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A microstructural investigation of electroplated damascene copper

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**A MICROSTRUCTURAL INVESTIGATION OF
ELECTROPLATED DAMASCENE COPPER**

A Thesis

Presented to

**The Faculty of the Department of Chemical and Materials Engineering
San Jose State University**

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Andrew Thomas Tzanavaras

December 2001

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ABSTRACT

A MICROSTRUCTURAL INVESTIGATION OF ELECTROPLATED DAMASCENE COPPER

by Andrew Thomas Tzanavaras

Electroplated Damascene copper is rapidly replacing aluminum-copper alloys for on-chip interconnect metallization in advanced semiconductor devices. A large grain size and high degree of (111) crystallographic texture are two microstructural characteristics that further enhance the performance and reliability of copper interconnects.

This investigation explores the effects of DC electroplating current density and brightening additive level on these microstructural characteristics after a high-temperature annealing treatment. In 1.3- μm thick blanket films, it was found that large, low-resistivity, highly (111)-textured grains with an average diameter of 1.7-1.9 μm could consistently be produced over a wide variety of electroplating conditions. The results also suggest a moderate degradation of the (111) texture component within a limited current density range. In Damascene trench features the current density, and to a lesser extent the additive level, are shown to be factors that will have an increasingly significant influence on the grain size within these features as geometries continue to shrink.

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TABLE OF CONTENTS

	Page
TABLE OF CONTENTS	vi
LIST OF FIGURES	x
LIST OF TABLES	xxi
Chapter 1 – Introduction	1
Chapter 2 – Literature Review	13
2.1 Microstructural Instability of Electroplated Copper Films	13
2.1.1 Microstructural and Sheet Resistance Changes	14
2.1.2 Film Stress Changes	18
2.1.3 Process Influences	22
2.1.4 Mechanisms of Microstructural Evolution	25
2.2 Grain Growth in Electroplated Copper Films	27
2.2.1 Grain Growth Limitations	27
2.2.2 Effect of Thermal Annealing on Grain Growth	31
2.3 Texture of Electroplated Copper Films	35
2.3.1 Barrier and Geometrical Influences on Texture	39
2.3.2 Development of Texture in Self-annealed Films	41
2.3.3 Effect of High-Temperature Annealing on Texture	42
2.3.4 Relationship between Stress and Texture	45
2.4 Literature Summary	50

	Page
Chapter 3 – Research Objectives	53
3.1 Research Objectives and Scope of Experimental Work	55
3.2 Experimental Matrix	56
3.3 Overview of Experimental Program	56
3.4 Description of Experimental Wafers	60
Chapter 4 – Experimental Methods	66
4.1 Electrochemical Deposition	66
4.1.1 Equipment and Materials	72
4.1.2 Electroplating Method	81
4.1.2.1 Deposition Rate	81
4.1.2.2 Preparation for Electroplating	82
4.1.2.3 Cathode Assembly Preparation	84
4.1.2.4 Substrate Preparation	84
4.1.2.5 Electrodeposition	86
4.2 Cyclic Voltammetric Stripping	94
4.2.1 Equipment and Materials	103
4.2.2 CVS Method	106
4.3 High-Temperature Annealing	115
4.3.1 Equipment and Materials	116
4.3.2 Annealing Method	124
4.3.3 Post-Annealing Inspection of Wafers	128

	Page
4.4 Sheet Resistance Measurements	133
4.4.1 Equipment and Materials	141
4.4.2 Measurement Method	141
4.5 Focused Ion Beam Imaging	147
4.5.1 Equipment and Materials	152
4.5.2 Imaging Method	156
4.6 X-ray Diffraction Measurements	162
4.6.1 Equipment and Materials	166
4.6.2 Measurement Method	172
Chapter 5 – Results and Discussion	178
5.1 Sheet Resistance Analysis	178
5.1.1 Assessment of Wafer Thickness Profiles	178
5.1.2 Statistical Comparison of Experimental Duplicates	180
5.1.3 Statistical Comparison of Experimental Conditions	196
5.1.4 Selection of Metrology Dice	196
5.1.5 Assessment of Copper Film Resistivity	198
5.2 Microstructure of Electroplated Copper Films	203
5.2.1 Microstructure of Blanket Copper Films	203
5.2.2 Grain Size and Distribution of Blanket Copper Films	212
5.2.3 Microstructure within Damascene Trench Features	228

	Page
5.2.4 Grain Size within Damascene Trench Features	234
5.2.5 Gap Filling within Damascene Trench Features	252
5.3 (111) Texture of Blanket Copper Films	259
5.3.1 General Approach for Texture Analysis	259
5.3.2 Bragg Scans	261
5.3.3 Rocking Curves	269
5.3.4 Texture (Fiber) Plots	271
Chapter 6 – Conclusions	285
Chapter 7 – Recommendations for Future Work	290
Chapter 8 – Bibliography	293
Appendix A – Sheet Resistance Statistics	303
Appendix B – Plan-view FIB Images of Blanket Copper Films	305
Appendix C – Tilt-view FIB Images of Blanket Copper Films	310
Appendix D – Tilt-view FIB Images of Trench Features	315
Appendix E – Tilt-view Electron Images of Trench Features	318

LIST OF FIGURES

Figure	Title	Page
Figure 1	Schematic of the multilevel interconnect scheme used in integrated circuits.	2
Figure 2	RC time delay versus feature size in integrated circuits.	4
Figure 3	The number of metal layers required for different interconnect materials options.	5
Figure 4	Experimental evidence of the improved electromigration performance resulting from the use of copper for on-chip IC interconnects.	6
Figure 5	The Damascene process used to fill via and trench structures in copper-based integrated circuits.	8
Figure 6	A figure illustrating how the microstructural changes accompanying the additive-induced, time-dependent, room-temperature recrystallization of electroplated copper films can be tracked by changes in sheet resistance.	16
Figure 7	FIB images of grains in a 1- μm thick electroplated Cu film for periods of (a) 90, (b) 180, and (c) 360 minutes after deposition.	17
Figure 8	The changes in film stress as a function of plating current both before and after the self-annealing process for 1- μm thick electroplated Cu films.	21
Figure 9	The effect of electroplating current density (bottom) and organic additive concentration (top) on the recrystallization kinetics and final sheet resistance of self-annealed, 1- μm thick, ECD Cu films.	23
Figure 10	Normalized sheet resistance as a function of time during room-temperature recrystallization for layers plated at 19.2, 14.2, 9.5, 4.8, 2.4, and 0.8 mA/cm^2 , going from left to right.	24
Figure 11	The evolution of grain size as a function of time for 1- μm thick ECD Cu films during the self-annealing process as a function of DC current density.	30

Figure	Title	Page
Figure 12	Two plan-view FIB images of 50 x 50- μm areas of ECD Cu films that were both self-annealed for 3 days at 21°C, followed by annealing treatments of a) 100°C for 30 minutes and b) 400°C for 30 minutes.	32
Figure 13	The orientation of the (111) crystallographic planes for Cu relative to the other two principal crystallographic planes (top) and the substrate surface and fiber axis (bottom) for a (111) fiber texture.	36
Figure 14	An example of a (111) fiber plot used to evaluate texture quality.	38
Figure 15	A plot of the surface-interface and strain energy differences between (111) and (200)-oriented grains.	47
Figure 16	Thermal hysteresis cycles to 400°C at 3°C/minute for five Cu films, with different initial stresses levels obtained by varying the plating current density.	49
Figure 17	(111) and (200) texture volume fractions as a function of annealing temperature.	51
Figure 18	A flowchart summarizing the basic processing, metrology, and analysis steps used in this investigation.	59
Figure 19	The mask layout for each of the identical 20-mm square die on the 200-mm CMP characterization wafers used in this study.	61
Figure 20	The row-wise numbering scheme used to identify each of the sixty-nine, identical, 20-mm square die on the experimental wafers.	62
Figure 21	A cross-sectional view of a typical Damascene trench structure for the wafers used in this investigation.	64
Figure 22	Two photographs of a typical 200-mm wafer used in this investigation prior to electrodeposition.	65
Figure 23	A schematic of the basic components typically used for the electrolytic deposition of copper from an aqueous solution.	67
Figure 24	A typical current density-potential curve for a copper electrodeposition process.	71

Figure	Title	Page
Figure 25	A schematic of the Jets Technology electroplating system showing all components and process piping.	75
Figure 26	A detailed view of the Jets Technology research and development electroplating cell showing all key components.	77
Figure 27	Two photographs of the Jets Technology electroplating cell without the removable cathode assembly that houses the substrates.	78
Figure 28	A schematic (top) and picture (bottom) of the six-inch rotating anode jet assembly (RAJA) embodied in the design of the Jets Technology electroplating cell.	79
Figure 29	A photograph of the removable cathode assembly that is designed to accommodate 200 mm Si substrates.	85
Figure 30	Backside (top) and frontside (bottom) views of the cathode assembly loaded with a 200 mm substrate prior to copper electrodeposition.	87
Figure 31	A flowchart summarizing the electrodeposition steps required to satisfy each unique condition of the experimental matrix.	88
Figure 32	Flow schemes used to fill the electroplating cell (top) and to electroplate (bottom).	91
Figure 33	The basic equipment requirements for cyclic voltammetric stripping.	95
Figure 34	An example of the repetitive, cyclic, triangular, potential excitation applied to the working electrode in a CVS analysis.	98
Figure 35	A typical cyclic voltammogram for a reversible chemical reaction of an electroactive chemical species.	100
Figure 36	The CVS equipment layout used in this study to determine the brightener additive activity.	104
Figure 37	A schematic (top) and photograph (bottom) of the CVS cell used in this study.	105

Figure	Title	Page
Figure 38	Partial cyclic voltammograms showing the anodic peak sweeps for each of the six additive concentrations used to generate a calibration curve.	109
Figure 39	The derived CVS calibration curve based on the anodic peak areas calculated from the cyclic voltammograms.	113
Figure 40	A schematic of the annealing system used in this investigation.	117
Figure 41	Two photographs of the inert-gas annealing system used in this study.	118
Figure 42	A photograph of the quartz preheater assembly used to heat the inert annealing gas prior to entering the chamber assembly.	119
Figure 43	A photograph of the gas distribution assembly.	120
Figure 44	The wafer holder assembly used to load the substrates and elevate them into the annealing chamber.	122
Figure 45	Top view (left) and bottom view (right) of the assembled annealing chamber.	123
Figure 46	A schematic of the wafer loading arrangement used during each annealing run.	126
Figure 47	A representative illustration of the thermal profile resulting from the annealing cycle used in this study.	127
Figure 48	Examples of the blisters seen on some of the experimental wafers after the high-temperature, isothermal annealing process.	131
Figure 49	Assorted examples of the blistering observed after the high-temperature annealing treatment of the experimental wafers.	132
Figure 50	A schematic of the eddy current method for determining sheet resistance.	136
Figure 51	Eddy current density as a function of penetration depth in an arbitrary material.	138

Figure	Title	Page
Figure 52	A typical liftoff curve illustrating the changes in the coil electrical parameters, as the probe is moved away from the sample for a material of constant resistance.	139
Figure 53	Families of liftoff curves and isodistance curves allow the resistance of an unknown test specimen to be determined from the coil electrical parameters.	140
Figure 54	A close-up photograph of the KLA-Tencor Omnimap® NC110, showing the probe, wafer chuck, and a sample wafer to be measured.	142
Figure 55	A die schematic showing the measurement location used for the blanket-film, eddy current sheet resistance measurements on each die.	144
Figure 56	An illustration of the location and direction of the 625-site, long (top) and 125-site, short (bottom) sheet resistance diameter scans used to assess the thickness profiles on the sample wafers.	146
Figure 57	A block diagram showing the basic operational components of a FIB system, which are very similar to those of an SEM.	148
Figure 58	The basic operational principles of a FIB system.	150
Figure 59	A schematic showing different atomic packing densities along three different crystallographic directions in a quartz crystal.	151
Figure 60	An FIB image of electroplated Cu in an array of, Damascene 0.35- μm trench features shortly after deposition showing the ion channeling effect.	153
Figure 61	Two different views of the FEI 820 Dual-beam FIB-SEM used in this investigation, showing the incident electron and ion beam sources.	154
Figure 62	A schematic of the die floorplan showing the region used for the Cu blanket-film FIB imaging.	157

Figure	Title	Page
Figure 63	A schematic showing the orientations of the ion and electron beam sources relative to the substrate, when imaging the top surface of the electroplated Cu films.	158
Figure 64	Electron beam images of the regions milled with the Ga ion source for cross-sectional views of the blanket film region (top) and trenched region (bottom).	159
Figure 65	A schematic showing how the sample is oriented relative to the Ga ion beam source during tilt-view, FIB imaging to examine the Cu grain structure in cross section.	161
Figure 66	A schematic of the geometry associated with Bragg's Law of Diffraction for a set of parallel, diffracting crystallographic planes.	163
Figure 67	A schematic of the geometry associated with rocking curve measurements.	165
Figure 68	Two views of the Scintag Model X2 Diffractometer with a θ - θ goniometer.	167
Figure 69	A diagram of the Scintag Model X2 Diffractometer set up for a Bragg-Brentano scan using a θ - θ goniometer.	168
Figure 70	A schematic illustrating how the diameter of the x-ray focusing circle decreases as the angle 2θ decreases.	169
Figure 71	The x-ray optics system in a typical diffractometer for both the incident and diffracted beams.	171
Figure 72	Two views of a Cu sample loaded in the sample holder and placed on the goniometer stage of the diffractometer.	174
Figure 73	Long-diameter sheet resistance scans for the experimental wafers of condition 5.	179
Figure 74	A bar chart that compares the mean sheet resistance values between duplicate wafers for all nine conditions.	182
Figure 75	Sheet resistance frequency histograms for the duplicate wafers of experimental condition 9, illustrating a skewed distribution and the presence of an extreme outlying value.	185

Figure	Title	Page
Figure 76	Sheet resistance die histograms by row (top) and column (bottom) for condition 9 duplicate wafers, showing dice with anomalous values.	186
Figure 77	Two sheet resistance contour maps for the first wafer of condition 9.	188
Figure 78	Average sheet resistance die histogram by row for all dice on all experimental wafers showing the recurrence of anomalous dice 49, 65, and 69.	189
Figure 79	A boxplot summary showing the distribution of sheet resistance values for the first wafer of condition 9.	191
Figure 80	Sheet resistance frequency histogram (top) and normal probability plot (bottom) for condition 9A, with dice 49, 65, and 69 removed.	193
Figure 81	A wafer schematic showing the subset of dice that were deemed suitable for subsequent metrology from each wafer.	199
Figure 82	Representative plan-view FIB images of the annealed copper microstructure for experimental conditions 2 (top) and 6 (bottom).	204
Figure 83	The atomic arrangement at the twinning plane in a face-centered cubic metal.	205
Figure 84	Examples of copper grains exhibiting a high degree of crystallographic twinning.	207
Figure 85	Examples of twin boundaries intersecting at 60° (left) and 90° (right).	208
Figure 86	Tilt-view FIB images at two different magnifications showing a cross section of the annealed copper microstructure for experimental condition 6.	210
Figure 87	Two tilt-view electron images of the annealed blanket copper films for experimental condition 2 showing thermal grooving (top) and a void (bottom).	211

Figure	Title	Page
Figure 88	Two plan-view images of the copper microstructure for experimental condition 8 showing the presence of voids at the grain boundaries.	213
Figure 89	Two plan-view FIB images from conditions 2 and 6 illustrating some complications arising from the use of FIB imaging for grain sizing.	215
Figure 90	A plot summarizing the grain sizing results for all nine experimental conditions.	219
Figure 91	A representative histogram of grain sizes obtained for experimental condition 5.	222
Figure 92	The lognormal probability density function for the distribution of grain sizes from experimental condition 5.	224
Figure 93	A normal probability plot of the logarithmically transformed grain size data from condition 5.	226
Figure 94	A graphical summary of the events leading to similar grain sizes in self-annealed, electroplated copper films, followed by a high-temperature thermal treatment.	229
Figure 95	Representative tilt-view FIB images taken at 35000 $\times$ magnification for condition 5, showing the grain structure within 0.50- μ m (top) and 0.35- μ m (bottom) Damascene trench structures in cross section.	230
Figure 96	Representative tilt-view FIB images taken at 50000 $\times$ magnification for condition 5, showing the grain structure within 0.50- μ m (top) and 0.35- μ m (bottom) Damascene trench structures in cross section.	233
Figure 97	A plot showing the trends in grain density within the 0.50- μ m trenches for all nine experimental conditions.	237
Figure 98	A plot showing the trends in grain density within the 0.35- μ m trenches for all nine experimental conditions.	238
Figure 99	Electron beam images of 0.50- μ m trenches illustrating the gap filling for conditions 1 (top) and 7 (bottom).	256

Figure	Title	Page
Figure 100	Electron beam images of 0.35- μm trenches illustrating the gap filling for conditions 1 (top) and 7 (bottom).	257
Figure 101	A representative high-resolution, Bragg-Brentano θ - 2θ scan for experimental condition 4 with the background intensity removed.	262
Figure 102	A comparison of the relative intensity values between the ICDD database for Cu and those obtained for experimental condition 4.	263
Figure 103	A detailed view of the Cu (111) peak obtained from a high-resolution, Bragg-Brentano θ - 2θ scan from experimental condition 4.	265
Figure 104	A comparison of Pearson VII fits to the Cu (111) $K\alpha_1$ Bragg peak data obtained from experimental condition 4.	268
Figure 105	A representative Cu (111) rocking curve obtained for condition 4.	270
Figure 106	An example of the defocusing and absorption corrections made to the (111) rocking curve for experimental condition 4, using “Texture Plus” software.	273
Figure 107	The mean, negative, and positive (111) fiber plots obtained from “Texture Plus” software for experimental condition 4.	275
Figure 108	A plot of the maximum (111) peak intensity as a function of the (111) textured fraction for all nine experimental conditions.	278
Figure 109	The (111) textured fraction as a function of current density for all three brightener activity levels.	280
Figure 110	Three fiber plots for experimental conditions 1, 4, and 5 that illustrate some of the key trends with respect to the electroplating variables used in this study.	281
Figure 111	Representative plan-view FIB images for experimental conditions 1 (top) and 2(bottom).	305
Figure 112	Representative plan-view FIB images from experimental conditions 3 (top) and 4 (bottom).	306
Figure 113	Representative plan-view FIB images from experimental conditions 5 (top) and 6 (bottom).	307

Figure	Title	Page
Figure 114	Representative plan-view FIB images from experimental conditions 7 (top) and 8 (bottom).	308
Figure 115	Representative plan-view FIB image from experimental condition 9.	309
Figure 116	Representative tilt-view FIB images for experimental condition 1 (top) and 2 (bottom) showing the blanket copper films in cross section.	310
Figure 117	Representative tilt-view FIB images for experimental condition 3 (top) and 4 (bottom) showing the blanket copper films in cross section.	311
Figure 118	Representative tilt-view FIB images for experimental condition 5 (top) and 6 (bottom) showing the blanket copper films in cross section.	312
Figure 119	Representative tilt-view FIB images for experimental condition 7 (top) and 8 (bottom) showing the blanket copper films in cross section.	313
Figure 120	Representative tilt-view FIB image for experimental condition 9.	314
Figure 121	Representative tilt-view images of 0.50 and 0.35- μm trench features for experimental conditions 1 (top), 2 (middle), and 3 (bottom).	315
Figure 122	Representative tilt-view images of 0.50 and 0.35- μm trench features for experimental conditions 4 (top), 5 (middle), and 6 (bottom).	316
Figure 123	Representative tilt-view images of 0.50 and 0.35- μm trench features for experimental conditions 7 (top), 8 (middle), and 9 (bottom).	317
Figure 124	Representative tilt-view electron images of 0.50 and 0.35- μm trenches for experimental condition 1 (top), 2 (middle), and 3 (bottom).	318
Figure 125	Representative tilt-view electron images of 0.50 and 0.35- μm trenches for experimental condition 4 (top), 5 (middle), and 6 (bottom).	319

Figure	Title	Page
Figure 126	Representative tilt-view electron images of 0.50 and 0.35- μm trenches for experimental condition 7 (top), 8 (middle), and 9 (bottom).	320

LIST OF TABLES

Table	Title	Page
Table 1	A compilation of some referenced literature results illustrating the changes in film stress accompanying the self-annealing process.	19
Table 2	The (111) fiber texture results obtained from two studies that used high-temperature annealing treatments of blanket ECD Cu films, with Ta barrier layers in an inert-gas environment.	44
Table 3	A summary table outlining the experimental matrix for this investigation.	57
Table 4	A summary of the equipment provided for this study by the collaborating industrial organizations.	58
Table 5	The Enthone-OMI premixed CUBATH® M acid copper sulfate electrolyte components as specified by the manufacturer.	73
Table 6	A summary of the electrodeposition parameters used for the three current density levels to achieve a nominal film thickness of approximately 1.5 μm .	83
Table 7	The electrochemical deposition parameters common to all nine conditions of the experimental matrix.	90
Table 8	A summary of the electrodeposition parameters used for the three current density levels that includes the voltage values recorded from the DC power supply.	93
Table 9	The chemicals required to perform the CVS analyses for brightener activity.	107
Table 10	A summary of the anodic peak areas obtained from the cyclic voltammograms.	112
Table 11	A table summarizing the interpolated CVS peak areas for future use in monitoring and maintaining the proper additive levels, during subsequent electrodeposition work.	114
Table 12	A summary of the process steps employed to anneal the substrates using the inert-gas sweep method.	125

Table	Title	Page
Table 13	A summary of processing defects based on post-annealing observations.	130
Table 14	The NC110 instrument performance capabilities and equipment configuration for this investigation.	143
Table 15	The basic equipment specifications for the FEI 820 Dual-beam FIB-SEM used in this investigation.	155
Table 16	The diffractometer equipment configuration used for this study.	173
Table 17	A summary of the high-resolution, Bragg-Brentano step scan ranges performed for each Cu peak that was identified in the high-speed, continuous scans.	175
Table 18	Sheet resistance z-test results at the 95% confidence level between all duplicate pairs of wafers for each condition, based on the entire raw data set.	184
Table 19	A summary of the boxplot analysis results for each set of duplicate wafers for all conditions, in relation to dice 49, 65 and 69.	192
Table 20	Sheet resistance z-test results at the 95% confidence level between all duplicate pairs of wafers for each condition, with the removal of dice 49,65, and 69.	194
Table 21	ANOVA results at the 95% confidence level comparing the mean sheet resistance values between all nine experimental conditions.	197
Table 22	A table summarizing the dispositions of the dice selected for subsequent metrology.	200
Table 23	A summary of the calculated resistivity values for each condition, based on the thickness and sheet resistance measurements of the FIB metrology dice.	202
Table 24	Univariate grain sizing statistics of the blanket copper films for all nine experimental conditions.	218
Table 25	The distribution parameters derived for the lognormal probability density function for all nine experimental conditions.	225

Table	Title	Page
Table 26	A summary of the grain density results for the 0.5- μm trench features.	235
Table 27	A summary of grain density results for 0.35- μm trench features.	236
Table 28	ANOVA results at the 95% confidence level for the entire 0.50- μm grain density data set.	240
Table 29	Modified ANOVA results at the 95% confidence level for the 0.50- μm grain density data that considers only the low and high current density levels, for all three additive levels.	242
Table 30	Modified ANOVA results at the 95% confidence level for the 0.50- μm grain density data that employs a trench area correction to experimental condition 8.	243
Table 31	ANOVA results at the 95% confidence level for the entire 0.35- μm grain density data set.	245
Table 32	Modified ANOVA results at the 95% confidence level for the 0.35- μm grain density data that consider only the low and medium current density levels, for all three additive levels.	246
Table 33	Modified ANOVA results at the 95% confidence level for the 0.35- μm grain density data that consider only the medium and high current density levels, for all three additive levels.	247
Table 34	Key geometrical features pertaining to the Damascene trenches used to observe gap filling.	255
Table 35	A summary of the relative intensity data for all nine experimental conditions, based on normalizing the peak areas taken from the Bragg scans to that of the Cu (111) peak.	264
Table 36	A list of the information required for the Texture Plus program, in addition to the Bragg and rocking curve intensity data for the peak of interest.	272
Table 37	A summary of the data obtained from fiber plots used to evaluate the (111) fiber texture for all nine experimental conditions.	277

Table	Title	Page
Table 38	ANOVA results at the 95% confidence level to assess the statistical significance of the impact electroplating variables have on the (111) textured fraction.	282
Table 39	Sheet resistance summary statistics for low brightener level.	303
Table 40	Sheet resistance summary statistics for medium brightener level.	303
Table 41	Sheet resistance summary statistics for high brightener level.	304

CHAPTER 1

INTRODUCTION

Since the early 1960's aluminum, and more recently aluminum-copper alloys, have been the materials of choice for global on-chip interconnects in integrated circuits. During this period there has been a steady trend of decreasing interconnect feature sizes, increased packing densities, vertical integration of metallization levels, and increasing die sizes to accommodate the need for faster devices capable of performing more diverse functions. The use of aluminum-copper alloys as an interconnect material is now being seriously challenged by these technological trends with respect to both interconnect performance and reliability. Figure 1 schematically illustrates the multilevel interconnect scheme used to route power and signals between functionalized groups of transistors, or cells, within the integrated circuit (IC) [1].

An inevitable consequence of these technological trends is that the line resistance, R , and capacitance associated with the dielectric, C , are now becoming the dominant factors in determining IC performance, instead of the intrinsic gate delay of the transistor [1,2]. This performance is typically measured by a parameter known as the RC time delay, where R and C represent the resistive and capacitive contributions to the delay time. The RC time delay is given by

$$RC \approx \frac{\rho}{t_M} \frac{L^2 \epsilon_{ILD}}{t_{ILD}} \quad (1)$$

Figure 1: Schematic of the multilevel interconnect scheme used in integrated circuits [1].

where ρ , L and t_M , are the resistivity, length, and thickness of the interconnect, and ϵ_{ILD} and t_{ILD} are the permittivity and thickness of the interlayer dielectric (ILD) [3]. The effective resistance attributable to the global interconnects has significantly increased with the decreased cross-sectional areas and increased lengths of the conductor lines. The relative contributions of the interconnects and transistor gates to the RC time delay as a function of feature size is shown in Figure 2 [4].

Since the early 1990s, research efforts to minimize the RC time delay in advanced integrated circuits have centered around using lower resistivity materials, such as copper, to reduce resistance and lower dielectric constant materials to reduce interline capacitance. The benefits of using copper and low-k dielectrics are illustrated in Figure 3 [5]. As the figure illustrates, the number of metal layers can be reduced, resulting in simpler process flows and significant cost reductions to the IC manufacturer.

The decreased cross-sectional areas of the interconnects has also resulted in a trend of increasing current densities, making the aluminum-based interconnect electromigration reliability a growing concern amongst IC manufacturers. A current density of 2×10^5 A/cm² is considered an upper limit for aluminum-based interconnect lines [6]. Copper is now coming of age as a replacement for interconnect metallization, due to its lower resistivity and improved electromigration resistance as compared to aluminum-based alloys. The allowable current density for copper lines has been reported to be 5×10^6 A/cm² and the activation energy for electromigration up to twice that of aluminum [7]. Figure 4 illustrates the difference in electromigration lifetime as a function of temperature for test structures composed of Al-0.5% Cu, and pure copper [5]. The reader should note

Figure 2: RC time delay versus feature size in integrated circuits. Interconnects start to dominate the RC time delay below feature sizes of approximately $1.0 \mu\text{m}$ [4].

Figure 3: The number of metal layers required for different interconnect materials options [5].

Figure 4: Experimental evidence of the improved electromigration performance resulting from the use of copper for on-chip, IC interconnects [5].

that for the 2- μm wide interconnect line data shown in this figure, the steeper slope of the graph for the copper electromigration experiment is indicative of a higher electromigration activation energy as compared to that of the Al-0.5%Cu alloy. An additional advantage that stems from the use of copper is the reduced IC power requirements resulting from its lower resistivity, making it very attractive for mobile applications.

The transition to copper as the conductor and to a better insulator began with widespread research and development efforts in the early 1990's, which eventually led to IBM's product announcement in September 1997 and first product shipment in June 1998 [8]. The four most commonly reported challenges which have delayed the implementation of copper for approximately forty years include the method of deposition, patterning the metal, its tendency to corrode, and its high diffusivity in silicon and silicon dioxide. Since copper contains energy levels deep within the bandgap of silicon, there is a very significant potential for device contamination. These problems are being resolved with the use of a process that the semiconductor industry has coined as the "Damascene" process in conjunction with appropriate barrier and passivation thin film layers that address the diffusion and corrosion problems.

Unlike its aluminum counterpart, copper patterning, whether it is for via or trench structures, is achieved by an additive, or Damascene, process as shown in Figure 5. This method essentially consists of copper deposition into preformed silicon dioxide trenches, followed by chemical-mechanical planarization. Similarly, copper lines and vias can be

Figure 5: The Damascene process used to fill via and trench structures in copper-based integrated circuits.

formed simultaneously with a dual-Damascene process flow. The advantages of Damascene processing include patterning without metal etching and avoiding oxide gap-filling challenges encountered by conventional aluminum processes. This process, however, is not without its own challenges. The burden of oxide gap filling has now shifted to metal gap filling, an equally challenging task. It is also important to note that the high diffusivity of copper in silicon dioxide and silicon requires the use of a conformal diffusion barrier layer, such as Ta, Ti, or TaN, in the trench or via of any Damascene structure prior to copper deposition.

The methods of depositing copper into Damascene vias or trenches include physical vapor deposition (PVD), chemical vapor deposition (CVD) and electrochemical deposition (ECD). Since PVD is a line-of-sight type deposition process, it is inherently limited in step coverage and gap-filling capabilities for aggressive geometries, thus making it unattractive for copper Damascene processes. While MOCVD and other CVD methods are still considered by some to be viable techniques for submicron Damascene processing, some major drawbacks have been reported. These include, but are not limited to, (1) a high level of film contamination, (2) poor electromigration resistance due to small grain sizes and a lack of (111) film texture, (3) a relatively low deposition rate, (4) high processing cost and deposition tool complexity [9]. Additive-enhanced ECD has received the most attention as the method for filling Damascene structures due to its high deposition rate, low cost of tool ownership, and the ability to fill deep submicron Damascene features.

The electrochemical deposition of metallic copper involves the electrochemical reduction of cupric ions (Cu^{2+}) from an aqueous, conductive electrolyte to metallic copper (Cu^0) according to the chemical reaction

This reaction does not happen spontaneously, but rather requires an external source of energy, such as a power supply, that provides two electrons to deposit each copper atom. In the scope of the current discussion, ECD refers to electrolytic chemical deposition in an acidic electrolyte and should not be confused with electroless methods that use reducing agents as a source of electrons. Currently, copper electroplating of interconnects is performed with commercially available sulfuric acid-cupric sulfate plating solutions utilizing proprietary additives similar to those used for printed circuit board processes [10].

The additives used for copper electroplating are generally organic compounds used in very small concentrations that affect the local kinetics of electrocrystallization process by acting as inhibitors, grain refiners and ductilizers and may be co-deposited with the copper electrodeposit [10,38]. The key components in most additive packages used for copper electroplating are generally referred to as brighteners, levelers, and suppressing agents [10]. The control of plating current density and additive levels in this application allows submicron interconnect features to be filled by a “bottom-up” or “superfilling” mechanism that prevents the formation of defects such as voids and seams within these

features [11]. A common theme in the “bottom-up” filling mechanism is that the deposition rate at the trench corners and the surrounding field area is suppressed and the deposition rate from the trench bottom is enhanced. Terms such as leveling, gap filling, and throwing power are frequently used in the literature to describe the ability of a given electroplating process to fill these fine via or trench structures. Of the three key additive components present in most copper electroplating additive packages mentioned above, brighteners, which act as grain refiners, have been reported to have the largest affect on throwing power for studies done in the printed circuit board industry [12].

An unexpected aspect of the electroplated copper process is the time-dependent change in the deposited film structure and properties that occurs after electroplating. Many investigators have reported that over a period of hours to days blanket or patterned copper films deposited in acidic copper baths with plating additives undergo a room-temperature recrystallization. The driving force for this behavior is now being associated with high grain boundary energy and defect densities, as well as the potential for chemical gradients that exist in the films resulting from plating additive incorporation into the growing films. After recrystallization, the copper grain size, which is on the order of 0.1 μm , can increase to several microns in blanket films after recrystallization is complete. The large grains produced by copper ECD, coupled with a high degree of (111) film texture, have been demonstrated the best combination of performance and reliability [7].

The grain structure and texture in any Damascene structure has implications for the performance and reliability of the interconnect, as well a possible implications for the

chemical mechanical planarization process which ensues. Since plating parameters, such as additive concentration and current density, mediate the kinetics of the electrodeposition processes, a systematic study to determine any possible effects on the final microstructure is warranted. Most pertinent journal articles are very secretive about plating bath formulations and ECD process parameters, so a very limited amount of detailed experimental information is available. The scope of this work is to evaluate the microstructure of recrystallized Damascene copper films for nine different electroplating conditions that vary both the current density and brightening additive concentration. To deposit the copper films, a unique high-rate, rotating-anode, jet-type, electroplating cell will be employed [13]. A post-deposition, high-temperature annealing process in an inert-gas atmosphere will be used due to its technical relevance to current semiconductor processes. The microstructural features of primary interest are grain size, grain structure, and crystallographic texture.

CHAPTER 2

LITERATURE REVIEW

The microstructure of electrodeposited copper in a Damascene materials system has been extensively studied due to its relevance to the performance and reliability for on-chip interconnects in semiconductor devices. This broad and complex topic invites further study to complement the existing body of scientific knowledge and to better understand the evolution of microstructural features that may benefit semiconductor manufacturers. There are many conflicting and contradictory results present in the literature stemming from the complexity of this system. This review highlights some of the key factors that lead to the evolution of microstructure in these electroplated Cu films. The primary focus will be on the changes in stress, grain size, and crystallographic texture that accompany the recrystallization process.

2.1 Microstructural Instability of Electroplated Copper Films.

Several research groups have reported the tendency of additive-enhanced, electroplated copper films to recrystallize at room temperature over periods ranging from hours to weeks. For example, it has been experimentally determined that a 1.5- μm electroplated copper film will recrystallize at room temperature in slightly less than 50 hours [10]. Accompanying this process are changes in the electrical, mechanical, and microstructural characteristics of the films. These include increases in grain size along with decreases in sheet resistance (or resistivity) and hardness, as well as changes in film stress and texture. Room-temperature recrystallization has been observed in both continuous films [14] and copper deposited into Damascene trench structures [15]. The

recrystallized grains are frequently described as being large, columnar, and highly twinned after this process.

Recrystallization is a diffusion-controlled, thermally activated process that follows an Arrhenius-type relationship of the form

$$k = Ae^{-E_a / RT} \quad (3)$$

where k is a rate constant, A is a pre-exponential constant, E_a is the activation energy, R is the universal gas constant, and T the absolute temperature [16]. The activation energy for this process has been reported to be approximately 0.9 to 1.1 eV, which is consistent with a process controlled by the grain boundary diffusion of Cu [17-19]. Since this recrystallization process occurs at low temperatures, the misleading term “self-annealing” has been coined in the pool of scientific literature to describe this process. It is also very interesting to note that electrodeposited films prepared under additive-free conditions or at very low current densities do not exhibit this self-annealing behavior, thus underscoring the importance of additives in this process [20]. In order to be consistent with the literature, the term self-annealing will be used in subsequent discussions.

2.1.1 Microstructural and Sheet Resistance Changes

During the self-annealing process, it has frequently been reported that the mean grain size in blanket films changes from approximately 0.1 μm in the as-deposited state to greater than 1 μm after the self-annealing process is completed. Accompanying this grain growth process are decreases of up to 20% in sheet resistance after a short

incubation period where the sheet resistance remains relatively constant. The rate at which this transformation occurs has been found to depend critically on the film thickness [21] and the current density used during electrodeposition [22,23]. In-situ focused ion beam (FIB) microscopy studies have shown that these changes in sheet resistance correlate very well with the fractional area recrystallized during this transient period, which is illustrated in Figure 6 [14].

Other FIB and transmission electron microscopy (TEM) studies have also shown the grain growth process that accompanies self-annealing can be characterized as an abnormal grain growth process in which select grains nucleate and grow rapidly within a background matrix of small grains [17,24,25]. With normal grain growth the entire population of grains grows simultaneously, which has not been observed during the self-annealing process. An example of this observation, which comes from an FIB study by Harper, is shown in Figure 7 [17]. The three FIB images on the left-hand side of the figure show a 1- μm thick electroplated copper film at 90, 180, and 360 minutes after deposition. The sketches to the right of each FIB image represent areas of large grains (black) and small grains (white). This illustration shows that within the population of small grains, only select grains nucleate and grow rapidly, which is characteristic of abnormal grain growth. Abnormal grain growth may occur when there is an additional driving force for grains to grow beyond the normal limit or when the normal grain growth process is hindered by a particle pinning mechanism [17]. Abnormal grain growth has also frequently been referred to as secondary grain growth in the literature on electroplated copper.

Figure 6: A figure illustrating how the microstructural changes accompanying the additive-induced, time-dependent room-temperature recrystallization of electroplated copper films can be tracked by changes in sheet resistance [14].

Figure 7: FIB images of grains in a 1- μm thick electroplated Cu film for periods of (a) 90, (b) 180, and (c) 360 minutes after deposition. The sketches shown to the right of each image show the fractional area recrystallized in black, which is composed of much larger grains than the surrounding matrix. The fractional areas recrystallized were determined to be (a) 14%, (b) 53%, and (c) 88% [17].

Brongersma further characterized the self-annealing process using in-situ FIB imaging and found that it consists of two distinct events in blanket films [26]. First, an initial top-down recrystallization occurs immediately after deposition, with nucleation occurring at the surface and subsequent growth proceeding downward to a thickness of approximately 0.5 μm . Then, on a much longer time scale, a lateral recrystallization takes place in the underlying untransformed regions, during which large grains start to form at the expense of the surrounding smaller grains.

2.1.2 Film Stress Changes

The changes in stress and sheet resistance that accompany self-annealing are two independent phenomena. As mentioned previously, FIB studies have reported that the decrease in sheet resistance that accompanies self-annealing correlates very well with secondary grain growth in electroplated Cu films [17]. Changes in stress, on the other hand, have been found to correlate well with the desorption of incorporated plating additives during the self-annealing process [27]. Furthermore, the changes in stress and sheet resistance are two non-correlated variables, as their changes during the self-annealing process occur on two different time scales [26]. Based on these results, film stress is apparently not a major driving force for the room-temperature recrystallization process. Results reported in the literature on electroplated Cu showed some conflicting results on the nature of the stress changes occurring during the room temperature transient period [10,17,26,28,30,31]. A summary of the results obtained in the literature may be found in Table 1. Apparently, the film thickness and plating current density can

Table 1: A compilation of some referenced literature results illustrating the changes in film stress accompanying the self-annealing process. There are some indications that the film thickness and electroplating current density play a role in this process.

ECD Conditions	Initial Stress (MPa)	Final Stress (MPa)	Stress Change (MPa)	Film Thickness (μm)	Reference
Unspecified	-45	0	45	1.0	17,30
Unspecified	70	0	-70	0.5	26
Unspecified	70	25	-45	0.75	26
Unspecified	70	50	-20	1.0	26
Unspecified	80	50	-30	1.0	27
3 mA/cm ² , Pulse	-40	0	40	1.0	28
5 mA/cm ² , Pulse	-40	15	55	1.0	28
7-40 mA/cm ² , Pulse	-40	80	120	1.0	28
10 mA/cm ² , DC	-14	0	14	0.35	28
10 mA/cm ² , DC	-15	4	19	0.55	28
10 mA/cm ² , DC	-22	80	102	1.00	28
10 mA/cm ² , DC	-27	85	112	1.80	28
Unspecified	-3	20	23	Unspecified	10
Unspecified	6	4	-2	0.8	31
Unspecified	-4	18	22	1.6	31
Unspecified	-20	28	48	3.3	31

influence both the initial and final stress of ECD Cu films both before and after self annealing, based on the results shown in this table.

Most recently, Brongersma has shown some of these conflicting results can be explained in terms of differing degrees of additive incorporation in the films resulting from the use of different current densities, as well as different plating chemistries [29]. Figure 8 illustrates some of the important results from this study for a 1- μm thick ECD Cu layer. In this figure it is apparent that the initial film stress after deposition can be varied over a wide range of tensile and compressive values with a crossover at approximately 2.5 Amperes (7.9 mA/cm^2), while the final stress also depends slightly on current density. Apparently it is the inclusion of plating additives in the bulk of the grains that are responsible for the dependence of the initial stress on the plating current. The fact that the stress is reduced in absolute terms for both initial tensile and compressive stresses illustrates that these changes are not a consequence of grain boundary elimination [29]. Such an occurrence would be expected to result in an increase in the tensile stress after self-annealing as a consequence of the reduction in film volume. The study presented earlier by Lee in Table 1 does, however, suggest that some plating chemistries might result in a significant volume contraction after the self-annealing process, as evidenced by the high residual tensile stress values obtained for films thicker than 1 μm or plated at higher current densities [28].

A recent kinetic analysis by Hau-Riege and Thompson reported that the moving grain boundaries of abnormally growing grains would, in effect, push all the impurities to the grain boundaries [25]. The limited volume of these boundaries will result in the

Figure 8: The changes in film stress as a function of plating current both before and after the self-annealing process for 1- μm thick electroplated Cu films. The current density range corresponding to these plating currents is 0.8 mA/cm^2 at the lowest level and 19 mA/cm^2 at the highest level. The film plated at the lowest current density level was reported to not have fully recrystallized [29].

observed desorption of impurities and a concurrent reduction in stress. A decrease in film volume is not expected as the volume in the original boundaries can be filled with the impurities originally present in the grains. Therefore, a large increase in tensile stress due to grain boundary volume elimination is not frequently observed. Hau-Riege and Thompson also showed that the accumulation of impurities at the grain boundaries not only slows the recrystallization kinetics but also contributes to the energetics that drives the transformation to a large-grained microstructure [23].

2.1.3 Process Influences

While there have been several studies on the factors affecting the recrystallization kinetics of electrodeposited Cu films, very few have focused on the effects of electrodeposition parameters. Ritzdorf recently published one of the best comparative studies in this area [20]. A graphical summary of these results may be found in Figure 9. In the study it was shown that films plated at higher current densities take less time to complete the "self-annealing" process than those deposited at lower current densities. The final sheet resistance is also slightly affected by the current density, with lower sheet resistance values at lower current densities. This finding, however, contradicts other authors who have reported that faster recrystallization kinetics derived from the use of higher current densities results in a lower final sheet resistance [22,29]. One example is presented in Figure 10. In any case, differing sheet resistance values after self-annealing can be explained in terms of differing recrystallized grain sizes or degrees of additive incorporation in the films stemming from the use of different current density conditions. Additionally, Ritzdorf also reported that a higher concentration of additives resulted in

Figure 9: The effect of organic additive concentration (top) and electroplating current density (bottom) on the recrystallization kinetics and final sheet resistance of self-annealed, 1- μm thick, ECD Cu films [20].

Figure 10: Normalized sheet resistance as a function of time during room-temperature recrystallization for layers plated at 19.2, 14.2, 9.5, 4.8, 2.4, and 0.8 mA/cm², going from left to right. These results suggest that plating at higher current densities results not only in faster recrystallization kinetics but also a lower final sheet resistance [29].

slower recrystallization kinetics and a higher final sheet resistance, which is also shown in Figure 9. Similarly, these results also suggest higher levels of additive incorporation or smaller grain sizes in films deposited with higher bulk additive concentrations. Self-annealing is not observed in cases where either no additives or very low current densities are used [20,22,29].

2.1.4 Mechanisms of Microstructural Evolution

Perhaps one of the most comprehensive papers which models the film changes during self-annealing was recently presented by Harper, and the following discussion summarizes some of the relevant results [30]. Using the Zener model, it is shown that the only mechanism that accounts for both the small, as-deposited grain size and the subsequent abnormal grain growth behavior is particle pinning of the grain boundaries. The Zener model considers particles that occupy the grain boundaries to reduce the overall grain boundary energy by an amount that is proportional to the occluded grain boundary area. These particles, in effect, impose a pinning pressure that opposes the grain growth pressure stemming from a high grain boundary energy density. Harper's analysis reported that an as-deposited grain size of 0.05-0.2 μm for electroplated Cu can be stabilized by a particle volume fraction range of 0.1-3.0 atomic percent for particle sizes ranging from atomic size up to 4.5 nm. Total impurity concentrations in electroplated Cu greater than 0.1 atomic percent have been reported in the literature [22]. It should be emphasized, however, that the exact nature of these pinning sites is as of yet undetermined and may include not only incorporated electroplating additives, but also point and line lattice defects such as vacancies and dislocations.

The observed incubation time before the onset of abnormal grain growth and the concurrent decrease in resistivity frequently reported in the literature can also be explained by particle pinning. Harper uses the argument that in order for a pinned grain boundary to break free and initiate abnormal grain growth, an Ostwald ripening of the pinned particles must be occurring during the incubation period, through which the film resistivity remains relatively constant for the first few hours after deposition [30]. During this period, the particles coarsen, their average spacing decreases, and their ability to pin grain boundaries consequently decreases. Eventually, certain grain boundaries will break free and undergo abnormal grain growth. This mechanistic model shows that room-temperature recrystallization is merely an abnormal grain growth process that does not necessarily involve the nucleation of new grains.

Harper's investigation also shows the primary driving force for self-annealing is the grain boundary energy density in the fine-grained, as-deposited film [30]. Based on an initial grain size of 0.1 μm and a final grain size of 1.0 μm , Harper estimates the energy released by copper grain growth during self-annealing to be 15 MJ/m^3 , equivalent to 1.1 meV/atom . The energy released during this process is directly proportional to the grain boundary energy density and inversely proportional to the initial grain size in cases where the initial and final grain sizes differ by more than an order of magnitude. Under conditions of abnormal grain growth, the energy density driving grain growth is determined by the small grain size of the matrix of as-deposited grains that have not yet grown. Hence, the pressure for grain growth, which is proportional to the grain boundary energy density, remains independent of the growing grain size, allowing abnormally

growing grains to greatly exceed the film thickness. Using a similar line of reasoning, Harper also demonstrated that the energy density associated with dislocations is not a major driving force for grain growth [30].

2.2 Grain Growth in Electroplated Copper Films

There is an increasing amount of evidence in the literature that suggests electroplating conditions can affect not only the recrystallization kinetics but also the final grain size of self-annealed electroplated copper films [28]. In particular, different current density conditions or additive levels lead to different levels of incorporated impurities from the electroplating bath that can pose grain-growth limitations. For this reason, high-temperature annealing treatments are now actively being explored and implemented [19,31-36].

2.2.1 Grain Growth Limitations

In the field of electrodeposition, it is generally accepted that additives can be consumed at the cathode by incorporation into the electrodeposit, or by the electrochemical reactions occurring at the cathode or anode [37]. The degree to which additives are incorporated into the growing deposit is a function of the bulk concentration or the deposition rate [38]. Higher concentrations or lower current densities will therefore generally lead to a higher degree of additive incorporation in the deposited film [38]. Several groups have shown that electroplated Cu will not recrystallize at room temperature if additives are not used in the electrodeposition process, thus underscoring their importance in the self-annealing process [20,22,23,29].

Brongersma, who pioneered much of the early work on the behavior of copper during the self-annealing process, was the first to propose that the degree of additive incorporation not only impacts the self-annealing kinetics but also the final grain size in such films [21]. In his work, Brongersma used the Avrami-Johnson-Mehl Equation (JMAK Theory) to model the changes in sheet resistance during self-annealing. In particular, he demonstrated that changes in the Avrami exponent and resistivity can be modeled if one assumes a constant nucleation rate and, more importantly, that a secondary grain can never grow beyond a certain critical size. It was also proposed that the existence of such a limit on the final grain size could be due to the purification of the bulk grains during recrystallization and the resulting accumulation of impurities at the grain boundaries. This could hamper grain boundary motion and therefore inhibit grain growth. Within the same time frame, Hau-Riege also performed a complementary study that modeled the changes in the fractional area recrystallized from a time series of TEM micrographs using JMAK theory and reached similar conclusions [25]. Both of these studies are in agreement with Harper's study which, as previously discussed, proposed a grain boundary pinning mechanism to account for the film changes that occur during the self-annealing process [30]. The results of these three kinetic studies suggest that impurities play several important roles in the room-temperature, self-annealing process of electroplated Cu films [21,25,30]. First, three-dimensional normal grain growth of the grains in the untransformed matrix is impaired by solute drag due to the presence of incorporated impurities from the electroplating process. The resulting stabilized small grain size, and to some degree impurity rejection from the grains, contribute to the high

driving force for the abnormal grain growth associated with self-annealing. Finally, the accumulation of rejected impurities at the grain boundary interface can slow the rate of transformation and impede further grain growth. Such a mechanism would explain the widely varying results in the literature on the final grain size in electroplated Cu films after self-annealing, despite reporting similar as-deposited grain sizes immediately after deposition. Such microstructural studies generally do not report relevant process details such as the current density or additive levels employed during the electrodeposition process.

In a recent study by Lee, it was reported that the evolution of grain size in electroplated Cu films is a strong function of the current density [23]. Lee demonstrated that increasing the current density, which lowers the degree of additive incorporation, results not only in faster recrystallization kinetics but also a larger final grain size. A summary of these results is shown in Figure 11 [23]. The faster recrystallization kinetics associated with the use of higher current densities is consistent with the work previously mentioned by Ritzdorf, which used sheet resistance as the metric to monitor the self-annealing process [20]. Lee attributed the faster kinetics to an increase in the dislocation loop densities resulting from the use of higher current densities in the as-deposited films, which were observed with TEM imaging.

Although Lee failed to comment on the reason for differences in the final grain size, different degrees of growth inhibition resulting from different degrees of additive incorporation can explain his results. The larger final grain sizes associated with the use of higher current densities are, however, not in agreement with Ritzdorf's work [20] but

Figure 11: The evolution of grain size as a function of time for 1- μm thick ECD Cu films during the self-annealing process as a function of DC current density. The data suggest both faster kinetics and larger final recrystallized grain sizes for increasing values of current density [23].

are in agreement with the work of Brongersma [29]. As previously shown in Figures 9 and 10, Ritzdorf's results [20] suggest that the use of higher current densities result in slightly higher final sheet resistance values after the transient period is complete, whereas Brongersma [29] reported the opposite trend. The larger final grain sizes associated with the use of higher current densities shown in Lee's work [23] would be expected to lower sheet resistance values due to a decreasing electron scattering component attributable to the grain boundaries.

2.2.2 Effect of Thermal Annealing on Grain Growth

In a recent study by Gignac, the effects of a combination of self-annealing followed by two different thermal annealing treatments were investigated for 1- μm films deposited with unspecified electroplating conditions [14]. After allowing three days for the room-temperature transient to occur in both films, the grain size was approximately 1 μm . Afterward, the two films were annealed at 100°C (low-temperature treatment) and 400°C (high-temperature treatment) for a period of 30 minutes. The grain size of the film with the low temperature treatment was $1.9 \pm 1.0 \mu\text{m}$, whereas the film with the high temperature treatment was $1.6 \pm 1.0 \mu\text{m}$.

A visual comparison of the plan view FIB images presented by Gignac are presented in Figure 12 [14] and suggest that fine grains may have been trapped in a matrix of larger grains for the low-temperature treatment. This, in turn, should result in a smaller grain size and larger standard deviation. Furthermore, these results imply that the microstructural transformation may have not been completed after self-annealing followed by the low-temperature treatment. Even though Gignac reported a smaller grain

Figure 12: Two plan-view FIB images of 50 x 50- μm areas of ECD Cu films that were both self-annealed for 3 days at 21 $^{\circ}\text{C}$, followed by annealing treatments of a) 100 $^{\circ}\text{C}$ for 30 minutes and b) 400 $^{\circ}\text{C}$ for 30 minutes. The latter treatment appears to have produced larger, more distinct grains. [14].

size for the high-temperature treatment, a visual inspection of the image shows larger, more distinct grains and a noticeable absence of any fine-grained component. Gignac raises the possibility that the grain sizing results of the film exposed to the lower temperature may be less accurate due to the fact that the “indistinct” grain boundaries made grain sizing more difficult.

Gignac’s results [14], along with the previously discussed dependence of grain size on current density demonstrated by Lee [23], suggest that the secondary grain growth associated with self-annealing in electroplated copper layers is incomplete after the sheet resistance and stress appear to have stabilized. Instead, the layer is apparently in an intermediate or metastable state with a grain size that depends on the degree of growth inhibition imposed by different levels of additive incorporation in the films, which is dependent on the electroplating conditions.

This conclusion is further supported by the fact that Dubin has reported further decreases in the Cu film resistivity after a thermal annealing treatment ($\approx 400^{\circ}\text{C}$), the degree of which is dependent on the film thickness within a range of 200 to 1200 nm [35]. In all cases, however, the post-annealing resistivity approached $1.7\ \mu\Omega\text{-cm}$, which is the bulk resistivity of copper. Brongersma has also confirmed experimentally that annealing at high temperatures ($\approx 400^{\circ}\text{C}$) results in an additional considerable enlargement of the grain structure accompanied by an additional decrease of the sheet resistance and desorption of the impurities that are incorporated during electroplating [29]. As a result, additional high-temperature annealing studies, which use various types

of annealing techniques, are now becoming more prevalent in the body of literature related to Damascene electroplated copper [31-36].

In addition to the benefits of high-temperature annealing described above, two recent studies by Brongersma [29] and Ritzdorf [19], which address self-annealing in fine damascene features, further highlight the need for high-temperature annealing of electroplated Cu films. In Ritzdorf's study it is demonstrated that self-annealing does not ensure the recrystallization of Cu in fine trench lines, which has also been previously observed by Jiang [31]. In particular, it was demonstrated by Ritzdorf that electroplated copper in 0.25- μm trench feature would not recrystallize after one week at room temperature even though the overlying Cu film had recrystallized. This investigation also showed that the annealing conditions are a function of trench line width in that 0.25- μm trenches require more thermal energy to achieve full recrystallization than 0.75- μm trenches.

Brongersma's study [29] attributes the observed difficulty of self-annealing in fine trench features to the reduced number of nucleation sites within the small volumes encompassed by such features, which retards the nucleation rate of secondary grains. It should be mentioned that the term nucleation is used somewhat controversially in this context and is meant to describe the onset of secondary grain growth. Brongersma also mentions that the film thickness within the trenches relative to the trench sidewalls may be another related factor retarding self-annealing in the trench features, based on studies with blanket films. For film thicknesses greater than 2 μm , grain growth is three-dimensional, and it is the number of nucleation sites per unit volume that determines the

transformation rate. When the layer thickness becomes smaller, grain growth becomes two-dimensional, and it is the number of nucleation sites per unit area that controls the dynamics of the self-annealing process [25]. The number of such available sites is reduced with thickness, and there appears to be a critical thickness of approximately 0.5 μm , below which grain growth is absent [28]. Jiang has also observed that the physical dimensions of blanket Cu electrodeposits and the presence of Damascene features affect the self-annealing kinetics [31]. In Jiang's study, it was shown that thin copper films take longer to transform than their thicker counterparts, which was attributed to the physical constraints imposed on the grain growth.

2.3 Texture of Electroplated Copper Films

The dominant texture component generally seen in both the as-deposited and recrystallized states of electrodeposited Cu in a Damascene materials system is a (111) fiber texture component. This texture component can be described as one in which the (111) planes are oriented parallel to the substrate surface with the fiber axis parallel to the film normal as shown in Figure 13. A significant (200) fiber texture component is also frequently observed in such films along with weak (511) and untextured (random) components. The most common method used to characterize texture is x-ray diffraction (XRD), although electron back scattering diffraction (EBSD) has often been used to characterize the microtexture at the grain level, especially within small Damascene features such as trenches [40].

The most frequent representations of texture are by pole figures generated by either XRD or EBSD techniques, which show the pole density for a specific set of

Figure 13: The orientation of the (111) crystallographic planes for Cu relative to the other two principle crystallographic planes (top) [55] and the substrate surface and fiber axis (bottom), for a (111) fiber texture. The fiber axis coincides with the [111] direction and is normal to the film surface. Other equivalent (111)-type planes are tilted 70.5° from the (111) plane that is parallel to the film surface.

crystallographic planes as a function of specimen orientation [41]. Both methods yield similar results for thin films with a strong fiber texture, but very weak textures are more readily detected by EBSD [40]. In the case of x-ray diffraction, the Schultz reflection method is commonly used to generate pole figures [42]. For fiber textures such as a (111) fiber texture, the use of pole figures is redundant due to their circular symmetry [43]. Therefore fiber plots, which are also referred to as texture plots, in which the diffracted intensity is plotted as a function of tilt angle (ω or φ) from the fiber axis, are commonly used. From such plots texture can be quantified for a particular crystallographic component in terms of its volume fraction and its maximum intensity ($I_{(111)\text{max}}$). In cases where the maximum intensity is displaced from the fiber axis, such textures are referred to as near-fiber textures [43]. The width of the texture distribution is also another important figure of merit frequently used to evaluate texture and can easily be derived from fiber plots. In these cases the width of the distribution is expressed as the tilt angle, or angular width, corresponding to a particular volume fraction for the texture component of interest. In the literature the 50, 63, 90, and 95 percent volume fractions, expressed as ω_{50} , ω_{63} , ω_{90} , and ω_{95} respectively, are the most common volume fractions used. Figure 14 exemplifies a hypothetical (111) fiber plot and illustrates some of the important points discussed above. In relation to fiber plots and the associated figures of merit discussed above, a high-quality texture component is considered to have a high maximum intensity, little or no displacement from the fiber axis and, more importantly, a large volume fraction and narrow distribution [43]. Many other less thorough and accurate methods of evaluating texture have been presented in the literature

Figure 14: An example of a (111) fiber plot used to evaluate texture quality. The peak area shown in dark blue corresponds to the 90% volume fraction of material with a (111) fiber texture. ω_{90} is the angular width of the distribution that corresponds to this 90% volume fraction. The light blue region near the bottom of the plot represents the untextured fraction or, more accurately, the volume fraction of material that does not exhibit a (111) fiber texture.

on electroplated Damascene Cu, which makes direct comparison of experimental results very difficult [23,28,44,46,51,52].

2.3.1 Barrier and Geometrical Influences on Texture

The barrier material and its degree of crystallinity have frequently been reported to influence the degree of (111) texture in the Cu seed layer, which, in turn, influences the (111) texture of the electrodeposit [44]. Ta and TaN are the two most common barrier materials found in the literature on electroplated Cu. Ta has been found to produce a strong (111) texture component, whereas TaN produces a very weak (111) texture [45]. The tendency of a strong (111) texture with the use of a Ta barrier layer has been attributed to a heteroepitaxial relationship at the barrier-seed layer interface [44,46,47]. This has been observed using transmission electron microscopy and does not exist in the case of amorphous TaN [44,46,47]. Wong has also shown that a strongly (111)-textured Cu seed layer, which has a low degree of surface roughness, will tend to promote a similar texture in the electrodeposited Cu [46]. He also showed that in-situ deposition of the barrier and seed layers is essential for developing a strong (111) texture in the seed layer [46]. In-situ deposited samples have a (111) texture that is about ten times stronger than that of a sample which is briefly exposed to air between the deposition of the two layers. In another study by Jiang, it was shown that a lower Cu seed layer deposition temperature (50°C) on a PVD Ta barrier resulted in a stronger texture in the Cu electrodeposit than for a seed layer deposited at 150°C [48].

With respect to Damascene features, Vanasupa [40,49] and Lingk [50] have shown using pole figure and texture plot analyses that the quality of the Cu (111) fiber texture

measured relative to the sample surface in interconnects fabricated with a Ta barrier layer and subsequently annealed generally degrades with decreasing linewidths. Blanket Cu films were also shown to exhibit a stronger (111) fiber texture than their counterparts within trench features [40]. In cases where the copper overlying the trenches (overburden) is removed prior to recrystallization, the degradation is associated with an increasing tendency for development of a sidewall (111) texture component with decreasing linewidths, since the fiber texture is measured relative to the film surface [40,50]. A (111) sidewall texture component originates from Cu grains that have their (111) crystallographic planes oriented parallel to the sidewalls of the trench. In contrast, a strong (111) fiber component and the absence of a (111) sidewall component were observed in cases where recrystallization occurs with the Cu overburden intact [40,50].

These results suggest some interesting features about the evolution of texture in Damascene Cu trench features. Firstly, the development of a (111) sidewall texture component during recrystallization suggests an increasing proportion of sidewall nucleation and growth with decreasing trench widths. Furthermore, this phenomenon exemplifies the fact that surface and interfacial energy minimization play a significant role in the development Cu texture in general, as the (111) crystallographic planes are the lowest surface energy planes for Cu [51]. Secondly, the absence of a (111) sidewall component intimates that the overlying Cu layer plays a dominant role in the evolution of texture within these fine features. In particular, it has been observed in FIB studies that Cu grains nucleate at the trench corners and propagate into the trenches during the self-annealing process [15,24,34,36]. In these cases, it would be expected that the texture

within the trenches is inherited to some degree by the superior (111) fiber texture of the overlying Cu layer.

2.3.2 Development of Texture in Self-annealed Films

To date there have been several studies that have addressed the development of (111) texture in blanket electroplated Cu films after room temperature recrystallization [23,45,48,52]. There appears to be conflicting reports in the literature as to whether the (111) texture degrades or improves pursuant to the self-annealing process, many of which are only semi-quantitative. Most of the studies that will be described below will focus on Ta as a barrier material with blanket Cu films due to their relevance to this investigation.

The study previously mentioned by Lee demonstrated that larger self-annealed grain sizes could be achieved with the use of higher electroplating current densities [23]. In the same study it was also reported that increasing the current density within the range of 5 to 50 mA/cm² resulted in an improvement in the (111) texture, based on a narrowing of the Bragg (111) peak. These results are complementary to the work of Wong who showed a correlation between the (111) texture quality and the self-annealed grain size [46]. In Wong's case the maximum intensity ratio of the Cu (111) and (200) peaks ($I_{(111)}/I_{(200)}$), based on texture plots of these two texture components from the Schultz reflection method, was used as the metric to evaluate texture. An increase in this ratio implies an increased number of (111) planes aligned with the fiber axis, which is normal to the film surface. Using this metric of texture, larger grains generally resulted in a higher $I_{(111)}/I_{(200)}$ intensity ratio and therefore a higher degree of (111) texture. In another study by Grunow, it was also shown that the (111) texture improves significantly after self-

annealing, which was supported by an increase in diffracted intensity and narrowing of both the (111) Bragg peaks and rocking curves [52].

In a study by Faust, which investigated Ta, TaN, and TaSiN as barrier materials, it was shown that there was a tendency toward a degradation of the (111) texture after an eleven-day self-annealing period for all barrier materials except TaSiN, which demonstrated a marked improvement in texture [45]. Faust used (111) fiber plots to evaluate the textures but failed to quantify his work in terms of the figures of merit that can be derived from such plots. Upon examination of his texture plots, however, it appears the degradation in texture took the form of a lower (111) maximum intensity as well as possibly lower (111)-textured fractions. With respect to Ta as a barrier material, which is most pertinent to this investigation, the electroplated copper films with a 10-nm thick barrier material suffered less texture degradation than those with a 25-nm thick barrier material. In the previously mentioned study by Jiang, which explored the effects of Cu seed deposition temperature on texture, it was also shown that the texture degrades significantly after a forty-eight hour self-annealing period [48]. The seed layer that was deposited at the lower temperature (50°C), however, suffered less degradation based primarily on the maximum (111) intensity from fiber plots.

2.3.3 Effect of High-Temperature Annealing on Texture

The aforementioned benefits of high-temperature annealing have inspired many studies to investigate the effects on texture [10,28,34,40,44,45,48,50]. There appears to be an increasing amount of evidence in the literature that the texture of Damascene electroplated Cu films degrades upon high-temperature annealing [10,44,45,48]. Several

studies have used annealing periods of thirty minutes to one hour at temperatures in the range of 400°C in an inert-gas environment [28,34,40,44,45,48,50]. Again, the results presented below will focus on results in which Ta was used as a barrier material due to its relevance to this investigation.

The previously mentioned studies by Faust [45] and Jiang [48] both demonstrate a further degradation in the (111) texture after a high-temperature annealing treatment that follows self-annealing. Both studies present fiber plots, but fail to quantify their results in terms of the figures of merit previously mentioned. The general trend illustrated in these plots is a significant lowering of the maximum (111) intensity and an apparent decrease in the (111) textured fraction. Dubin, on the other hand, has reported that the texture improves significantly after high-temperature annealing [34]. In this case the (111)-textured fraction decreased from 17 to 4 percent, with the width of the texture distribution decreasing by approximately a factor of two. For example, ω_{50} , the angular spread corresponding to the 50 percent (111) volume fraction, decreased from 1.07° to 0.55° after an annealing period of 30 minutes at a temperature of 400°C. A summary of the quantitative texture results produced from two different studies that employed inert-gas, high-temperature annealing of electroplated Cu films with Ta barrier layers may be found in Table 2. In both cases the figures of merit for texture were obtained from fiber plots derived from XRD pole figures.

Table 2: The (111) fiber texture results obtained from two studies that used high-temperature annealing treatments of blanket ECD Cu films, with Ta barrier layers in an inert-gas environment. The first study reported using a 400°C treatment for an unspecified period of time, while the second study reported using a 400°C treatment for 30 minutes in a forming gas. Both films are highly textured with respect to the (111) orientation and neither study reported the presence of other texture components. The intensity results are not directly comparable, as they are equipment dependent.

Film Thickness	ω_{50}	ω_{63}	ω_{90}	ω_{95}	$I_{(111)max}$	% Random	Reference
1.5 μm	0.55	0.77	3.4	4.29	1.25×10^5	4	35
1.5 μm	0.51	-	1.44	1.82	7000	< 5	40

2.3.4 Relationship between Stress and Texture

The results of the studies presented above illustrate conflicts in the literature on the evolution of texture in Damascene electroplated copper, both after self-annealing or high-temperature annealing. It is now becoming increasingly clear that the evolution of texture during recrystallization is related not only to the minimization of the surface and interfacial energies but also to the degree of residual stress in these films, which explains the wide variety of texture trends seen in the literature.

As previously mentioned, (111) and to a lesser degree (200) fiber texture components are the most commonly reported for electrodeposited Damascene copper. Riege recently presented a paper that modeled the evolution of texture in Damascene interconnects and blanket films [53]. In this work it is shown that the energy-minimizing texture in Cu results from a simultaneous minimization of both the strain and surface energies. Since the close-packed (111) plane is the lowest surface energy plane for Cu, conditions that favor surface energy minimization produce a (111) crystallographic orientation. A (100) orientation, on the other hand, is favored in cases where strain energy minimization is favored, which results from the crystallographic anisotropy of Cu. It is important to realize that a (100) orientation is used interchangeably in the literature with a (200) grain orientation, as both orientations are crystallographically equivalent in that both planes are parallel in the Cu unit cell. The interplanar d-spacings of (200) planes are, however, one-half those of (100) planes. In order to avoid confusion in future discussions, the (200) notation will be used as (100) Bragg reflections are theoretically impossible for Cu.

Reige further explains that grains with different textures have different elastic constants both in and out of the wafer surface, so the strain energy will differ from grain to grain. Grains with orientations leading to low strain energy densities will grow at the expense of grains with other orientations. In FCC metals such as Cu, Young's Modulus is a maximum in the $\langle 111 \rangle$ direction and a minimum in the $\langle 100 \rangle$ direction [54]. Films with a low strain energy density will thus have a (200) texture and those with a high strain energy density will have a (111) texture. The difference in strain energy density between (111) and (200) oriented grains in Cu has been reported to be $1.46\epsilon^2 \text{ GJ/m}^3$, where ϵ represents strain [44]. The surface energy density difference between (200) and (111) grains, on the other hand, is estimated as 20 kJ/m^3 for a $1\text{-}\mu\text{m}$ thick Cu film [44].

In another investigation, Lee used calculated values of ϵ , as well as measured values of elastic modulus, to determine a critical, thickness-dependent, threshold biaxial stress (σ_T) above which the (111) texture starts to degrade and a (200) texture emerges [28]. For the films used in his study, Lee calculated threshold stress values of 120, 96, 71, and 53 MPa for films with thicknesses of 0.35, 0.55, 1.0, and $1.8 \mu\text{m}$, respectively. These results are illustrated graphically in Figure 15 [28]. Lee verified these theoretical considerations experimentally using thermal cycling and did find that the (111) and (200) x-ray intensities decreased and increased respectively for a given film thickness once the critical stress was surpassed.

Based on the foregoing discussion, it is apparent that the wide variety of conflicting texture results in the literature are primarily due to the differences in the final film stress

Figure 15: A plot of the surface-interface and strain energy differences between (111) and (200)-oriented grains. The horizontal dashed lines are the surface-interface energy differences between (111) and (200)-oriented grains, for the four film thicknesses shown. The blue line is the strain energy difference between the (111) and (200)-oriented grains. A critical threshold stress (σ_T) is indicated for films of four different thicknesses and is determined by the stress level where the two curves intersect (black vertical lines). A copper film will start to develop a (200) fiber texture, once this critical stress is exceeded for a given film thickness [28].

in these Cu films, which result from different electroplating conditions, additive chemistries, and thermal histories. The behavior of incorporated film additives at the grain boundaries and the degree of grain growth leading to grain boundary elimination during recrystallization are both factors that can apparently lead to different residual stress levels in the resulting films. Geometrical factors such as film thickness, in the case of blanket films, or aspect ratio, in the case of trench or via features, are also factors to be considered [40].

In the aforementioned study by Brongersma which used a TaN barrier, it was shown that the initial (as-deposited) and final (self-annealed) film stresses in Cu films increase in the tensile direction as a function of current density for the plating chemistry used in that investigation [29]. These results were summarized in Figure 8 [29]. The stress is reduced in absolute terms for both initial tensile and compressive stresses during the self-annealing process. Based on this trend, Brongersma attributed the changes in stress to differing degrees of additive incorporation in the self-annealed films rather than grain boundary elimination. It was also shown that thermal cycling of these films at 3°C/minute up to 400°C after self-annealing resulted in some differences in the final film stresses, which tended to increase with current density after this high-temperature treatment. This trend is illustrated in Figure 16 [29]. Unfortunately, Brongersma did not characterize the texture of these films to determine if the (111) texture degraded as a result of the increased stress developed from this thermal cycling. Furthermore, the author made no mention of the possible sources of this trend of increasing residual stress levels in the annealed films in relation to increasing current densities.

Figure 16: Thermal hysteresis cycles to 400°C at 3°C/minute for five Cu films with different initial stresses levels obtained by varying the plating current density. Going from bottom to top, the current densities used were 2.38, 4.75, 9.5, 14.25, and 19 mA/cm². The results suggest that current density plays a role in the development of stress in electroplated Cu films after high-temperature annealing cycles [29].

In an independent experiment presented in the same paper [29], he did however measure the (111) and (200) texture components as a function annealing temperature for a film deposited at a current density of 0.75 mA/cm^2 , which would be expected to have a very high degree of additive incorporation [38]. The resulting trends are shown in Figure 17 [29]. The sudden increase in the (200)-textured fraction between 100 and 400 °C suggests an increase in the film tensile stress from grain boundary volume elimination [28,53].

Quite interestingly, Brongersma took one of the self-annealed films that was plated at 0.75 mA/cm^2 and performed an additional high-temperature anneal for 20 hours at 400°C and noted additional desorption of additive impurities, additional grain growth, and grooving at the grain boundaries [29]. He attributed the thermal grooving to grain boundary volume elimination resulting from additional grain growth. Unfortunately, Brongersma failed to characterize the final film stress or texture of this film.

2.4 Literature Summary

The ability to achieve a stable, low-resistivity, large-grained, copper microstructure with a high degree of (111) fiber texture in a Damascene materials system is dependent on many processing and materials factors. Even though the self-annealing process is of fundamental importance in the area of materials science, there are many drawbacks making its use impractical for semiconductor manufacturers. Electroplating variables such as current density and brightening additive can influence the recrystallization kinetics and can lead to metastable microstructures that are only partially recrystallized due to the presence of remnant incorporated plating additives.

Figure 17: (111) and (200)-textured volume fractions as a function of annealing temperature. The sudden increase in the (200) fraction between 100 and 400°C suggests an increase in the tensile stress level in the film. [29].

Even though the resistivity and stress levels in self-annealed films eventually stabilize, further secondary grain growth can be kinetically inhibited by the plating additives that remain in grain boundaries. Annealing at higher temperatures can lead to additional enlargement of the grain structure accompanied by additional decreases in resistivity due to the desorption of remnant incorporated electroplating impurities in blanket films. There has yet to be a systematic study, however, to determine if the final grain size in blanket copper films is independent of current density or brightening additive level after a high-temperature annealing treatment. Furthermore, there is no indication in the literature as to whether or not such electroplating variables influence the final grain size in fine interconnect features after high-temperature processing.

Annealing Damascene copper films at high temperatures can also lead to high tensile stress levels that are a consequence of grain boundary elimination stemming from extensive grain growth. Lee has shown that a critical stress exists, above which the (111) fiber texture begins to degrade and a less-desirable (200) crystallographic component begins to evolve due to the crystallographic anisotropy of copper [28]. Brongersma has also reported a current density dependence on the final film stress after high-temperature annealing cycles [29]. This dependence, however, has yet to be fully explored with respect to its potential influence on the (111) texture component.

CHAPTER 3

RESEARCH OBJECTIVES

A successful copper electroplating process for semiconductor on-chip interconnects using a Damascene materials system must consistently produce defect-free, large-grained films with a high degree of (111) fiber texture. Such film characteristics enhance the post-deposition CMP removal rate and uniformity [20] and, more importantly, provide a high degree of electromigration resistance and improve performance for semiconductor devices working at very high current densities over prolonged periods of time [57]. Electroplated Damascene copper films are typically deposited in the presence of organic brightening additives that are used in conjunction with other organic and inorganic additives to promote the "bottom up" filling of fine interconnect features [11]. Such films show a remarkable tendency to recrystallize at room temperature and the semiconductor industry has coined the term "self-annealing" to describe this process [17].

The period required for the self-annealing process to occur can take from hours to weeks, depending on process-dependent variables such as electroplating current density and brightener concentration, as well as the film thickness and level of geometrical constraint [20,21,31]. These electroplating variables can lead to different defect densities in the as-deposited films that influence not only the kinetics of the transformation but also the final grain size and degree of (111) fiber texture [23]. The grain size dependence is apparently related to the degree of impurity incorporation in the grain boundaries after the self-annealing process, which poses limitations to further grain growth [21,25,29]. The electroplating current density and brightener concentration are two process variables

that can lead to different degrees of impurity incorporation in electroplated copper films [38].

As a practical manner, a delay between process steps greater than 48 hours to allow self-annealing to occur is not acceptable in a fabrication environment. Some type of thermal annealing is therefore required to complete the recrystallization process so that the flow of product may not be interrupted or extensively delayed. In this vein, various forms of high-temperature annealing treatments either after deposition or self-annealing are being actively pursued by semiconductor equipment and device manufacturers and are becoming increasingly prevalent in the literature on Damascene copper for on-chip interconnects [31-36].

In addition to increasing production throughput, thermal annealing of the self-annealed copper microstructure has been reported to have additional materials benefits. These include a slight lowering of the final film resistivity to near-bulk values [35], additional grain growth [23], along with higher CMP removal rates of the copper overburden [20]. These benefit the integrated circuit manufacturer by improving the chip performance by further reducing the RC delay time [57], improving electromigration performance [57], and increasing the CMP production throughput and yield [20].

The quality of the (111) fiber texture component is primarily dependent on a competition between surface-interface and strain energy minimization [28,53], which may either improve or degrade after thermal annealing processes [34,45,48]. For this reason, development of residual film stresses that accompany grain growth after extensive high-temperature annealing can lead to a degradation of the (111) texture

component and the development of significant (200) component, which is undesirable for electromigration resistance [57]. The residual stresses in such films have been shown to depend on the electroplating current density not only after self-annealing but also after an extensive thermal annealing treatments in an inert-gas environment [29].

3.1 Research Objectives and Scope of Experimental Work

The primary purposes of this investigation are to quantitatively evaluate the final in-plane Cu grain size and distribution as well as the quality of the (111) fiber texture in blanket, unpatterned electroplated copper films after an extensive high-temperature annealing treatment using a wide range of electroplating conditions. Additionally, a thorough description of the annealed Cu microstructure in both these unpatterned films, as well as Damascene trench features with line widths of 0.50 and 0.35 μm , will be performed for all experimental conditions.

The electroplating variables of current density and brightening additive level will be employed in this investigation, using the jet-agitation electroplating method. The electroanalytical technique of cyclic voltammetric stripping (CVS) will be used to monitor and adjust the brightening additive level in the electroplating bath, based on its chemical activity. High-temperature annealing will be accomplished using the inert-gas sweep method. Sheet resistance measurements, using the non-destructive eddy current method, will be used to compare experimental duplicates and different experimental conditions. These measurements will also be used to assess the final resistivity of the blanket Cu films after the high-temperature treatment of these films. High-resolution focused ion beam (FIB) imaging in plan view and cross section will be employed for

grain sizing purposes, as well as a comprehensive description of key microstructural features in both the patterned and unpatterned film regions. X-ray diffraction will be used to assess the (111)-textured fraction and its associated distribution in the blanket film regions. The x-ray data, which includes Bragg-Brentano scans and rocking curves, will be processed in a novel way that is comparable to the (111) fiber (texture) plots obtained from the time-intensive pole figure method commonly found in the literature.

3.2 Experimental Matrix

The experiments to be performed will be conducted within the framework of a 3^2 full-factorial experimental design. A total of nine unique experimental conditions, which simultaneously vary both brightener additive level and electroplating current density, will be performed using 200-mm Si wafers with a Damascene materials system which contain both blanket and patterned film regions. Three extreme levels, designated as low, medium and high, will be used for each of these two electroplating variables. Two replications will be performed for each unique set of conditions. A summary of the electroplating variables to be used in this study may be found in Table 3. Each of these nine conditions will be referred to frequently herein by only the condition number. The contributions of each collaborating organization to the processing and metrology required for this study is found in Table 4.

3.3 Overview of Experimental Program

A flow chart summarizing the processing, metrology, and analysis steps required for this investigation may be found in Figure 18. Steps 1-4, which involve preparation and analysis of the plating bath as well as electrodeposition, will be repeated twice for

Table 3: A summary table outlining the experimental matrix for this investigation. There are two electroplating variables, each at three levels, making this a 3^2 full-factorial design experiment.

Condition	Current Density (mA/cm²)	Additive Level (ml/l)
1	15 (low)	0.75 (low)
2	45 (medium)	0.75 (low)
3	105 (high)	0.75 (low)
4	15 (low)	1.50 (medium)
5	45 (medium)	1.50 (medium)
6	105 (high)	1.50 (medium)
7	15 (low)	2.25 (high)
8	45 (medium)	2.25 (high)
9	105 (high)	2.25 (high)

Table 4: A summary of the equipment provided for this study by the collaborating industrial organizations.

<i>Equipment Type</i>	<i>Manufacturer/ Model</i>	<i>Organization</i>	<i>Purpose</i>
<i>CVS System</i>	Custom	Jets Technology	Brightener Activity
<i>Jet-agitation ECD System</i>	Custom	Jets Technology	Cu Electrochemical Deposition
<i>Inert-gas Annealing System</i>	Custom	Steed Technology	High-Temperature Annealing
<i>Eddy Current Sheet Resistance System</i>	Prometrix NC100	KLA-Tencor	Sheet Resistance Measurements
<i>XRD System</i>	Scintag X2	Thermo-ARL	(111) Texture Analysis
<i>FIB-SEM System</i>	FEI 820	Accurel Systems	Cu Microstructure and Grain Size Analysis

Figure 18: A flowchart summarizing the basic processing, metrology, and analysis steps used in this investigation.

each experimental condition as two wafers will be processed. After approximately a one-week period, annealing will be done in lot sizes of six wafers, corresponding to three current density levels at a given additive level, starting with the lowest additive level first. The entire process will be repeated twice to accommodate the medium and high additive levels and complete the matrix. With the wafer processing completed, the sheet resistance measurements will be done as a group of 18 wafers, which encompasses the entire experimental matrix. After the sheet resistance measurements and analysis are completed, the duplicate wafers corresponding to each condition are to be divided into two metrology groups: the first for x-ray diffraction and the second for FIB-SEM imaging. (111) texture and microstructural analysis, including grain sizing, will then be performed on the raw data sets corresponding to each set of metrology wafers, respectively.

3.4 Description of Experimental Wafers

Twenty-four Damascene copper CMP characterization wafers with a wide array of pre-fabricated Damascene trench and via structures with different pitch densities are provided by Jets Technology [58]. These wafers have a total of 9 identical dice with a mask floorplan that is shown in Figure 19 [59]. The row-wise numbering scheme that will be used to identify each of the 20-mm square die is illustrated in Figure 20. These wafers are 200-mm, (100) Si wafers with an etched 0.8- μm PETEOS SiO_2 layer, a 25-30 nm CVD Ta barrier layer, and a 125-nm composite CVD-PVD Cu seed layer. A cross-sectional view of a typical trench structure, which includes the electroplated copper, is

Figure 19: The mask layout for each of the identical 20-mm square die on the 200-mm CMP characterization wafers used in this study. The 0.5/0.5 and 0.35/0.35 pitch density trench structures, as well as selected unpatterned blanket film regions, were used in this investigation. A 0.5/0.5 structure implies 0.5- μm linewidths, with 0.5- μm line spacings [59].

	1	2	3	4	5			
	6	7	8	9	10	11	12	
13	14	15	16	17	18	19	20	21
22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39
40	41	42	43	44	45	46	47	48
49	50	51	52	53	54	55	56	57
	58	59	60	61	62	63	64	
	65	66	67	68	69			

Figure 20: The row-wise numbering scheme used to identify each of the sixty-nine, identical, 20-mm square die on the experimental wafers. Note that some dice, such as 65, are only partial dice, in that they are not truly 20-mm squares.

shown in Figure 21 [59]. A representative photograph of one of the experimental wafers prior to electrodeposition is shown in Figure 22.

Figure 21: A cross-sectional view of a typical Damascene trench structure for the wafers used in this investigation . The layer thickness for each of the materials in this system are indicated. The wafers were provided as shown with the exception of the electroplated Cu, which was deposited in this study [59].

Figure 22: Two photographs of a typical 200-mm wafer used in this investigation prior to electrodeposition. The small colored squares seen in the top photograph are arrays of trench structures with different linewidths and pitch densities.

CHAPTER 4

EXPERIMENTAL METHODS

4.1 Electrochemical Deposition

The basic components of a typical electroplating cell used for the electrodeposition of copper is shown schematically in Figure 23. Electrodeposition of a metal is performed by immersing a conductive surface into a solution containing ions of the metal to be deposited. With copper electrodeposition, the electrolyte is highly acidic and typically is composed of aqueous copper sulfate (CuSO_4) and a support electrolyte such as sulfuric acid (H_2SO_4) to make the solution more electrically conductive [10]. The conductive surface onto which material is to be deposited is electrically connected to an external power supply and current is passed through the solution. In the case of electrodeposition of copper onto a silicon wafer with a barrier metal, the wafer is first typically coated with a thin conductive layer of copper (seed layer) approximately 100 nm in thickness and immersed in a solution containing cupric ions. After electrical contact is made to the seed layer, current is passed through the solution to reduce the copper ions to metallic copper on the wafer surface.

Since cupric ions are reduced to solid copper at the wafer surface, the wafer is referred to as the cathode. The reduction reaction occurring at the cathode is represented by Equation (2). To complete the electrical circuit, another electrically active surface, known as the anode, is required in the conductive solution. To maintain electrical neutrality of the solution, an oxidation reaction occurs at the anode to balance the current flow at the cathode. In the absence of any side reactions, the total charge delivered to the

Figure 23: A schematic of the basic components typically used for the electrolytic deposition of copper from an aqueous solution.

cathode during electroplating is directly proportional to the amount of metal deposited [60-65]. This is known as Faraday's Law of Electrolysis.

In addition to the basic components described above for a typical acid copper sulfate electroplating bath, organic and inorganic plating additives are also commonly used. In this particular application, they have a dramatic effect on the filling mechanism within fine submicron Damascene features such as via or trench structures [10,11]. Key components in most commercially available additive packages include organic compounds that act as inhibitors, grain refiners, and ductilizers. Used alone, these additives have a minimal effect on the leveling of the deposit. When formulated together, they impart a synergistic effect that maximizes the leveling effect [10]. In this application, the use of the term leveling refers to uniform deposition within fine features (i.e. filling up fine recesses), also commonly referred to as gap filling.

Brighteners, which are of prime importance in this study, are generally organic compounds that contain sulfur and other functional groups. Examples include thiourea, 4,5-dithiooctane-1,8-disulfonic acid, and mercapto-propane sulfonic acid [10]. Brighteners have a grain-refining effect in that they produce small-grained deposits that appear bright to the eye. They function by preventing the formation of copper at preferred locations through enhancing the formation of new-deposit nuclei, as opposed to the growth of existing nuclei [10]. In addition to brighteners, two other classes of additives used for Damascene copper electroplating include levelers and suppressors (inhibitors). These additives will not be discussed here, but a good general review may be found in a recent paper by Mikkola [10].

Many processes that occur at the metal-solution interface dictate the rate at which any cathodic reduction reaction occurs. This interface is commonly and most simply characterized as an electrical double layer (Helmholtz layer or diffusion layer) in which the metal surface is negatively charged and the bulk solution is positively charged. These two layers of charge are separated by a thin stagnant layer of solution in which potential and concentration gradients exist.

When an electrode is made part of an electrochemical cell through which current flows, its potential will differ from the equilibrium potential. The difference between the two potentials is known as the overpotential. The overpotential required to surpass the hindrance of the electrode reaction is composed of several partial reactions, any of which can control the overall reaction rate. These reactions include charge-transfer, diffusion, chemical, and crystallization [38]. Even though the slowest partial reaction is the rate-determining step, several partial reactions can have low reaction rates and can therefore be rate-determining [38]. The rate-determining step in acid copper sulfate electroplating has been reported to be the charge transfer reaction [30]

The surface diffusion of copper adatoms or adions, which is related to crystallization, is also another important factor in the kinetics of the overall reaction [70]. The use of plating additives further complicates the kinetics and mechanisms of the electrodeposition process at the metal-solution interface and is beyond the scope of the

current discussion. A good review on the mechanisms by which additives act at the metal-solution interface may be found in a paper published by Franklin [69].

The general relationship between electroplating current and electrode potential was first established empirically by Tafel in 1905 [38]. Under conditions typical of most electroplating processes, the current flow is approximated by an exponential relationship [38]. Figure 24 shows a current density-potential curve typical of a copper electrodeposition process [71]. As the potential is scanned from equilibrium to more negative values, the current increases in an exponential manner (Tafel region), where the overall deposition rate is determined largely by charge-transfer kinetics at the cathode. As the potential continues to increase, mass transfer effects become predominant and a limiting current plateau is reached. This results when the species reacting at the cathode (Cu^{2+}) no longer reach the metal-solution interface at a rate sufficient to maintain the high reaction rate. As a general rule, most plating processes are operated at current densities no greater than 30-50% of the limiting current in order to maintain quality deposits [38,71].

To ensure the mass transfer rate is large compared to the overall reaction rate and uniform across the wafer surface, various methods of solution agitation are used [71]. Convection is the most important mode of mass transport, and can vary from laminar to turbulent flow [71]. In electroplating cells, convection is generally achieved by some form of solution agitation, which ultimately allows the use of higher current densities and cathode efficiencies to achieve higher deposition rates. Agitation, in effect, decreases the width of the diffusion layer between the cathode and the bulk electrolyte and thus allows

Figure 24: A typical current density-potential curve for a copper electrodeposition process. In the Tafel region the current starts to rise exponentially [71].

for more efficient mass transport [72]. Cathode rocker motion, ultrasonics, solution pumping, and moving paddles are common methods to achieve adequate solution agitation. Rapid cathode rotation in conjunction with the impingement of jets of solution have been shown to be the best combination to sustain very high current densities and will be the method employed in this study [72].

4.1.1 Equipment and Materials

The materials required for electroplating were Shipley-Ronal Copper Gleam® PPR Carrier (Carrier) [73], Shipley-Ronal Copper Gleam® PPR Additive (brightener) [73], and Enthone-OMI premixed CUBATH® M acid copper electrolyte [74]. These three components comprise the contents of the electroplating bath used in this investigation. The chemical makeup of the acid copper electrolyte solution, as specified by the manufacturer, is shown in Table 5 [74].

In this electrolyte, the copper sulfate provides as source of Cu^{2+} ions that are reduced to Cu metal during electrodeposition. The sulfuric acid is included to reduce the solution resistance thus making the electrolyte more conductive, and the Cl^- (from HCl) functions as an inorganic additive that works synergistically with the organic additives [10,58]. Each five-gallon lot of the electrolyte is carbon purified, analyzed, and performance tested by the manufacturer, thus making it ready for immediate use. Using a commercially available pH meter (Orion Model 763), the pH of the Enthone-OMI premixed CUBATH® M acid copper electrolyte was found to be approximately 0.5. Additional materials required for electroplating included standard Pyrex® laboratory

Table 5: The Enthone-OMI premixed CUBATH® M acid copper sulfate electrolyte components as specified by the manufacturer [74].

<i>Component</i>	<i>Nominal Value</i>	<i>Operating Range</i>
<i>Copper Sulfate</i>	170 g/l	150-225 g/l
<i>Sulfuric Acid</i>	67 g/l	59-75 g/l
<i>Chloride Ion (from HCl)</i>	70 mg/l	50-90 mg/l

glassware such as volumetric pipets, graduated cylinders, and Griffith beakers for measuring solution volumes and taking samples from the plating cell for CVS analysis. The CVS technique, which was used to analyze and monitor the brightening additive activity in the electroplating bath, will be discussed in Sub-section 4.2.

The primary equipment required for electroplating included the Jets Technology electroplating system and the CVS equipment described in Sub-section 4.2 [13,58]. A schematic of the electroplating system, along with all process piping that connects the various components, is exhibited in Figure 25. This tool is a research and development system that operates entirely without automation. The primary components are the electroplating cell, the 50-liter reservoir tank, the filtration unit, the recirculating chiller, and a high-pressure chemical pump. Instrumentation to regulate process parameters such as pressure, flow rate, and temperature are also included with the system.

The particular valve configuration used depends on the function being performed. Such functions include electrodeposition, filling the cell with fresh electrolyte, removal of organic bath additives, and solution homogenization. For example, during electroplating the plating solution will flow from the pump, through the isolated 0.1- μm filter (located on the left-hand side of the filtration unit), and into the left-hand side of the plating cell via the pressure and flow instrumentation. From the plating cell, the solution will then flow over a weir (within the cell), into the reservoir, and finally back to inlet of the chemical pump. At any given time during the electroplating process, the cell contains approximately 10 liters of the total 50-liter volume. The continuous flow of plating fluid

Figure 25: A schematic of the Jets Technology electroplating system showing all components and process piping.

through the cell during the electrodeposition process allows for the continuous replenishment of fresh, homogenized plating solution.

A detailed view of the electroplating cell is shown schematically in Figure 26 and pictorially in Figure 27. This system is designed with a stationary cathode (wafer) and a rotating anode jet assembly (RAJA) [13], which are in close proximity and coaxial with respect to one another. In this figure, the electrical components and connections required for electrodeposition are also shown. In the configuration shown, the equipment is set up for direct-current (DC) plating with a primary power supply (Kepco Model ATE36-30M DC power supply) and the option for a DC bias voltage (Kepco Model 20-10M Bipolar Operational Amplifier/Power Supply) that can be applied separately to the substrate (wafer). With the appropriate power supplies and a waveform generator, the system can also be operated in the pulse and pulse-reverse current modes. Further details on the design and functionality of the cell may be in US Patent 5,421,987 issued to Cohen and Tzanavaras [13].

One of the novelties of this work is embodied in the design of the anode utilized in this electroplating cell. Cohen and Tzanavaras describe the anode as a rotating anode jet assembly (RAJA) [13]. A front view of the RAJA is shown in Figure 28. Six pie-shaped anode segments composed of phosphorized (certified 0.045% phosphorous by weight) copper are interposed between six rows of high-pressure jet nozzles, which form a "virtual anode circle," according to the description given in the patent [13]. The anode segments are connected electrically to a common metal ring on their backside. With the cathode (wafer) and RAJA facing each other in close proximity and oriented vertically in

Figure 26: A detailed view of the Jets Technology research and development electroplating cell showing all key components. Note that the electrodes are oriented vertically with respect to the horizontal.

Figure 27: Two photographs of the Jets Technology electroplating cell without the removable cathode assembly that houses the substrates.

Figure 28: A schematic (top) and picture (bottom) of the six-inch rotating anode jet assembly (RAJA) embodied in the design of the Jets Technology electroplating cell [58].

the plating cell as previously shown in Figure 26, the high-pressure jet nozzles expel the electrolyte in a conical shape that is essentially normal to the wafer, with partial overlap between adjacent fluid cones. These impinging powerful jets create a uniform turbulent flow at the substrate surface and provide efficient agitation and solution replenishment in both high and low aspect ratio features.

As compared to more conventional methods of solution agitation, this method facilitates improved leveling and allows the use of significantly higher current densities by decreasing the length of the diffusion layer [13,72]. The higher current densities, in turn, allow for plating at substantially higher rates without sacrificing the strict gap-filling requirements of the copper Damascene process. Cohen has reported plating rates in excess of 1.5 microns per minute while being able to fill 0.06- μm features with aspect ratios of approximately 28:1 [75]. Most commercially available plating systems that are used in copper Damascene applications (such as fountain platers or paddle cells), typically report deposition rates of approximately 0.15-0.30 μm per minute. Cohen has suggested that the rotation speed of the RAJA, which affects the frequency of jet pulsation, is a critical factor in determining the micro-uniformity or gap-filling capabilities of the electrodeposit [13]. It is also noteworthy that the anode-cathode area ratio is less than one for this cell. In most designs, which do not use impinging jets, this ratio typically assumes a value greater than one [72].

4.1.2 Electroplating Method

4.1.2.1 Deposition Rate

Similar to other deposition process, electroplating often requires the use of calibration curves under a specific set of conditions to establish the deposition rates to a reasonable degree of accuracy. In the present work, the copper deposition rate was estimated from fundamental principles. The time, t , required to electrodeposit a metal film of thickness, h , at a current, i , may be expressed as

$$t = \frac{h\rho AnF}{iM} \quad (5)$$

where t is the time expressed in seconds, h is the film thickness in cm, ρ is the theoretical density of Cu expressed in g/cm³, A is the surface area of the cathode expressed in cm², n is the number of electrons transferred in the reduction reaction, F is Faraday's constant (96,487 Coulombs per gram-equivalent weight), i is the current expressed in A or C/s, and M is the gram molecular weight expressed in g/mol [58]. This expression assumes that every two electrons produce one Cu atom in the reduction process according to the reduction reaction described in Equation (2) occurring at the cathode surface. In other words, Equation (5) assumes a 100% cathode efficiency. This expression has its basis in Faraday's Law of Electrolysis, which states that the quantity of substances undergoing chemical change at each electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolytic cell.

Using Equation (5), the plating times and DC currents required to achieve a 1.5- μm thick Cu film at the three current densities of interest were calculated and are summarized in Table 6. It should be noted that current density is defined in terms of the actual electrodeposition setup or process as

$$j = \frac{i}{A} \quad (6)$$

where j is the current density, A , the total electrode (wafer) area, and, i , the DC plating current. For clarity, it should be noted that the current densities shown in Table 6 are approximate from the standpoint that they are based on the surface area of a blanket, or unpatterned, 200-mm wafer with an edge exclusion of about 2 mm. In actuality, the true current density would be somewhat smaller due to the additional surface area encompassed by the many trenches and vias contained within the 69 patterned dice on each wafer. In practice, electroplating current densities for wafer-type applications are generally presented using the former approach, which assumes unpatterned wafers.

4.1.2.2 Preparation for Electroplating

To purge the electroplating system of any organic contaminants, deionized water (20 $\text{M}\Omega$) was allowed to cycle through the entire system, including the activated carbon filter, for approximately 48 hours. After removing the water, 50 liters of fresh, certified Enthone-OMI CUBATH® M additive-free acid copper electrolyte were introduced into the reservoir of the plating system.

Table 6: A summary of the electrodeposition parameters used for the three current density levels to achieve a nominal film thickness of approximately 1.5 μm .

Current Density (mA/cm²)	DC Current (A)	Plating Rate ($\mu\text{m}/\text{min}$)	Plating Time (seconds)
15	4.5	0.35	256
45	18.0	1.4	64
105	31.0	2.4	37

With the electrolyte circulating through the system, 750 ml of Shipley-Ronal Copper Glean® PPR Carrier (carrier) were then introduced and thoroughly mixed with the electrolyte using a 10-minute homogenization cycle. 11.25 ml of Shipley-Ronal Copper Glean® PPR Additive (brightener) were then carefully measured using volumetric pipets and added to the recirculating volume of plating solution to achieve an absolute volume concentration of approximately 0.75 ml/l of brightener.

4.1.2.3 Cathode Assembly Preparation

The removable cathode assembly onto which the substrate is loaded is shown in Figure 29. Electrical contact is made between the primary electrical terminal and the front side of the wafer through an electrically-conductive, elastomeric O-ring situated on the backside of the cathode assembly. Prior to each deposition, the O-ring was soaked in a 50-g/l oxidizing solution of ammonium persulfate to remove any powdery copper deposits from previous work. The O-ring was then thoroughly rinsed with DI water, wiped dry, and properly seated into the O-ring groove. Electrical continuity between the electrical terminal on left-hand side of the cathode assembly and the O-ring was then verified at 45° increments around the circumference of the O-ring using a standard ohmmeter. During the actual deposition work, electrical continuity was checked before each deposition and the O-ring treated with ammonium persulfate as needed.

4.1.2.4 Substrate Preparation

Before each deposition, the substrate was placed face down with the film (seed layer) side against the O-ring of the cathode assembly. It was then secured against the O-ring by tightening four screws that pass through four equally-spaced Teflon clips (wafer-

Figure 29: A photograph of the removable cathode assembly that is designed to accommodate 200-mm Si substrates.

retaining clips), which press against a plastic wafer-shaped retainer situated between the backside of the wafer and the clips. Front and backside views of the cathode assembly loaded with a substrate are shown in Figure 30. Electrical resistance between the edge of the copper seed layer on the front side of each wafer and the primary electrical terminal on the top of the cathode assembly was checked using a standard ohmmeter. The resistance was measured at 45° intervals on each wafer and recorded. As suggested by Cohen, the maximum allowable resistance between the seed layer and the contact was 1 Ω [58]. In most cases, the actual measured resistance ranged between 0.1 and 0.2 Ω .

4.1.2.5 Electrodeposition

The most efficient approach to satisfy the deposition requirements of the experimental matrix was to work in the order of increasing volume concentrations of brightener and increasing current densities. That is to say, starting with lowest brightener additive level (0.75 ml/l) that is based on the activity of fresh brightener from the anodic peak area of a derived CVS calibration curve (Sub-section 4.2), the wafers were deposited in order of increasing current density. The same approach was used for the intermediate (1.5 ml/l) and finally the highest additive level (2.25 ml/l) to complete the matrix.

A summary of the steps required to satisfy each unique combination of current density and additive level is shown in Figure 31. As indicated in this figure, an extensive number of CVS analyses were needed to maintain strict control of the brightener activity at a constant carrier level of 15 ml/l. In order to be consistent with the methodology used to establish a CVS calibration curve (Sub-section 4.2), 50-ml samples were taken directly

Figure 30: Backside (top) and frontside (bottom) views of the cathode assembly loaded with a 200-mm substrate prior to copper electrodeposition.

Figure 31: A flowchart summarizing the electrodeposition steps required to satisfy each unique condition of the experimental matrix.

from the plating solution before and after each deposition and diluted to a total volume of 250 ml and achieve a 4:1 dilution factor. Adjustments were then made to the bath to achieve an anodic peak area that was within $\pm 5\%$ of the target value defined by the CVS calibration curve. In the vast majority of the cases, it was necessary to add brightener after each deposition to achieve the desired peak area. In the rare cases of overshoots, it was necessary to reduce the brightener activity by plating a dummy wafer over extended periods of time and reanalyzing the plating solution. The electrodeposition parameters common to all depositions that were suggested by Cohen and based on previous experimentation with this equipment are shown below in Table 7 [58].

At the beginning of each set of experimental runs, the chemical pump and recirculating chiller were energized. The plating solution was then allowed to flow in a closed loop between the reservoir and pump through the 0.1- μm cartridge filter for 15 minutes to remove any particulates, homogenize the additive constituents in the plating solution, and achieve the desired plating temperature. The plating cell was then filled by diverting flow to the bottom inlet of the cell using the closed-loop flow scheme shown in the top diagram of Figure 32. With the electroplating cell filled and solution continuously flowing over the weir, solution flow was then diverted to the side inlet of the cell to create the closed-loop flow pattern shown in the bottom diagram of Figure 32. A sample was then taken from the bath near the weir for CVS analysis and the bath adjusted as required to achieve the desired brightener activity. The valve to the RAJA was then adjusted to achieve the necessary pressure and flow requirements outlined in Table 7.

Table7: The electrochemical deposition parameters common to all nine conditions of the experimental matrix.

<i>Parameter</i>	<i>Value</i>
<i>Jet Nozzle Pressure</i>	40 PSI
<i>Plating Solution Flow Rate</i>	3.5 - 3.8 GPM
<i>RAJA Rotation Speed</i>	20 RPM
<i>Anode - Cathode Spacing</i>	2.8 cm
<i>Anode - Cathode Area Ratio</i>	0.75: 1
<i>Collimator Screen Position</i>	Not Used
<i>Wafer Bias Current</i>	Not Used
<i>Deposition Temperature</i>	21.5 +/- 1.0 °C

Figure 32: Flow schemes used to fill the electroplating cell (top) and to electroplate (bottom). The arrows indicate the direction of solution flow.

Before each deposition, the temperature of the plating solution was recorded and the appropriate current level preset on the DC power supply in accordance with Table 6. With the substrate properly secured in the cathode assembly and checked for electrical resistance, the fixture was then suspended vertically in the cell and allowed to sit idle in the acidic bath for 15 seconds to remove any surface oxidation on the copper seed layer. The power supply was then energized and the wafer plated for the appropriate time interval at the preset current level in accordance with Table 6. The applied potential corresponding to each current setting was also recorded from the power supply, and the results are summarized in Table 8.

After each deposition, the wafer was quickly removed from the cathode assembly, thoroughly rinsed in deionized (DI) water, dipped into a 10% solution of hydrochloric acid (HCl), re-rinsed with DI water, and blown dry with pressurized clean dry air (CDA). The HCl dip is necessary to minimize the occurrence of post-deposition haziness from surface oxidation [38]. The two DI water rinsing steps are also very critical in that post-deposition acidic attack of the electrodeposited copper film can occur if not performed quickly and thoroughly.

The brightener activity was then rechecked before the next deposition and adjusted as necessary. After each group of six wafers (corresponding to three current density levels at a given additive level, with two duplicate wafers for each condition) were completed, they were stored for one week in a clean environment for the subsequent high-temperature annealing process.

Table 8: A summary of the electrodeposition parameters used for the three current density levels that includes the voltage values recorded from the DC power supply.

<i>Current Density (mA/cm²)</i>	<i>DC Current (A)</i>	<i>DC Voltage (V)</i>	<i>Plating Time (seconds)</i>
15	4.5	0.5	256
45	18.0	1.0	64
105	31.0	2.5	37

4.2 Cyclic Voltammetric Stripping

The method used to analyze the brightener activity, one of two key variables in this investigation, is a technique known as cyclic voltammetric stripping (CVS) [60-65]. CVS is an analytical electrochemical technique for the quantitative determination of organic additives, their components, and contaminants in electroplating solutions such as those used in acidic copper sulfate electroplating [60]. The chemical activity, or effective concentration, of such components can not be determined by their absolute concentration due to the many interactions taking place between the components themselves and their oxidation byproducts [60]. It should be emphasized that this is an electrolytic method in which an external source of energy is supplied to drive an electrochemical reaction which would not normally occur [61]. The fundamental principles of electrochemical deposition are therefore also applicable to the CVS technique. In this application, the basis for measuring the additive activity is the magnitude of the effect the brightener additive has on the electrodeposition kinetics in the acid copper sulfate system. Similar to all other voltammetric techniques, the external driving force is an applied potential, and the resultant current is the analytical signal. [62].

The basic equipment requirements for a CVS analysis are shown in Figure 33 [64]. The analysis is performed in an electrochemical cell using a three-electrode system, which are known as the working electrode (WE), the secondary electrode (SE), and the reference electrode (RE). With this method, the potential of the inert WE is cycled at a constant rate in the plating bath so that a small amount of metal is alternately deposited on the electrode surface and stripped off by anodic dissolution. During the scan, the

Figure 33: The basic equipment requirements for cyclic voltammetric stripping [64].

current at the working electrode is measured as a function of potential, with the data being collected on a standard XY recorder. The potentiostat functions to allow accurate application of the potential from the signal generator to the WE and the measurement of the resulting current [62-64]. The potential of the WE, which is of primary interest, is always measured with respect to that of the RE, which remains constant throughout the course of the analysis. In the absence of any significant ohmic (IR) drops, this effective measured potential may thus be defined as [61]

$$E_{WE}(RE) = |E_{WE} - E_{RE}| \text{ as } IR \rightarrow 0 \quad (7)$$

In this expression, $E_{WE}(RE)$ is the potential of the WE with respect to the RE, E_{WE} the potential of the WE, E_{RE} the fixed potential of the RE, and IR the ohmic drop from the plating solution, which is assumed to approach 0 for highly conductive aqueous solutions. It is this value that is measured by the high impedance voltmeter (HIV) and recorded on the X-axis of the XY recorder shown in Figure 33 [64]. For simplicity and to be consistent with the literature, $E_{WE}(RE)$ will simply be expressed as E_{WE} herein, as it is always assumed that the potential of the WE is measured with respect to the RE. As a final note, it should be mentioned that the SE, the last of the three electrodes, merely functions as a source or sink of electrons for the electrochemical reaction of interest at the WE [63].

As the potential of the WE is changed in a pre-determined manner, a current will flow between the WE and the SE that originates from the complementary oxidation-reduction reactions occurring at each electrode-solution interface. In a CVS analysis, the

current flowing at the WE-electrolyte interface is measured by an electrometer circuit within the potentiostat as a function of E_{WE} , and is recorded on the Y-axis of the XY recorder shown in Figure 33 [64]. For reactions obeying Faraday's Law, the instantaneous current flowing to or from the WE is given by [63]

$$I = zFAJ \quad (8)$$

where I is the current in A, F is Faraday's constant in C/mol, z is the number of electrons transferred, and J is the flux of material reacting in mol/m². The current can thus be viewed as a measure of the rate at which an electrochemical reaction occurs, and this rate is determined by two factors [63]:

1. The rate of the overall electron transfer process occurring at the electrode surface.
2. The rate of mass transport of the electroactive species to the electrode.

An example of the repetitive cyclic triangular potential excitation that is applied to the WE-solution interface in CVS experiments is shown in Figure 34. Under normal operation, the potential at the WE-solution interface is scanned linearly from an initial value $E_{initial}$, to a final value E_{final} , and then back to $E_{initial}$ at a constant scan rate (v) by the signal generator to complete one cycle. $E_{initial}$ and E_{final} are generally referred to as the switching potentials of the WE. The labeled segments in Figure 34 may thus be interpreted the following way:

- a) Forward scan from -0.3 V to $+1.5$ V at a scan rate of 100 mV/s.
- b) Direction of scan switched at a switching potential of $+1.5$ V.

Figure 34: An example of the repetitive, cyclic, triangular, potential excitation applied to the working electrode in a CVS analysis.

- c) Reverse scan from +1.5V to -0.3V at a scan rate of 100 mV/s.
- d) Termination of first cycle.

Although the scan is frequently terminated at the end of the first cycle (point d), it can be continued for any number of cycles, which gives rise to a technique known as cyclic voltammetry. The CVS technique is considered to be a subset of cyclic voltammetry. The scan profile, or potential sweep range, used in a particular experiment is determined by the location of the oxidation-reduction couple of interest [63-65].

As mentioned above, with CVS experiments the current at the working electrode is measured as a function of the WE potential, with the data being collected on a standard XY recorder. Such a scan is known as a cyclic voltammogram, an example of which for a reversible chemical reaction of a single electroactive species is shown in Figure 35 [64]. It is important to realize that the potential axis is also a time axis, as a constant sweep rate is used throughout the entire experiment [60,62,64]. In examining Figure 35, one can see that two characteristic peaks develop. These peaks occur due to changes in the concentration gradient of the analyte in the diffusion layer, and the exact shape of these peaks depends on solutions to Fick's Second Law of Diffusion with appropriate boundary conditions. The peak that occurs during the negative potential sweep at negative current values is referred to as the cathodic peak and is indicative of a reduction reaction occurring at the WE [62,63,64]. Similarly, the positive peak that appears during the positive potential sweep is referred to as the anodic peak and represents an oxidation reaction. It should be apparent that the WE can function as either an anode or cathode, depending on the direction of the potential sweep.

Figure 35: A typical cyclic voltammogram for a reversible chemical reaction of an electroactive chemical species [64].

In consideration of the fact that the potential axis is also a time axis, the area under the cathodic peak represents the total charge transferred during a reduction reaction [60,62,64]. Using similar reasoning, the area under the anodic peak must therefore represent the total charge transferred during an oxidation reaction [60,62,64]. These two observations are merely restatements of the fundamental physical relationship that relates the charge passed (Q) for a given electrical current (I) over a given time interval (dt). Mathematically, this may expressed as [64]

$$Q = \int I dt \quad (9)$$

If one then considers Faraday's First Law, the amount of material deposited or stripped off a given electrode is proportional to the quantity of charge passed during a reduction or oxidation reaction, respectively [60,62].

The most noticeable effect that additives have on electroplating is on the electrodeposition kinetics [12]. In the presence of the appropriate plating bath components, a higher brightener concentration causes an increase in the plating rate [12,60]. It is for this reason that brighteners are sometimes referred to as accelerators in the literature. Brightening additives have the capacity to affect the film growth process by changing the concentration of nucleation sites on the surface of the growing film and therefore have a grain refining effect [37]. They function by preventing the deposition of copper at preferred locations by enhancing the formation of new-deposit nuclei, as opposed to the buildup of existing nuclei [10].

The chemical activity, or effective concentration, of an additive is therefore reflected in the plating rate of a metal onto an electrode [60]. With organic additives it is important to realize that the effective concentration, and not the absolute concentration, is of analytical interest. CVS is particularly well suited for such determinations as the activity, or effective concentration, of brightening or leveling additives in a plating solution can be determined by the effect these additives have on the electrodeposition rate. In particular, the area under the stripping peak (anodic peak) can be related to the effective concentration of the additive in solution since it corresponds to the charge required to oxidize the metal [60,62,67]. This, in turn, is proportional to the average deposition rate for that cycle. The anodic peak area can thus be used as a metric in a CVS experiment to evaluate the activity of an additive, even in proprietary formulations. Because CVS is based on the plating process, it is the only analytical technique that provides a true measure of the activity of the organic additive [60].

During the electrodeposition process, organic additives undergo various chemical transformations such as oxidation, reduction, fragmentation, and polymerization [38,60,67]. Most of these transformations result in species that are still electroactive and therefore still affect the plating process [60,67]. Since it is the fresh additive that is used as a standard in making CVS calibration curves, the concentration of additive in a production bath can be expressed as the equivalent activity of the fresh additive. With the use of CVS, the replenishment of the bath to the proper additive level, based on its equivalent activity to fresh additive, is thus very convenient and necessary for a well-controlled process [67]. The purpose of using CVS in this investigation is to create an

empirical calibration curve that relates the activity of fresh brightener, based on the anodic peak area derived from a cyclic voltammogram, to its absolute concentration. This information can then be used to adjust the brightener level during the course of the electrodeposition process, which was previously discussed in Sub-chapter 4.1.

4.2.1 Equipment and Materials

The CVS equipment layout used in this investigation to determine the brightening additive (Copper Gleam® PPR Additive [73]) activity is shown in Figure 36. The EG&G Princeton Applied Research Model 173 Potentiostat/Galvanostat was used in the potentiostatic mode to control the potential between the WE and the RE and to measure the current flowing at the WE-electrolyte interface using an electrometer circuit. In order to generate the triangular waveform that is applied to the WE, the potentiostat was used in conjunction with an EG&G Model 175 Universal Programmer. The programmer functions as a waveform generator by producing a DC voltage sweep at a programmed rate between the two switching potentials, which is then input into the potentiostat and applied to the WE. Since the kinetics of oxidation-reduction reactions are temperature-dependent, the temperature was monitored during CVS analyses using a Cole-Parmer Model 8402-00 Thermistor Thermometer.

As previously mentioned, CVS requires a three-electrode electrochemical cell. The configuration of the cell used in this study was designed and constructed by Jets Technology and is shown in Figure 37 [58]. A high-purity, gold wire (0.127-mm diameter, 99.999% purity, Johnson-Matthey) functioned as the WE, a circumferential sheet of oxygen-free, high-conductivity copper (99.95% purity, Alfa Metals) as the SE,

Figure 36: The CVS equipment layout used in this study to determine the brightener additive activity.

Figure 37: A schematic (top) and photograph (bottom) of the CVS cell used in this study. In the photograph on the bottom, the Ag/AgCl reference electrode is not in the CVS cell but rather is in a separate vessel containing copper sulfate holding solution.

and a commercially available silver-silver chloride anion electrode as the RE. The vessel used for the cell was a 500-ml Pyrex® Griffith beaker. During each analysis, the gold WE was placed concentrically in the beaker and immersed in the solution to a level of approximately 5 cm. The SE copper sheet was placed circumferentially around the inner wall of the beaker and completely immersed in the analyte. Lastly, the Ag/AgCl RE was placed at a distance of approximately 1.5 cm from the WE. The chemicals required for the CVS analyses are shown in Table 9. It is important to realize that these chemicals are identical to those required for acidic copper sulfate electroplating. Additional materials required for CVS include standard Pyrex® laboratory glassware such as volumetric pipets, graduated cylinders, and Griffith beakers for measuring solution volumes and making dilutions.

4.2.2 CVS Method

9.85 liters of a fresh acidic copper sulfate plating solution (Enthone-OMI CUBATH® M) were poured into a large container that contained all typical inorganic components in the volume concentrations recommended by the manufacturer for this application. 150 ml of the carrier additive (PPR organic carrier) was then added to the 9.85 liters of plating solution to achieve a carrier volume concentration of 15 ml/l. This 10 liters of solution, which will be referred to as "CVS stock solution" herein, was then thoroughly homogenized. For each CVS analysis, one liter of the CVS stock solution was poured into another container and appropriate volumes of brightener were added using a precision volumetric pipet to achieve the brightener volume concentration of interest. 250 ml of this brightener-containing solution were then transferred to the CVS

Table 9: The chemicals required to perform the CVS analyses for brightener activity. These chemicals are identical to those required for acid copper sulfate electroplating.

<i>Description</i>	<i>Manufacturer</i>	<i>Product Code</i>
<i>Acid Copper Electrolyte</i>	Enthone-OMI	CuBath® M
<i>Carrier Additive</i>	Shipley-Ronal	Copper Gleam® PPR Carrier
<i>Brightener Additive</i>	Shipley-Ronal	Copper Gleam® PPR Additive

electrochemical cell described above for analysis. The range of absolute concentrations used to construct the calibration curve was 0.0-2.50 ml/l in increments of 0.50 ml/l, requiring a total of six data points. Note that the first data point, which has no brightener added, served as a reference, or baseline, point on the calibration curve.

The method used to generate the cyclic voltammograms was recommended by Jets Technology and was developed during previous work with this system for this particular application [58]. It should be emphasized that this is a hydrostatic technique in that the electrodes remain stationary throughout the analysis. Many CVS references in the literature report a hydrodynamic technique that utilizes platinum rotating-disk electrodes [38,60,67,68]. Before each analysis, the pen of the XY recorder was zeroed at the origin of the potential-current axes. After placing the three electrodes in the CVS cell, the sample was then scanned a total of seven times between the switching potentials of -2.3 and 1.5 V. To condition the sample and establish a concentration gradient at the WE, the first three scans were done at a sweep rate of 500 mV/s and not recorded. The next four scans were done at a rate of 100 mV/s, with only the last three being recorded on the XY recorder for each calibration point.

The family of voltammograms obtained for each brightener concentration required to generate the calibration curves is shown in Figure 38 and is similar in form to those found in the literature for the acidic copper sulfate system [66,67]. Note that the cathodic peak was not recorded during the reverse (cathodic) scan as only the stripping peak (anodic peak) is generally used to determine the additive activity [60,66,67]. During the forward (anodic) scan, a large asymmetric peak was observed at approximately 0.2 V.

Figure 38: Partial cyclic voltammograms showing the anodic peak sweeps for each of the six additive concentrations used to generate a calibration curve. The area under each of the anodic peaks is representative of the brightener activity for a given concentration of fresh additive.

This peak corresponds to the stripping (oxidation) of deposited copper from the WE and is the peak of analytical interest in this study.

The asymmetry of this peak suggests an irreversible electrochemical process. There are several reasons that might explain the electrochemical irreversibility of this process [58]. First, additives adsorb on the surface of the metal during electrodeposition, thus rendering the metallic surface impure. In fact, the pure electrolyte without additives starts the deposition at a lower cathodic potential than that of an electrolyte containing additives. In essence, the additives render the system to be interface-controlled, rather than transport-controlled. Second, the anodic peak is created by the exhaustion of the plated copper from the gold wire. In other words, the current decreases due to depletion of copper from the gold wire. It is arbitrarily determined by the scanning potential range and the scan rate. Similarly, the cathodic peak is arbitrarily determined by the point where the potential scan is reversed and its magnitude is also affected by the scanning rate. Finally, the scanning rate is too fast to enable a reversible reaction. If the electron transfer kinetics are slow, the peak position will shift and the peak magnitude will change by altering the scan rate, which is characteristic of an irreversible reaction. This behavior was observed when varying the scan rate in this investigation.

An additional, but much smaller, peak was also observed on the tail of the anodic dissolution peak, which occurred in all scans at approximately 0.45 V. It is speculated that this peak is associated with the stripping of underpotential deposited monolayers of Cu, based on the work of Eliadis [66]. Cohen has speculated that this small peak may also correspond to the desorption of additives from the electrode [58]. There is also a

suggestion that an additional small peak of the same variety might exist between 0.25 and 0.30 V, based on the observation that three subtle inflection points often appeared in this potential range on the voltammogram [58]. More generally, this peak appears as a ripple that is superimposed on shoulder of the copper stripping peak.

After completion of the CVS work, the peak areas corresponding to each absolute brightener concentration were calculated in units of milliCoulombs (mC) and the results are shown in Table 10. Before the areas were calculated, the WE potentials were converted to units of time (in seconds), as a constant sweep rate of 100 mV/s was employed. Figure 39, which is a graphical representation of the same data, clearly indicates a linear relationship ($R^2 = 0.993$) between the anodic peak area and the brightener concentration. Bratin has also reported similar results [67]. From the relationship illustrated, it is clear why brighteners are often called accelerators in ECD processes. It should also be mentioned, however, that brighteners have very little affect on the deposition rate in the absence of other additives such as inorganic Cl^- ions and carrier-type ("suppressor") additives, which illustrates the synergism that exists between them [10]. Based on the equation corresponding to the regression line in Figure 39, the peak areas corresponding to the three brightener concentrations of interest in this study were calculated and the results summarized in Table 11. These areas were used for future CVS analyses in relation to the electroplating work described in Sub-chapter 4.1. Based on the normalized peak areas in Table 10, an arbitrary activity number, A_B , was also assigned to each of the three brightener concentrations of interest, which is also shown in Table 11.

Table 10: A summary of the anodic peak areas obtained from the cyclic voltammograms. Two analytical methods were used to obtain the average peak areas shown. The data were also normalized to the baseline condition of brightener-free electrolyte.

Brightener Concentration (ml/L)	Area 1 Trapezoidal Rule (mC)	Area 2 Cubic-spline Fit (mC)	Average Area (mC)	Normalized Area (unitless)
0	1.537	1.536	1.536	1
0.5	3.240	3.257	3.248	2.114
1	4.953	4.976	4.964	3.231
1.5	7.934	7.939	7.936	5.165
2	10.023	10.022	10.022	6.523
2.5	11.810	11.750	11.780	7.667

Figure 39: The derived CVS calibration curve based on the anodic peak areas calculated from the cyclic voltammograms.

Table 11: A table summarizing the interpolated CVS peak areas for future use in monitoring and maintaining the proper additive levels, during subsequent electrodeposition work. An arbitrary activity number, based on peak area ratios, was also assigned to each of these three additive levels.

Brightener Concentration (ml/l)	CVS Peak Area (mC)	A_B
0.75	4.45	2.78
1.50	7.65	4.94
2.25	10.84	7.10

4.3 High-Temperature Annealing

The thermal processing of oxygen-sensitive semiconductor materials, such as electrolytically deposited copper, requires an annealing ambient that is free of oxygen, moisture, or particulate contaminants. The three primary methods to ensure such an environment are 1) load lock 2) vacuum priming and 3) inert-gas purge. All three methods are currently being used in the semiconductor industry. The load lock method refers to a pre-chamber that is vacuum evacuated, or purged, prior to inserting the substrates into the primary chamber where they are exposed to elevated temperatures. The vacuum priming method refers to vacuum evacuation of the primary chamber prior to exposing the substrates to elevated temperatures. The last method, known as inert-gas purge or inert-gas sweep, refers to the purging of the major chamber with an inert gas prior to annealing the substrates.

The method used in this study to anneal the ECD copper samples is the inert-gas sweep method. With this method, the purge volumes of inert gas displace any oxidizing media present within the major chamber, thus rendering the environment inert. A previous study, which used rapid thermal annealing, reported that oxidation is minimized for 1- μm Damascene Cu films annealed at 100-400°C for 15-120 seconds in a forming gas composed of 4% H_2 and 96% N_2 , with less than 5 parts per million (ppm) O_2 [32]. Based on cross-sectional FIB imaging and sheet resistance measurements, these films were found to be completely stabilized, with no further increases in grain size or lowering of the sheet resistance.

4.3.1 Equipment and Materials

A schematic of the inert-gas sweep annealing apparatus supplied by Steed Technology for use in this investigation is shown below in Figure 40 [76]. The major system components consist of a gas pre-heating unit connected to a gas source, a chamber assembly, and a control panel that is interfaced with a computer system to control and monitor the temperature within both units in real time. Photographs of the annealing system are shown in Figure 41.

The gas pre-heater is a conventional, tubular, high-temperature furnace similar to those employed in semiconductor manufacturing and functions to superheat a flowing inert gas upstream of the chamber assembly. An example of such a furnace may be found in the U.S. patent by Bayne and Guiver [77]. The furnace is composed of a spiral quartz tube with concentric, radiant, heating lamps made of quartz, through which the inert annealing gas flows and acquires thermal energy before entering the annealing module via a gas feedthrough. A photograph of the pre-heater components described above is shown in Figure 42.

The annealing capsule, which creates a controlled diffusion environment for 200-mm substrates, consists of a cylindrical quartz chamber that encloses a gas distribution assembly and vertically-oriented wafer holder. The gas distribution assembly, which is shown in Figure 43, is composed of a gas feedthrough that is attached to eight diametrically-opposed injector tubes made of quartz.

The injector tubes have multiple rows of high aspect ratio (approximately 10:1) orifices extending along its length that function to disperse N_2 or forming gas uniformly

Figure 40: A schematic of the annealing system used in this investigation [76].

Figure 41: Two photographs of the inert-gas annealing system used in this study. A view of the entire system (top) and a close-up view of the chamber assembly where the wafers are annealed (bottom).

Figure 42: *A photograph of the quartz preheater assembly used to heat the inert annealing gas prior to entering the chamber assembly.*

Figure 43: A photograph of the gas distribution assembly.

across the wafer surfaces, thus providing a controlled diffusion environment. A vent at the bottom (distal end) of the annealing capsule is provided as a gap around the feedthrough of the injector tube. With this venting method, a positive pressure is easily maintained with a low flow of inert gas into the capsule, thus avoiding seepage of contaminating or oxidizing gases into the capsule. Also shown in Figure 43 is the surrounding cylindrical quartz chamber that is attached to the gas distribution assembly.

The wafer holder, which is used to support the substrates during annealing, is shown in Figure 44. The holder accommodates 25, 200-mm wafers that are loaded horizontally and has baffles made of circular metal plates on opposite ends to direct the flow of inert gas and create a uniform annealing environment for all wafers. This assembly is attached to an aluminum baseplate, which elevates the entire assembly into the annealing chamber when the thumbwheels are rotated on each of four leadscrews. Top and bottom views of the assembled annealing chamber are shown in Figure 45.

To control and monitor the temperature of the pre-heater radiant quartz lamps and the wafers within the annealing chamber, a Watlow Anafaze PPC 2000 Computerized Control System was used. This control system, which is capable of monitoring and controlling 50 independent data channels, interfaces with a standard personal computer and receives temperature information from the annealing system via thermocouples. Temperature uniformity was initially characterized using a 17-point thermocouple wafer. This wafer is a 200-mm silicon wafer with Type R thermocouples spot-welded to the wafer surface. High-temperature thermocouple wires are then connected to the control

Figure 44: *The wafer holder assembly used to load the substrates and elevate them into the annealing chamber. A vertically-oriented quartz boat supports the wafers.*

Figure 45: Top view (left) and bottom view (right) of the assembled annealing chamber.

system with both control and monitoring circuits that interface with the computer via a data acquisition printed circuit board. Previous characterization of the system yielded a $\pm 5\%$ wafer temperature uniformity across 200-mm wafers. During the actual processing of the experimental wafers, a similar monitor wafer was used that had a single-point thermocouple at the center of the wafer surface.

4.3.2 Annealing Method

The process steps used to anneal the experimental wafers are summarized in Table 12. It should be noted that vacuum priming was not used in this investigation, as no vacuum port was available on the annealing system at the time the first group of wafers were ready for processing. Additionally, no gas-bypass circuit was available on the system at the time of this study that would allow direct cooling of the substrates. Every annealing run consisted of six experimental wafers and two dummy wafers that serve as baffles due to the small lot size. This wafer-loading scheme within the annealing chamber, along with the radial flow pattern of heated forming gas across the wafers, is shown in Figure 46.

A representative thermal profile of the annealing cycle performed for the first lot of six wafers corresponding to experimental conditions 1, 2 and 3 is shown in Figure 47. Referring to this figure, one can see three distinct regions that include a ramp-up cycle, an isothermal period (400°C, 30 minutes), and a ramp-down cycle. While the rate of temperature increase is fairly typical for this method of annealing, the rate of temperature decay for the ramp-down cycle is shown to be excessively long in comparison. The primary reason for this behavior is related to the equipment design. After the thirty-

Table 12: A summary of the process steps employed to anneal the substrates using the inert gas-sweep method. The inert-gas environment was a 4% H_2/N_2 forming gas mixture.

Step	Description
1	Load specified lot of substrates into annealing chamber
2	Elevate substrates and statically seal chamber
3	Begin flow of forming gas (40slpm) and purge chamber for 10 minutes
4	Activate quartz heating lamp at pre-heater to heat forming gas
5	Establish 1050°C pre-heater temperature and 750°C gas temperature
6	Flow pre-heated gas planar to substrates
7	Ramp substrates to 400°C and hold for 30 minutes
8	Turn off quartz lamps while maintaining gas flow
9	Allow substrates to cool to room temperature
10	Unload and inspect substrates

Figure 46: A schematic of the wafer loading arrangement used during each annealing run. Also shown is the flow pattern of the heated inert gas through the system.

Figure 47: A representative illustration of the thermal profile resulting from the annealing cycle used in this study.

minute, 400°C, isothermal annealing period, the quartz lamps were extinguished as was previously shown in step 8 of Table 12. Since the gas pre-heater assembly is well-insulated, residual heat remains in the system for extended periods of time, to which the forming gas is continuously exposed during the ramp-down cycle. A much better design would include a gas bypass that provides a direct route from the gas source to the chamber assembly for more efficient cooling of the wafers.

4.3.3 Post-Annealing Inspection of Wafers

After annealing the wafers, they were inspected carefully to identify any processing defects. Blistering, haziness, and occasional dark blemishes (spots) were three categories of macroscopic defects found on many of the wafers. Of these three defects, blistering was by far the most prevalent and considered the most serious. Blistering can best be described as a hemispherical bubble-like defect protruding from the surface of the Cu film. These defects, while generally not reported in the literature, have been known to occur in damascene Cu processes after inert-gas annealing. It is also important to note that these defects were not present prior to the annealing process, even though the samples were stored for a one-week period. A brief summary of the post-annealing defect observations corresponding to each wafer is given in Table 13. The blistering and haziness are shown to occur primarily near the edges of the wafers. Inspection of the wafers revealed that the occurrence of blisters was primarily confined to the two outermost rows and columns of dice on the experimental wafers, as shown in Figure 48.

The blisters were further examined with a metallurgical microscope to better characterize their morphology, examples of which are shown in Figure 49. There exist a

wide variety of shapes and sizes assumed by these bubble-like defects, and their occurrence is predominantly in the patterned regions occupied by trenches and vias. The source of this defect is unknown at this time, but it is speculated that the use of high temperatures in conjunction the H_2 component of the forming gas might be a possible cause. If the hydrogen atoms were to disassociate, diffuse into the film, recombine, and coalesce, trapped gas bubbles would be the net result. These trapped gas bubbles, in conjunction with the high annealing temperatures, would result in high gas pressures that would ultimately cause the trapped bubbles to burst. The occurrence of the blisters almost exclusively in the patterned regions may have been due to the fact that these areas of the wafer are regions of higher localized film stress, as compared to their unpatterned counterparts.

Table 13: A summary of processing defects based on post-annealing observations. The occurrence of blistering and haziness was primarily confined to the edges of the wafers.

Condition	Blisters		Haziness		Dark Spots	Annealing Run
	Center	Edge	Center	Edge		
1A	None	None	None	None	Very Few	1
1B	Few	Few	Yes	Yes	Some	1
2A	None	None	None	Yes	Some	1
2B	None	None	None	None	Very Few	1
3A	None	Many	None	None	Some	1
3B	None	Many	Yes	Yes	None	1
4A	Very Few	Very Few	None	Yes	Very Few	2
4B	Few	Few	Yes	Yes	Some	2
5A	Some	Some	None	Yes	Very Few	2
5B	Very Few	Very Few	None	Yes	Some	2
6A	None	Many	None	Yes	Very Few	2
6B	None	Many	None	Yes	Very Few	2
7A	Many	Few	None	Yes	Very Few	3
7B	Few	Many	None	Yes	Very Few	3
8A	None	None	None	Yes	Very Few	3
8B	Very Few	Very Few	None	Yes	Very Few	3
9A	None	Many	None	Yes	Very Few	3
9B	None	Many	None	Yes	Very Few	3

Figure 48: Examples of the blisters seen on some of the experimental wafers after the high-temperature, isothermal annealing process. Their occurrence was primarily confined to the outermost two rows and columns of dice on the wafers.

Figure 49: Assorted examples of the blistering observed after the high-temperature annealing treatment of the experimental wafers. Their occurrence was primarily confined to the patterned regions near the edge of the wafer.

4.4 Sheet Resistance Measurements

Sheet resistance, R_s , is a commonly measured electrical parameter in many types of thin film work and is based on Ohm's Law. R_s is measured in units of ohms per square ($\Omega/\square$). Valence electrons are the charge carriers that allow the electrical conduction in metals. The conductivity, σ , of a metal is a measure of its ability to conduct electrical current in the presence of an applied electrical field. Conductivity is given by the expression

$$\sigma = nq\mu \quad (10)$$

where n is the density of charge carriers (m^{-3}), q is the charge carried by each carrier (Coulombs), and μ is the mobility of each carrier ($m^2/V-s$) [56]. The resistivity is a measure of a material's ability to oppose electrical conduction that is induced by an electric field. Resistivity, ρ , is a characteristic electrical property of a material and is defined as [78]

$$\rho = \frac{1}{\sigma} \quad (11)$$

The resistance of a material is related to the physical dimensions of a sample and the resistivity by

$$R = \frac{\rho L}{A} \quad (12)$$

where R is resistance (Ω), A is the sample cross-sectional area, and L is the sample length [78].

As mentioned above, thin films are more commonly described in terms of the sheet resistance, R_s , rather than the resistivity or resistance. In considering Equation (12) above, the cross-sectional area, A , may be considered as the product of the sample width (W) and thickness (t). The resistance is then related to the resistivity by [56]

$$R = \frac{\rho L}{tW} \quad (13)$$

If a thin sheet of material having thickness, t , is considered to be composed of squares of arbitrary area, then $L = W$ [79]. Or, alternatively, the resistance of a thin sheet is constant for any square area of the same material [78]. The sheet resistance, R_s , is then related to the resistivity and specimen thickness by [56,78,79]

$$R_s = \frac{\rho}{t} \quad (14)$$

The value of sheet resistance lies in the ability to calculate the resistivity of thin films knowing only the sample thickness.

The two most common methods of measuring sheet resistance for process monitoring are the four-point probe and eddy current methods [56]. Although the eddy current method is less well known than the four-point probe method, it was chosen for

this investigation as it is a non-contact, and therefore non-destructive, measurement method.

The basic principles of the eddy current method, which was used in this study, are shown in Figure 50 [56]. Referring to the figure, eddy current systems determine the sheet resistance of a thin film by creating a time-varying magnetic field from a wound coil. The coil radiates energy and, when placed close to a conductive layer, eddy currents are generated by the amount of energy absorbed by the conductive film. The eddy currents, in turn, create their own magnetic field, which then interacts with the primary coil by mutual inductance, thus changing the electrical characteristics of the coil. The more conductive the film, the greater the energy which gets trapped in the film to create eddy currents. The magnetic field produced by the coil drops off exponentially with penetration depth but will still penetrate through thin films typical of semiconductor processing and into the underlying films and substrate. The undesirable field developed in the substrate can lead to erroneous measurements and is the biggest limiting factor for eddy current use [56]. Electrical eddy currents require a sufficient volume to create a complete circular path. Any interruptions in this circular path will prevent eddy currents from being formed in that layer.

The eddy currents produced in a thin film are dependent on the film resistance and magnetic permeability [56]. Since the films used in the semiconductor industry have a relative permeability of one, they can be ignored in this application. The magnetic field created by these eddy currents and their effect on the primary coil circuit depend on the sheet resistance of the film [80]. The density of eddy currents will vary with penetration

Figure 50: A schematic of the eddy current method for determining sheet resistance. Eddy currents are induced in a nearby thin film, by placing a coil with a time-varying electric current near the sample [56].

depth as is shown in Figure 51 [56]. The depth at which the eddy current density has decreased to 37% of the surface value is called the standard skin depth of penetration. The standard skin depth for non-magnetic films can be approximated by

$$S = 50,000 \left(\frac{\rho}{f} \right)^{1/2} \quad (15)$$

where S is the standard skin depth in μm , and f is the frequency in Hertz [56]. Most eddy current systems operate at a frequency of approximately 10 MHz or lower. If the metal film resistivity is significantly lower than that of the substrate or underlying films, their effects can be ignored [56,80].

In making eddy current measurements, the changes in coil values rather than their absolute values are measured. Such measurements require the use of calibration curves, which are commonly referred to as a liftoff curves [56,80]. These curves plot the changes in coil resistance and reactance as the probe-to-film distance changes for a constant film resistance. Each unique film resistance will result in a unique liftoff curve, and the shape of such a plot is shown in Figure 52 [56]. A family of liftoff curves for different film resistances can thus be used to calibrate the eddy current probe system. If a series of resistance and reactance values are collected at a constant film height, they form another family of curves called isodistance curves [56,80]. These isodistance curves, in turn, may be overlaid on the family of liftoff curves as is also illustrated in Figure 53 [56]. The resistance (or sheet resistance) of an unknown sample can then be theoretically

Figure 51: Eddy current density as a function of penetration depth in an arbitrary material. One standard skin depth is defined as the depth at which the eddy current density falls to 37% of its surface value [56].

Figure 52: A typical liftoff curve illustrating the changes in the coil electrical parameters, as the probe is moved away from the sample for a material of constant resistance [56].

Figure 53: Families of liftoff curves and isodistance curves allow the resistance of an unknown test specimen to be determined from the coil electrical parameters [56].

determined from the coil resistance and reactance at a given height from the sample by interpolation.

4.4.1 Equipment and Materials

The instrument used to make the sheet resistance measurements in this investigation was a KLA-Tencor Omnimap™ NC110 non-contact metals monitoring system, which uses eddy current probe technology for making sheet resistance measurements [81]. The system accommodates wafer sizes up to 200 mm and has XY wafer mapping capabilities for measuring sheet resistance on over 1200 individual sites. It is also capable of performing long and short diameter scans for up to 625 individual sites. The location of the measurement probe, which houses the aforementioned primary induction coil, in relation to the wafer chuck is shown in Figure 54. A summary of the NC110 instrument performance capabilities and the equipment configuration used for this investigation are shown in Table 14 [81].

4.4.2 Measurement Method

In this investigation, three different measurement routines were utilized. The first routine was designed to take individual sheet resistance measurements from the blanket film regions on each of the 69, 20-mm dice for all eighteen experimental wafers. Using a Cartesian coordinate system, the measurement position on each die was (-2.5 mm, -7.5 mm) relative to the geometric center, or origin, of each die, which is shown in Figure 55. This region of the die is predominantly unpatterned but also has several regions of square-shaped vias, most of which have very large geometries. Based on the available areas to measure and the 3-mm measurement spot size, this region was deemed the

Figure 54: A close-up photograph of the KLA-Tencor Omnimap® NC110, showing the probe, wafer chuck, and a sample wafer to be measured.

Table 14: The NC110 instrument performance capabilities and equipment configuration for this investigation [81].

Parameter	Value
Coil Diameter	1 mm
Spot Size	3 mm
Skin Depth	15 μm
Frequency	10 MHz
Coil-Sample Spacing	Variable (75 μm -3 mm)
Range	1 m Ω/α - 1 Ω/α
Accuracy	$\pm 1\%$
Precision	< 0.2% (1 σ)
Measurement Speed	3 seconds per site

Figure 55: A die schematic showing the measurement location used for the blanket-film, eddy current sheet resistance measurements on each die [59].

closest approximation to a blanket Cu film. The second and third routines included a 625-point, 200-mm, long diameter scan, and a central 12-mm, 125-point, short diameter scan, respectively. These scans were made parallel to the wafer flat, as is illustrated in Figure 56.

From a practical standpoint, it should be noted that all the necessary information to calculate the sheet resistance was pre-programmed into the system. The liftoff curves were generated empirically by measuring the probe output voltage of standard samples of known sheet resistance as a function of probe distance at a frequency of 10 MHz. The sheet resistance of the measurement standards was determined using a calibrated four-point probe. This information was input into the NC110 computer system, thus allowing the sheet resistance of the experimental wafers to be determined by interpolation. In essence, the system measures the output voltage characteristics of the unknown samples for distances ranging from 3 mm to 75 μm at a frequency of 10 MHz to obtain a voltage-distance curve that is compared to the family of calibration curves.

Figure 56: An illustration of the location and direction of the 625-site, long (top) and 125-site, short (bottom) [59] sheet resistance diameter scans used to assess the thickness profiles on the sample wafers. The 12-mm short scan was performed on die 35.

4.5 Focused Ion Beam Imaging

A focused ion beam (FIB) workstation operates similar to a scanning electron microscope (SEM) in that both instruments take charged particles from a source, focus them into a beam through electromagnetic and electrostatic lenses, and then raster scan small areas of the sample using deflection plates or scan coils. Often both capabilities are integrated into one instrument, which is referred to as a dual-beam FIB-SEM.

A schematic showing the basic FIB components is shown in Figure 57 [82]. The primary difference between the two techniques is that an electron microscope uses electrons to form its imaging beam, whereas a FIB system uses gallium (Ga) ions from a field-emission, liquid-metal, ion source capable of analytical spot sizes less than 10 nm [83]. The finely focused beam of gallium ions can be used at low beam currents for imaging, or high beam currents for localized sputtering or milling the sample. During the imaging process, a detector collects secondary charged particles emanating from the sample and their signals are amplified to produce in-situ images of the surface of interest. The image provides topographical and materials contrast information and is used for navigation across the sample. In addition to imaging and milling samples, FIB systems can be used for compositional imaging via secondary ions, microfabrication, transmission electron microscopy sample preparation, and localized deposition and etching of metal or insulator structures [82]. In the current investigation only the milling and imaging features were used for plan-view and cross-sectional imaging of Cu blanket films and Damascene trench features.

Figure 57: A block diagram showing the basic operational components of a FIB system, which are very similar to those of an SEM. One of the primary differences is a gas nozzle, which serves as source of Ga ions for the incident beam [82].

Figure 58 illustrates the basic operational principles of FIB imaging. As the finely focused beam of gallium ions is scanned over the surface of the sample, the interaction of the ion beam with the sample sputters a small amount of material that leaves the surface as neutral atoms. This interaction also produces secondary ions and electrons, which are the species most commonly used for imaging [83]. Secondary electrons are produced by inelastic scattering (energy loss with negligible change in direction) of the primary beam ions by the sample atoms [84]. Inelastic scattering is caused by interactions with either the atomic nucleus or with bound electrons. If inelastic collisions occur between the loosely-bound electrons in the outermost orbitals of the sample material and the ion beam, energy is lost from the beam ions and the loosely bound electrons from the sample are ejected. The ejected electrons have energies that are typically less than or equal to 50 electron-volts (eV) and are called secondary electrons. The secondary electrons produced by the beam-specimen interaction vary from point to point around the specimen due to the local character of the specimen. The interaction may be affected by topography, composition, crystallographic orientation, and the magnetic or electric properties of the sample [84].

Unlike classical metallographic techniques, the primary grain contrast mechanism in FIB images is grayscale contrast. The grayscale contrast arises from differential gallium ion channeling through the individual grains that varies as a function of crystallographic orientation in a polycrystalline material [85]. The ion channeling effect arises from the different atom packing densities that are observed along different crystallographic directions, an example of which is shown in Figure 59 [84]. The large

Figure 58: The basic operational principles of a FIB system. An incident beam of Ga^+ ions interact with the sample to produce sputtered atoms (n^0), secondary ions (i^+), and secondary electrons (e^-). The secondary electrons (or ions) are collected by a detector and converted into an image, as the primary beam scans the sample.

Figure 59: A schematic showing different atomic packing densities along three different crystallographic directions in a quartz crystal. The degree of ion channeling will increase in going from left to right in the figure, due to the increasing “openness” of the structures [84].

energetic gallium ions suffer inelastic collisions with the host material, which produces low-energy (<50 eV) secondary electrons that escape from the host material. The secondary electron yield will depend on the number of collisions produced from the inelastic ion-solid interactions that occur during the channeling process and the depth within the material where the collisions occur [85]. Low-yield conditions will generally produce a darker region on the image, whereas high-yield conditions will produce a lighter region. Similar to scanning electron microscopy, the secondary electrons are collected by a secondary electron detector to produce an image on a phosphor screen that is subsequently amplified, captured electronically, and ultimately digitized. Such images are generally composed of 255 grayscales and have a pixel density that produces very high resolutions that range between 4-10 nm [83]. An example of a cross-sectional FIB image of Damascene electroplated copper shortly after deposition is shown in Figure 60 to illustrate the ion contrast mechanism [86].

4.5.1 Equipment and Materials

The equipment used for this investigation was an FEI 820 Dual-beam FIB-SEM system with both ion and electron imaging capabilities [87]. Photographs of the system are shown in Figure 61, which show both the electron and ion beam sources used for imaging purposes. The angle between the ion and electron beam sources is 52° , with the electron beam source being oriented vertically. The basic system specifications for this instrument are shown in Table 15 [87]. The system is equipped with an XY sample stage capable of accommodating intact 200-mm Silicon wafers, so no sample preparation or additional materials were required.

Figure 60: An FIB image of electroplated Cu in an array of Damascene 0.35- μm trench features shortly after deposition, showing the ion channeling effect. Note the grain-to-grain contrast arising from different grayscale levels [86].

Figure 61: Two different views of the FEI-820 Dual-beam FIB-SEM used in this investigation, showing the incident electron and ion beam sources.

Table 15: The basic equipment specifications for the FEI 820 Dual-beam FIB-SEM used in this investigation [87].

Parameter	Specification
<i>Ion Source</i>	Liquid Ga, 1500 hours
<i>Electron Source</i>	Hexalens™ Electron Column
<i>Beam Voltage (Electron Source)</i>	200 V-30kV
<i>Beam Voltage (Ion Source)</i>	5kV-30kV
<i>Image Resolution (SEM)</i>	3 nm
<i>Image Resolution (FIB)</i>	7 nm
<i>Beam Aperture Change Time</i>	< 10 seconds
<i>Base Pressure</i>	3×10^{-7} Torr
<i>Load/Unload Time</i>	< 2 minutes to base pressure
<i>Stage</i>	5-Axis XYZRT, 200 mm x 200 mm travel
<i>Sample Tilting</i>	Eucentric, up to 60°
<i>Sample Holder</i>	200 mm Diameter, Vacuum Chuck
<i>User Interface</i>	MS Windows™, Icon-driven
<i>Wafer (CAD) Navigation</i>	Optical Microscope 50X-600X

4.5.2 Imaging Method

In this investigation both plan-view and cross-sectional FIB images were acquired for the grain sizing and microstructural characterization of the annealed, electroplated copper samples in both the unpatterned and trenched regions of the sample wafers. Cross-sectional electron images were also acquired to assess gap filling within the trenches. All images acquired for this study will be presented and discussed in Chapter 5.

For the grain sizing and microstructural analysis, five plan-view (top surface) FIB images in the blanket film region of die 17 were obtained for each of the nine experimental conditions at 5000 $\times$ magnification. This region of the die is shown in Figure 62. For these images an ion beam voltage of 30 kV and beam current of 150 picoAmps (pA) were employed, and the sample was tilted 52° relative to the horizontal to make the ion beam normal to the substrate surface as shown in Figure 63. The region to be imaged was lightly milled using a beam current of 1000 (pA) to remove any surface oxide or other contamination prior to imaging. These images and the method used to process them for grain sizing will be presented in Chapter 5.

For further characterization of the Cu grain structure and morphology in the blanket film regions, 2-4 tilt-view images were acquired that allowed the microstructure to be seen in cross section. A beam voltage of 30kV and beam current of 5 pA were typically used with magnifications ranging between 25000-50000 $\times$. Before such images could be acquired, a rectangular region of the Cu film was first milled down to the Si wafer using a beam current of 2700 pA. Electron images of such milled regions in both the blanket-film and patterned areas of a sample die are shown Figure 64. The sample

Figure 62: A schematic of the die floorplan showing the region used for the Cu blanket-film FIB imaging. The locations of the 0.35 and 0.50- μm trenches are also shown [59].

Figure 63: A schematic showing the orientations of the ion and electron beam sources relative to the substrate, when imaging the top surface of the electroplated Cu films.

Figure 64: Electron beam images of the regions milled with the Ga ion source for cross-sectional views of the blanket film region (top) and trenched region (bottom).

was then tilted back to the horizontal position in order to make the ion beam impinge on the side wall of the blanket film region, as shown in Figure 65. In this orientation, the beam is oriented 38° from the wafer surface. This leads to a foreshadowing effect that requires the Y-axis dimension of the image to be corrected. The correction was made by dividing the Y-axis dimension of the image by the cosine of 38° . After a brief coarse (2700 pA) milling of the side wall, the beam current was reduced to 1000 pA to smoothen the same surface (fine milling) before imaging at 5 pA, which is below the sputtering threshold for copper [85].

In order to characterize the grain size and microstructure within the patterned regions, similar tilt-view FIB images were obtained in the 0.35 and 0.50- μm trenches using the methodology and beam current settings described above. In these cases, two images at magnifications of 35000 and 50000 $\times$ were acquired for both trench sizes. One electron image of these same trenches was also obtained at 65000 $\times$ magnification to assess the presence or absence of voids within these features. The location of these trench features was previously shown in Figure 62 [59].

Figure 65: A schematic showing how the sample is oriented relative to the Ga ion source during tilt-view, FIB imaging to examine the Cu grain structure in cross section.

4.6 X-ray Diffraction Measurements

In order to evaluate the quality of the (111), axisymmetric fiber texture present in the blanket Cu films, two commonly used x-ray diffraction (XRD) scans were performed on one sample for each experimental condition. These two scans required the use of only an ordinary powder diffractometer. The fundamental aspects of each scanning method will be described below, and the application of these scans to derive the necessary figures of merit for texture in Chapter 5.

The first of these scans is commonly known as a Bragg-Brentano, or θ - 2θ scan. Such a scan produces a plot of diffracted beam intensities as function of detector angle (2θ) over the angular range of interest. With this method, an incident beam of monochromatic x-rays is diffracted from a particular set of crystallographic planes in a fashion that satisfies Bragg's Law. Bragg's Law takes the general form

$$n\lambda = 2d \sin \theta \quad (16)$$

where λ is the wavelength of the incident beam radiation, d is the interplanar spacing for a particular set of crystallographic planes, and θ the angle between the incident beam and the set of diffracting planes [88].

The geometry of the Bragg condition is shown in Figure 66 and can be described in the following manner. Consider an x-ray beam incident on a pair of parallel diffracting planes (P1 and P2) of interplanar spacing d . These two parallel incident rays (I_1 and I_2) make an angle θ with these two planes. A reflected beam of maximum intensity will

Figure 66: A schematic of the geometry associated with Bragg's Law of Diffraction for a set of parallel, diffracting crystallographic planes.

result if the waves represented by I_1' and I_2' are in phase. The difference in path length between I_1-I_1' and I_2-I_2' must therefore be an integral number of wavelengths, λ , which is summarized mathematically in Equation (16). It is important to realize that the incident and diffracted beams, as well as the reflecting plane normal, must all be coplanar [88]. Additionally, the angle subtended by the incident and diffracted beams is always 2θ . In the literature 2θ is referred to as the diffraction angle and, for standard sample goniometers, it is this angle that is generally measured experimentally.

The possible interplanar d-spacings are defined by the Miller plane indices, (hkl), which are determined by the shape of the unit cell. Equation (16) can be arranged as

$$\sin \theta = \lambda/2d \quad (17)$$

In this form, it can be seen that the possible 2θ values are determined by the unit cell parameters. However, the intensities of the diffracted beam are determined by the distribution of electrons in the unit cell [88]. Since the highest electron densities are found around the atoms, these intensities depend on the type of atoms and their location in the unit cell [89].

The second type of scan to be used in this study is commonly referred to as a rocking curve, θ scan, or ω scan [88,90,91]. This method involves measuring the intensity of a Bragg peak whose diffracting planes are normal to the preferred crystallographic direction while tilting (rocking) the specimen, as shown in Figure 67. Unlike a θ - 2θ scan which only measures the intensity from planes parallel to the sample

Figure 67: A schematic of the geometry associated with rocking curve measurements. The sample is tilted (rocked) at a particular Bragg peak location to measure the diffracted intensity of planes that are tilted relative to the plane of the substrate.

surface, a rocking curve allows for the measurement of the diffracted intensity of planes that are tilted with respect to the substrate surface for a particular Bragg peak [90]. The width of a rocking curve is therefore a direct measure of the range of orientation present for a particular set of crystallographic planes [88].

4.6.1 Equipment and Materials

The x-ray diffractometer used to acquire the Bragg and rocking curve scans was a Scintag (Thermo-ARL) Model X2 Diffractometer, which is shown in Figure 68 [92]. The major components, which are also shown diagrammatically in Figure 69, include an x-ray source (x-ray tube), a goniometer, an x-ray detector, and the x-ray optics system [92]. The goniometer is a mechanical assembly that is comprised of the sample holder, detector arm, and gearing. In this study a θ - θ goniometer was employed, which is also illustrated in Figure 69. With a goniometer of this type, the sample is held stationary in the horizontal position as both the source and detector move simultaneously over the angular range θ . It should also be noted that the source, detector, and sample all lie on the same focusing circle, which is inscribed within a another circle called the diffractometer circle. During an x-ray scan, both the source and detector move simultaneously around this diffractometer circle, which is of constant radius. Based on geometrical arguments, it can be shown that this arrangement ensures that all diffracted beams from the specimen converge at a point, which in this case is the x-ray detector [88]. The focusing circle, which is centered on the specimen normal and passes through the source and detector, is not of constant radius. Instead, it decreases in radius as the angle 2θ decreases, which is shown in Figure 70. [88].

Figure 68: Two views of the Scintag Model X2 Diffractometer with a θ - θ goniometer. The bottom photograph shows the key system components.

Figure 69: A diagram of the Scintag Model X2 Diffractometer set up for a Bragg-Brentano scan using a θ - θ goniometer. All major system components are shown [89].

Figure 70: A schematic illustrating how the diameter of the x-ray focusing circle decreases as the angle 2θ decreases [88].

The diffractometer system also contains a very elaborate optical slit system for both the incident and diffracted beams, which collectively comprise the x-ray optics. A typical x-ray optics system is shown in Figure 71 [89]. The incident-beam optics include a divergence slit, soller slits, and a scatter slit. The diffracted-beam optics also include soller and scatter slits, in addition to a receiving slit located in close proximity to the detector.

The divergence slit is used to create a line source of emitted x-ray radiation which extends considerably above and below the plane of the diffractometer circle. The focusing optics mentioned above, however, require that the incident beam be parallel to the plane of the diffractometer circle. This condition is realized through the use of the soller slits, which are comprised of a set of closely-spaced, thin metallic plates parallel to the plane of the circle. Collectively, the divergence and soller slits define the divergence of the incident beam along the line of focus in the plane of the diffractometer circle [89]. Sometimes scatter slits are also placed between the soller slits and the sample to minimize the in-plane divergence of the incident beam.

Similar to the case of the incident beam, the beam diffracted by the specimen also passes through soller and scatter slits to limit divergence and confine the beam to the plane of the diffractometer circle. The receiving slit defines the width of the beam admitted to the counter and therefore defines the maximum intensity of the diffraction line being measured [88]. The width of the slit chosen represents a suitable compromise between intensity and resolution. It is for this reason that the area under a diffraction peak, or its integrated intensity, is of more fundamental importance than the maximum

Figure 71: The x-ray optics system in a typical diffractometer for both the incident and diffracted beams [89].

intensity [88]. The maximum intensity is dependent on the receiving slit width, whereas the integrated intensity is not [89].

4.6.2 Measurement Method

Before measuring any samples, the wafers selected for this phase of the analysis were diced into 20-mm squares, and the appropriate dice selected based on criteria that will be discussed in Chapter 5. The instrument configuration used for both the Bragg-Brentano and rocking curve scans is shown in Table 16. Each die was pressed onto a small piece of modeling clay located in a polymethylmethacrylate (PMMA) bulk sample holder until level with the reference surface of the holder. Careful attempts were made to center the sample in the holder and orient the sample the same way each time. With the sample loaded in the sample holder, the entire assembly was placed onto the goniometer stage of the diffractometer as shown in Figure 72.

The equipment was then set up to perform two Bragg-Brentano scans on each sample using the Scintag DMSNT (Version 1.37) measurement and analysis software package [92]. The first was a high-speed scan between 5 to 100° in 2θ , with 0.02-degree steps at 4° per minute. The purpose of this scan was to assess the overall intensities and peak locations for Cu and to look for substrate or barrier layer peaks. With the Cu peaks identified, a high-resolution, multi-range, step scan was performed for each Cu peak over the angular ranges shown in Table 17. This scan used a 0.02° step size at 5 seconds per point.

Using the data acquired from the step scans, the background intensity was removed from each peak using a horizontal linear fit of the background intensity surrounding each

Table 16: The diffractometer equipment configuration used for this study.

Description	Configuration
<i>X-ray Tube Type</i>	Long fine-focus, ceramic
<i>X-ray Tube Dimensions</i>	0.4 mm x 12 mm
<i>X-ray Tube Anode Material</i>	Copper
<i>X-ray Tube Current</i>	44 mA
<i>X-ray Tube Voltage</i>	45 kV
<i>Incident Beam Takeoff Angle</i>	6°
<i>Incident-beam Divergence Slit</i>	2 mm (1.2°)
<i>Incident-beam Soller Slit</i>	1.15°
<i>Incident-beam Scatter Slit</i>	4 mm (1.7°)
<i>Goniometer Type</i>	θ - θ
<i>Goniometer Radius</i>	250 mm
<i>Diffacted-beam Scatter Slit</i>	0.5 mm
<i>Diffacted-beam Soller Slit</i>	1.15°
<i>Diffacted-beam Receiving Slit</i>	0.2 mm
<i>Detector Type</i>	Si (Li) Solid State
<i>Detector Cooling</i>	Peltier-cooled
<i>Detector Active Area</i>	2 mm

Figure 72: Two views of a Cu sample loaded in the sample holder and placed on the goniometer stage of the diffractometer.

Table 17: A summary of the high-resolution, Bragg-Brentano step scan ranges performed for each Cu peak that was identified in the high-speed, continuous scans.

<i>Cu Peak</i>	<i>Scan Range (Degrees)</i>
<i>(111)</i>	42.90-44.00
<i>(200)</i>	50.00-51.20
<i>(220)</i>	73.70-75.00
<i>(311)</i>	89.50-90.80
<i>(222)</i>	94.80-96.00

peak. Such background radiation comes about from fluorescent radiation emitted by the sample, diffraction of the continuous spectrum, diffraction and scattering from sources other than the specimen, and diffuse scattering from the specimen itself [88]. The background-subtracted raw data for each Cu peak was then fit to Pearson VII profiles that combine the $K\alpha_1$ and $K\alpha_2$ components [93]. The Pearson VII curve fitting method will be discussed in Chapter 5. Based on the Pearson VII fits, the $K\alpha_1$ peak positions, peak widths at half-maximum intensity, maximum peak intensities, and peak areas were determined. It is important to note that the peak widths at half-maximum intensity are commonly referred to as full-width, half-maximum (FWHM) values in x-ray diffraction literature.

Rocking curve scans were then collected at the $2\theta_B$ values (peak positions) determined for each Cu (111) peak using the Pearson VII fits mentioned above. The step size of these scans was 0.05° degrees at 2 seconds per point. The scan range, or more accurately the tilting range, for any rocking curve for a particular Bragg peak is limited by its $2\theta_B$ value. The effective tilting range for a rocking curve, or θ scan, is limited to $\pm\theta_B$ due to the geometrical restrictions imposed by having a fixed scattering angle at $2\theta_B$ [90]. A low-index peak would then have a much more limited tilting range than a high index peak. For example, the Cu (111) peak occurs at $2\theta_B = 43.2978^\circ$, according to the International Center for Diffraction Data (ICDD) card number 4-386 [94]. The effective tilting range for a rocking curve of this peak would then be approximately $\pm 21.6^\circ$, which was the range used for the (111) rocking curves in this investigation. It should be noted that the tilt angle associated with rocking curves is also commonly referred to as ω in the

literature and the derived scans as ω scans. This latter terminology will be used in subsequent discussions. The intensity data for both the Bragg and rocking curves scans were saved for subsequent texture analysis.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Sheet Resistance Analysis

As mentioned in Chapter 4, sheet resistance measurements were performed on both duplicate wafers for all experimental conditions using the eddy current method. The measurements included long and short diameter scans along a diameter parallel to the wafer flat, as well as individual measurements in the unpatterned regions of each die. These measurements served the following purposes:

1. Assess the thickness profile on the sample wafers.
2. Statistically compare the mean sheet resistance values between duplicate wafers.
3. Statistically compare the mean sheet resistance values between conditions.
4. Identify dice to be used for subsequent metrology.
5. Assess the resistivity of the blanket film regions.

5.1.1 Assessment of Wafer Thickness Profiles

Figure 73 illustrates a representative 625-site, long-diameter sheet resistance scan for the wafers from condition 5. The general waviness seen in these scans is attributable to local changes in sheet resistance arising from the increased surface area in the patterned regions of each die. In view of the first objective listed above, it appears that the copper film thickness varies significantly across the wafer diameter. Recalling that the sheet resistance is inversely proportional to the film thickness, two regions are identified as being significantly thicker than the remaining regions scanned. These are the two

Figure 73: Long-diameter sheet resistance scans for the experimental wafers of condition 5. These scans were used to assess the copper thickness profiles across the wafer diameter for each condition. The suffix designations “A” and “B” refer to the first and second wafers produced for this experimental condition.

extreme edges located approximately 90 mm from the center and the central region, which encompasses a range of approximately ± 6 mm from the center of the wafer.

In the former case, the edge non-uniformity is attributable to the fact that no wafer biasing was used during the electrodeposition process. In the absence of wafer biasing, there will be an electrical potential gradient that decreases in going from the edge to the center of the wafer. This generally results in thicker films being deposited near the edge of the wafer. In fact, one can see that the sheet resistance gradually increases in going from 90 mm to approximately 6 mm from the wafer center.

The origin of the localized non-uniformity in the central region of the wafer may have been a consequence of the rotating anode jet assembly (RAJA) design. As previously shown, the RAJA has six rows of jet nozzles spaced 60° apart and extending radially outward, with an additional nozzle located on the central axis. In going from the center to the edge of this assembly, the linear velocity will increase linearly with radial distance from the central axis at a given angular velocity as the RAJA rotates. The central nozzle will therefore not have a linear velocity component, whereas the other nozzles will experience linear velocities that increase with radial distance during solution agitation. In fact, this may have also contributed to the thickness gradient in going from the center to the edge of the wafer. Removal of the central nozzle and additional experimentation would be required to validate this interpretation.

5.1.2 Statistical Comparison of Experimental Duplicates

As mentioned above, individual sheet resistance measurements in the blanket regions of all dice on each wafer were also performed. The primary goals of making

such measurements were to compare duplicate wafers based on their mean sheet resistance values and help identify the dice to be used for subsequent metrology, by eliminating die with extreme outlying R_s values. Such an assessment is extremely important, as only one die from each duplicate wafer was to be selected for subsequent metrology, each of which will follow a different metrology path.

A general statistical analysis was performed on all duplicate wafer pairs using the raw sheet resistance data obtained for all 69 dice on each wafer. The general, summary, variability, and distribution statistics are presented in Appendix A. These three tables indicate that the duplicate wafers for each set of experimental conditions show similar average sheet resistance values and degrees of variability in terms of the standard deviation. The largest difference between duplicates is exhibited by experimental condition 6, which yielded an 8.6% difference in the mean sheet resistance. A graphical comparison of the mean R_s values for each set of duplicate wafers by experimental condition may be found in Figure 74. The recurring, large, positive values of skewness and kurtosis shown in Appendix A indicate heavy-tailed, negatively-skewed distributions and the presence of one or more extreme outlying values for all conditions.

Before investigating the data for extreme outlying values that might be skewing the R_s distributions, statistical inference was performed on the entire raw data set. Since the number of R_s observations for each sample was greater than 50 for each wafer, a two-sample, two-tailed z-test was performed on the 69 R_s values for each pair of the duplicate wafers. The mean R_s values for each pair of duplicate wafers for all nine experimental conditions were compared at the 95% confidence level. The underlying assumption of

Figure 74: A bar chart that compares the mean sheet resistance values between duplicate wafers for all nine conditions. A total of sixty-nine points were measured on each wafer in the blanket film regions.

such a test is that the data is normally distributed, which, as mentioned above, is in question. The results are summarized in Table 18. Since the p-values are all greater than 0.05, it is concluded that the mean R_s values for all duplicate wafer pairs are equal at the 95% confidence level for all nine conditions, based on the entire raw data set.

The data were further investigated for extreme outlying values that might be skewing the distribution and invalidating the assumption of normality in the data. Such occurrences could possibly invalidate the conclusion that all experimental duplicates are statistically equivalent in terms of their sheet resistance values. In order to obtain a visual assessment of the shape of the distributions, sheet resistance frequency histograms were generated for each pair of duplicate wafers. An example is shown in Figure 75, which shows frequency histograms for the duplicates of experimental condition 9. The shapes of the distributions clearly confirm the presence of negatively-skewed distributions with heavy right-hand tails. Furthermore, it appears that at least one extreme value is the primary cause of the non-normality. All other wafers in this study were found to exhibit similar distributions.

To help identify the dice that were causing the abnormality and further assess the general trends in sheet resistance on the wafers, die histograms for the condition 9 duplicates were generated by column and by row. These two histograms are shown in Figure 76. Examination of these histograms indicates some very interesting trends that are undoubtedly related to the sheet resistance trends seen previously in the long-diameter scans. There is both a row-wise and column-wise periodicity that is primarily related to the thickness distribution on the wafer. Recalling that R_s is inversely proportional to

Table 18: Sheet resistance z-test results at the 95% confidence level between all duplicate pairs of wafers for each condition, based on the entire raw data set.

Condition	Mean Difference	Standard Error	Z_{test}	p-value	Confidence Intervals	
					Lower 95%	Upper 95%
1	0.00004	0.0007	0.062	0.951	-0.0013	0.0014
2	0.00034	0.0010	0.356	0.722	-0.0016	0.0022
3	0.00041	0.0011	0.357	0.721	-0.0026	0.0018
4	0.00023	0.0004	0.584	0.559	-0.0010	0.0005
5	0.00002	0.0012	0.019	0.985	-0.0023	0.0022
6	0.00101	0.0012	0.852	0.394	-0.0033	0.0013
7	0.00037	0.0005	0.813	0.416	-0.0013	0.0005
8	0.00007	0.0009	0.084	0.933	-0.0018	0.0017
9	0.00014	0.0010	0.143	0.886	-0.0021	0.0018

Figure 75: Sheet resistance frequency histograms for the duplicate wafers of experimental condition 9, illustrating a skewed distribution and the presence of an extreme outlying value. One measurement was performed in the blanket film region on each of the sixty-nine test die.

Figure 76: Sheet resistance die histograms by row (top) and column (bottom) for condition 9 duplicate wafers, showing dice with anomalous values.

thickness, the data suggest the thickness over the wafer surface would approximate an inverted hemisphere, with the film thickness increasing radially from the center to the edge of the wafer. The data also suggests that die numbers 49, 65, and 69 are outlying values, as they represent significant interruptions in the regular periodicity seen along columns and rows in the die histograms. It is also evident that die 65 is an extreme outlying value and is the primary cause of the aforementioned distortions in the distribution.

To further illustrate this point and gain a more comprehensive perspective on the distribution of sheet resistance values on the entire wafer, color sheet resistance contour maps were generated for one of the condition 9 wafers. Figure 77 shows two contour maps: one with all 69 measurements (top) and another with dice 49, 65, and 69 removed (bottom). The top map clearly distorts the sheet resistance distribution, in that the wafer appears deceptively uniform except for the regions in the vicinity of the three anomalous dice. The bottom map, on the other hand, shows a series of concentric contour lines that are indicative of a thickness gradient going from center to edge, with the film thickness being largest toward the edges. These are the same trends seen in the die histograms and diameter scans previously mentioned. All other wafers in this investigation showed the same sheet resistance trends and the occurrence of the three anomalous dice (49, 65, and 69). This is evidenced by Figure 78, which shows a composite row-wise histogram for the average R_s values by die number for all 18 wafers used in this study.

Figure 77: Two sheet resistance contour maps for the first wafer of condition 9. The top map has all sixty-nine measurements, and the bottom map has the values for dice 45, 65, and 69 removed. In the bottom figure a gradient in sheet resistance can easily be seen, in going from the center to the edge of the wafer.

Figure 78: Average sheet resistance die histogram by row for all dice on all experimental wafers, showing the recurrence of anomalous dice 49, 65, and 69.

Further analysis of these three dice by the boxplot method revealed that, in all cases, die 65 was an extreme outlying value. An example of such a boxplot is shown in Figure 79. Die 49, on the other hand, was found to be either an extreme or moderate outlier in most cases. Lastly, die 69 was a moderate outlier in only four of eighteen cases, and a non-outlier for the remaining conditions. These results are summarized in Table 19. Furthermore, the outlying R_s values were not within the 3σ limit currently used in the semiconductor industry for die acceptance. Based on these results, dice 49, 65 and 69 were not considered for subsequent metrology for any of the 18 samples.

With the three anomalous dice removed from the pool of R_s data, the assumption of normality in the data was reinvestigated. Figure 80 shows both frequency histograms and normal probability plots for one of the condition 9 wafers. It is clear from this figure that removal of these three dice results in normally distributed data. Similar results were obtained for the all the remaining wafers. Z-tests were again performed on all wafer pairs in the fashion previously described and the results are shown in Table 20. Again, the p-values are all substantially larger than 0.05, indicating that duplicate wafers for each condition have statistically equivalent mean R_s values at the 95% confidence level with the three dice removed.

One possible explanation for the anomalous sheet resistance measurements on these three dice takes into account the fact that the measurement locations on these three dice are much closer to the edge of the wafer than equivalent dice which are diametrically opposed. Recall that the measurement location on each die was at coordinates $x = -2.5$ mm, $y = -7.5$ mm, relative to the geometric center, or origin, of the 20-mm square die. If

Figure 79: A boxplot summary showing the distribution of sheet resistance values for the first wafer of condition 9. Three outlying values are identified.

Table 19: A summary of the boxplot analysis results for each set of duplicate wafers for all conditions, in relation to dice 49, 65 and 69. “E” refers to an extreme outlier, “M” a moderate outlier, and “X” a non-outlier.

Condition	Wafer	Die 49	Die 65	Die 69
1	1A	M	E	X
	1B	M	E	X
2	2A	E	E	X
	2B	E	E	M
3	3A	E	E	X
	3B	E	E	X
4	4A	X	E	X
	4B	M	E	X
5	5A	E	E	M
	5B	E	E	X
6	6A	X	E	X
	6B	E	E	X
7	7A	X	E	X
	7B	X	E	X
8	8A	M	E	X
	8B	M	E	X
9	9A	M	E	M
	9B	X	E	M

Figure 80: Sheet resistance frequency histogram (top) and normal probability plot (bottom) for condition 9A, with dice 49, 65, and 69 removed.

Table 20: Sheet resistance z -test results at the 95% confidence level between all duplicate pairs of wafers for each condition, with the removal of dice 49,65, and 69.

Condition	Mean Difference	Standard Error	z_{test}	p-value	Confidence Intervals	
					Lower 95%	Upper 95%
1	0.00016	0.0002	0.995	0.320	-0.0005	0.0002
2	0.00029	0.0002	1.270	0.204	-0.0002	0.0007
3	0.00019	0.0002	0.837	0.403	-0.0006	0.0003
4	0.00025	0.0001	1.745	0.081	-0.0005	0.0000
5	0.00067	0.0012	0.574	0.566	-0.0016	0.0030
6	0.00007	0.0002	0.285	0.776	-0.0005	0.0004
7	0.00029	0.0002	1.619	0.106	-0.0006	0.0001
8	0.00003	0.0002	0.150	0.881	-0.0004	0.0004
9	0.00003	0.0002	0.129	0.897	-0.0004	0.0004

one compares the shortest distance to the wafer edge between the measurement locations on dice number 5 and 65, which are diametrically opposed, die 5 is approximately 20.5 mm from the edge of the wafer, while die 65 is only approximately 5.5 mm from the edge. As previously mentioned, eddy current measurements rely on a sufficient volume of material to create a complete circular path within the material being measured. Any interruptions in this circular path, such as the edge of a wafer, will disrupt the eddy currents and could result in erroneously high measurements. It is conceivable that such an effect may have contributed to the erroneous measurements seen on dice 49, 65, and 69.

Another effect that could be distorting the measurements on these dice is related to the fact that near the edge of the wafer a significant portion of the magnetic energy from the probe is not being coupled to the film. In other words, the magnetic field lines emanating from the probe extend beyond the edge of the wafer and get coupled to the surrounding air in the absence of any copper film. This occurrence represents lost magnetic energy and introduces the possibility of erroneously high sheet resistance values on dice with measurement locations very close to the wafer edge.

A last possible effect is related to the edge exclusion on the wafer. As previously mentioned, the electroplated copper film does not extend to the wafer edge, as the tooling (cathode assembly) used for electroplating requires good electrical contact to the copper seed layer, which itself does not extend to the wafer edge. Careful inspection near the edges of all wafers used in this investigation revealed some exposed Si and Ta, which both have significantly higher resistivities than Cu. It is quite possible that the eddy

current probe was receiving a portion of its signal from these edge regions, which could also raise the sheet resistance values and produce anomalous readings. In other words, a portion of the signal from the probe came from materials that have resistivities which greatly exceed that of copper.

5.1.3 Statistical Comparison of Experimental Conditions

Another extremely important component of this analysis was to compare the mean sheet resistance values between all nine conditions. This was accomplished using the one-way analysis of variance (ANOVA) approach with the data from both duplicate wafers, but with the dice 49, 65, and 69 removed from the populations. Such an analysis allows the mean values of a variable for several different treatment groups to be compared statistically. The data in Appendix A give a very good indication that the sheet resistance values are very similar, but such an assessment is only qualitative. The results of this analysis, which were performed at the 95% confidence level, are summarized in Table 21. The very small mean square values indicate that very little variability exists both within and between groups. The derived p-value of 0.173 indicates that there is no difference in the mean sheet resistance between all nine experimental conditions at the 95% confidence level. This implies that the Cu microstructures for the nine different treatment groups have similar defect densities, but not necessarily the same grain size.

5.1.4 Selection of Metrology Dice

Based on the analyses presented here and previous discussions, one 20-mm die from each wafer was selected for subsequent metrology. The primary criteria used to select the dice were as follows:

Table 21: ANOVA results at the 95% confidence level comparing the mean sheet resistance values between all nine experimental conditions.

Source of Variation	df	SS	MS	Fcalc	Fcrit	p-value
Between Conditions	8	1.54E-05	1.93E-06	1.4440	1.946	0.173
Within Conditions	1179	0.001572	1.33E-06			
Total	1187	0.001588				

1. The die must have no visual film defects.
2. The central die and all its adjacent neighbors are excluded.
3. All edge dice and their interior adjacent neighbors are excluded.
4. The die selected must have an R_s value that is within 1σ of the mean value.

Criterion 2 is based on the fact that the diameter scans exhibited a localized central lobe of non-uniformity in sheet resistance approximately 12 mm in diameter. The contour maps suggested that this local non-uniformity might extend into adjacent dice for some wafers. The bases for criterion 3 are: 1) anomalous dice 49, 65, and 69 are included in this subset; 2) the long diameter scans and contour maps indicated these dice to be contained within regions of thickness non-uniformity; 3) these dice were the most prone to the processing defects mentioned in criterion 1.. Criterion 4 ensures that the die chosen is reasonably representative of the wafer in terms of its mean R_s value.

In consideration of the selection criteria listed above, the dice that served as the best candidates for subsequent metrology are shown in Figure 81. Attempts were made to choose the same dice from wafer pairs for each experimental condition in this study. Processing defects, however, prevented this additional condition to be satisfied for all wafer pairs. A list of the dice selected and their metrology dispositions are shown in Table 22.

5.1.5 Assessment of Copper Film Resistivity

A final objective was to assess the resistivity in the blanket regions of the dice selected for microstructural analysis. To perform this analysis, a detailed knowledge of the film thickness is required. Thickness values in blanket regions of each die were

Figure 81: A wafer schematic showing the subset of dice that were deemed suitable for subsequent metrology from each wafer. These dice are highlighted in gray.

Table 22: A table summarizing the dispositions of the dice selected for subsequent metrology. The sheet resistance values for each die are shown for reference.

Condition	Duplicate	Die	$R_s (\Omega/\alpha)$	Metrology Disposition
1	1A	17	0.01267	Focused Ion Beam Imaging
	1B	24	0.01194	X-ray Diffraction
2	2A	17	0.01276	Focused Ion Beam Imaging
	2B	17	0.01236	X-ray Diffraction
3	3A	17	0.01291	Focused Ion Beam Imaging
	3B	33	0.01286	X-ray Diffraction
4	4A	17	0.01220	Focused Ion Beam Imaging
	4B	37	0.01201	X-ray Diffraction
5	5A	53	0.01228	X-ray Diffraction
	5B	17	0.01252	Focused Ion Beam Imaging
6	6A	17	0.01266	Focused Ion Beam Imaging
	6B	33	0.01309	X-ray Diffraction
7	7A	55	0.01198	X-ray Diffraction
	7B	17	0.01291	Focused Ion Beam Imaging
8	8A	17	0.01259	Focused Ion Beam Imaging
	8B	53	0.01256	X-ray Diffraction
9	9A	17	0.01266	Focused Ion Beam Imaging
	9B	37	0.01298	X-ray Diffraction

determined from tilt-view FIB images, which show the Cu film in cross-section. Examples of these images will be presented and discussed in Sub-chapter 5.2. Since FIB imaging is a destructive test, the resistivities of the dice selected for texture analysis were not analyzed. A total of six thickness measurements were taken from two different FIB images. The resistivities were then calculated, based on the sheet resistance and thickness values for each die, and the results are shown in Table 23. The table clearly indicates that the films used in this investigation approach the bulk resistivity value for Cu of $1.673 \mu\Omega\text{cm}$, which suggests a large-grained microstructure. This data also suggest that the Cu films for all nine conditions have similar crystalline defect densities, but not necessarily the same average grain size. Theoretical and experimental studies have shown that the grain boundary scattering contribution to the resistivity remains small and constant after the mean grain size exceeds approximately $1 \mu\text{m}$ [17].

Table 23: A summary of the calculated resistivity values for each condition, based on the thickness and sheet resistance measurements of the FIB metrology dice.

Condition	Die	R_s ($\Omega/$)	Thickness (μm)	Resistivity ($\mu\Omega\text{-cm}$)
1A	17	0.01267	1.34	1.70
2A	17	0.01276	1.29	1.65
3A	17	0.01291	1.30	1.68
4A	17	0.01220	1.35	1.65
5B	17	0.01252	1.32	1.65
6A	17	0.01266	1.30	1.65
7B	17	0.01291	1.26	1.63
8A	17	0.01259	1.28	1.61
9A	17	0.01266	1.29	1.63
Average		0.01265	1.30	1.65
Maximum		0.01291	1.35	1.70
Minimum		0.01220	1.26	1.61
Standard Deviation		0.00022	0.03	0.03
Standard Deviation (%)		1.7	2.2	1.6

5.2 Microstructure of Electroplated Copper Films

5.2.1 Microstructure of Blanket Copper Films

Typical plan-view FIB images obtained for this investigation, which use gallium ion channeling contrast, are shown in Figure 82. The images depict the surface of 1.3- μm , annealed Cu films in the unpatterned region of die 17 for experimental conditions 2 and 6. Additional images for all conditions may be found in Appendix B. From the images, one can discern large, distinct copper grains, which are indicative of complete recrystallization and subsequent grain growth of the Cu microstructure. In comparing the images for all experimental conditions (Appendix B), one can see that some differences exist in the range of grayscales present in the images for the different experimental conditions, the significance of which is unclear at this time. Some images, such as one for condition 9, were also found to exhibit a more textured appearance, which suggest some possible topographical differences in the microstructures. In some cases a high degree of faceting was observed in the larger grains, which previously has been reported in the literature after high-temperature annealing treatments of electroplated copper [33].

The recrystallized microstructure also exhibits a very high degree of crystallographic twinning. Face-centered cubic (FCC) metals, such as copper and aluminum, frequently exhibit this type of defect, which comes about from stacking fault errors of the (111) close-packed planes. Figure 83 shows the atomic arrangement of a twinning plane for a typical FCC metal. As the figure indicates, there are two twin boundaries, or interfaces, that separate the twin and the parent crystal. A twin boundary is often a coherent interface, in that the atomic positions of the parent and twin match

Figure 82: Representative plan-view FIB images of the annealed copper microstructure for experimental conditions 2 (top) and 6 (bottom).

Figure 83: The atomic arrangement at the twinning plane in a face-centered cubic metal. The black and white circles represent atoms on different levels.

along the boundary (coincident lattice sites) and no dislocation need be present [16]. The interfacial energy of a twin boundary is generally only about one-tenth that of a grain boundary. In the case of copper, it has been determined to be 0.044 J/m^2 , which is very much smaller than the copper-copper grain boundary energy of 0.646 J/m^2 [16]. In light of these facts, a twin boundary is generally considered to be a subgrain boundary and not a true grain boundary. This type of crystalline defect can arise from either mechanical deformation or annealing [16]. In the latter case, they are generally referred to as recrystallization or annealing twins. In some cases the twinned grains exhibited very high twin densities, examples of which are illustrated in Figure 84.

Figure 85 illustrates two cases where adjacent grains both contain twins. In the first case, the angle at the intersection of the twin boundaries is 60° , while in the second case they form an angle of 90° . Previous studies have shown that grains having a (111) crystallographic orientation will have the twin boundaries that form an angle of 60° , while (200)-oriented grains have twin boundaries that intersect at an angle of 90° [33]. Both types of grains were found for all nine experimental conditions, which suggests that both (111) and (200) texture components are present in the annealed copper films prepared for this investigation. The 60° twin boundaries, however, were observed to occur more frequently than the 90° boundaries, which raises the possibility of a larger (111) texture component.

To further complement a qualitative description of the copper microstructure, tilt-view FIB and electron images of the blanket film regions were examined. Representative FIB and electron images that depict the copper grain structure in cross section may be

Figure 84: Examples of copper grains exhibiting a high degree of crystallographic twinning.

Figure 85: Examples of twin boundaries intersecting at 60° (left) and 90° (right).

found in Figures 86 and 87. Additional tilt-view FIB images for each experimental condition may be found in Appendix C. From these pictures one can easily discern that the microstructure is comprised of large columnar grains that are generally of a height comparable to that of the film thickness. Similarly, the twins contained within such grains span the entire film thickness. These types of grains are most common in compact thin films and often come about as a result of preferred growth in certain crystallographic directions [38]. This is not surprising since Damascene copper frequently exhibits both (111) and (200) texture components. Randomly oriented grains, on the other hand, are generally small in comparison to the film thickness [38].

A frequent observation in some of these images is a textured appearance on the film surface, giving such films the appearance of having a high degree of surface roughness. This occurrence may be related to the textured appearance also seen in the plan-view images and may have come about from the annealing process. A similar degree of surface roughening was also illustrated in a study by Brongersma, in which an electroplated Cu film was annealed for 20 hours at 400°C [29].

Occasionally, very small grains were observed at the barrier-copper interface, as exemplified in Figure 86. At this magnification, it is unclear whether these grains are associated with the seed layer or the electroplated copper. Ryu has reported that copper seed layer grains persist after self-annealing using high-resolution TEM imaging, but the applicability of his result to this study is unclear [96].

Figure 87 also shows evidence of some thermal grooving in the region where the grain boundaries meet at the top surface. The occurrence of thermal grooving is

Figure 86: Tilt-view FIB images at two different magnifications showing a cross section of the annealed copper microstructure for experimental condition 6.

Figure 87: Two tilt-view electron images of the annealed blanket copper films for experimental condition 2 showing thermal grooving (top) and a void (bottom).

generally associated with high-temperature annealing and is a direct result of surface tension factors [16]. Diffusion of atoms over the free surfaces is believed to be the most important factor involved in the transport of atoms out of the grooved regions during the formation of the grooves [16]. Brongersma also reported extensive grain boundary grooving in electroplated Cu films annealed at 400° for extended periods of time [29]. However, he attributed this grooving to the grain boundary volume reduction that accompanies extensive grain growth at elevated temperatures, which generally leads to high residual tensile stresses in the films.

Lastly, circular pores, or voids, that are approximately 0.1-0.3 μm in diameter were also frequently observed, as is also shown in Figure 87. Additional visual evidence of these voids is present in the plan-view images of Figure 88 at two different magnifications, which suggest they occur primarily at the grain boundaries. The origin of this undesirable film defect is unknown at this time and would require further investigation. However, void formation has been associated with conditions of high tensile stress in soft metals that exceed the yield point [16]. In such cases, material is selectively transported out of certain regions of the film to relax the stress elsewhere. High residual tensile stresses have been shown to develop in recrystallized, electroplated Cu films during the self-annealing process for some plating chemistries [10], or after high-temperature thermal cycling [29].

5.2.2 Grain Size and Distribution of Blanket Copper Films

The method used to analyze the grain size and associated grain size distributions utilized image analysis software [112] in conjunction with plan-view FIB images taken at

Figure 88: Two plan-view images of the copper microstructure for experimental condition 8 showing the presence of voids at the grain boundaries. The top image uses conventional metallurgical light microscopy and the bottom image focused ion beam imaging.

5000× magnification. A total of five plan-view images in the blanket film region of die 17 were acquired for each of the nine experimental conditions for grain sizing purposes. Since copper grains frequently exhibit crystallographic twins, completely automated grain sizing is not possible with FIB or even TEM photomicrographs. When grain sizing polycrystalline FCC metals, it is customary not to count the twins within the copper grains separately, as they are generally considered to be subgrain boundaries. However, image analysis software packages use grayscale contrast to differentiate between grains or particles. Using automated grain detection would obviously yield erroneous results, since a grain containing a single twin, which usually has a significantly different grayscale value, would, in effect, be treated as three separate grains.

A frequently used approach to circumvent these problems is to manually trace the grain boundaries from a printed image onto an overlaid transparency and digitally scan the results into an image analysis program to calculate the individual grain areas [95]. Other problems encountered in the use of FIB images for grain sizing include adjacent grains having similar grayscale levels and the occurrence of very complicated networks of twins. Examples of these two problems are shown in Figure 89. Acquiring multiple images in the same area of the sample at different tilt angles can also aid in grain identification, but was not used in this study [14].

In this investigation, a combination of both manual and automated techniques were employed to determine the grain sizes and associated distributions. To perform the grain size analysis, the automatic particle detection feature of the software utility was not employed for the reasons stated above. After appropriate spatial calibration of the image

Figure 89: Two plan-view FIB images from conditions 2 and 6 illustrating some complications arising from the use of FIB imaging for grain sizing.

to be analyzed, the grayscale thresholding feature was utilized to narrow the grayscale detection range to approximately 20-30 grayscale levels, starting with the low (dark) side of the grayscale level spectrum. Grains that were discernable to a reasonable degree of confidence within a given grayscale range were then manually traced directly on the image (using the "wand tool") and numbered. Special precautions were taken to ensure accurate grain identification in cases where the grains were twinned, had very similar grayscale levels, or indistinct grain boundaries. This included utilization of image enhancement features such as zoom, contrast, brightness, and the application of various image filters contained within the software utility.

The areas of each numbered grain in this collection were then calculated with the area analysis feature of the software. The process was then repeated approximately ten times for each image to encompass the entire range of grayscales contained within the image. Five plan-view, 5000 $\times$ -magnification FIB images, such as the ones previously exhibited in Figure 82, were utilized for each of the nine experimental conditions to calculate the areas of approximately 500-600 grains for each of these conditions. The results were then exported into spreadsheet software for further analysis.

The in-plane, mean grain size and standard deviation for each condition were determined from a Gaussian fit to the distribution of grain sizes. This method assumes circular two-dimensional grains, since the data were generated from areal FIB images. Hence, the area values determined for each grain were converted to a grain diameter by assuming circular grains. In essence, this method assumes a linear correlation between two-dimensional (areal) and three-dimensional (volume) recrystallization. This method

is commonly used and well documented in the literature for studies that employ FIB plan-view imaging for grain sizing [14,33].

A summary of the basic univariate statistics for all nine experimental conditions is shown in Table 24. The mean grain diameters ranged between 1.7 to 1.9 μm , with standard deviations that ranged between 0.5 to 0.8 μm . A grain size that is large in comparison to the film thickness has been attributed to abnormal, or non-uniform, growth during the annealing process [43]. This is consistent with the contention of many authors that additive incorporation in Cu grain boundaries is a factor that contributes to the initiation of abnormal grain growth during the recrystallization process [17,25,30].

These results, which are also summarized graphically in Figure 90, show that a high-temperature annealing treatment of blanket, self-annealed copper films produces large grains of similar dimensions that are independent of the DC current density or additive level used during the copper electrodeposition process. Considering the degree of overlap of the 95% confidence intervals shown in Figure 90 and the inherent potential for some error to be generated in the grain sizing process, these data suggest that no statistically significant difference in the mean grain sizes exists after high-temperature annealing. The grain size results are also in agreement with the resistivity results previously presented, which showed no significant differences in resistivity for any of the nine experimental conditions. Films with similar grain sizes would be expected to have similar resistivities, assuming the same film thickness and similar defect densities. However, the reader should be cautioned that the resistivity increase attributable to grain

Table 24: Univariate grain sizing statistics of the blanket copper films for all nine experimental conditions. The upper and lower 95% confidence intervals are also shown.

Condition	Count	Mean Diameter (μm)	Standard Deviation (μm)	Maximum (μm)	Minimum (μm)	Upper 95% C.I.	Lower 95% C.I.
1	536	1.763	0.765	6.666	0.437	1.829	1.699
2	606	1.818	0.845	6.372	0.500	1.885	1.750
3	558	1.710	0.691	4.976	0.580	1.767	1.652
4	584	1.742	0.575	4.206	0.574	1.789	1.695
5	593	1.835	0.654	5.453	0.681	1.887	1.782
6	584	1.781	0.580	4.507	0.602	1.828	1.734
7	614	1.905	0.692	6.315	0.724	1.962	1.848
8	638	1.705	0.543	4.872	0.703	1.747	1.663
9	595	1.852	0.540	4.215	0.855	1.895	1.808

Figure 90: A plot summarizing the grain sizing results for all nine experimental conditions. The vertical error bars shown in red represent the 95% confidence intervals.

boundary scattering in Cu thin films becomes relatively insignificant ($< 5\%$) once the grain size reaches approximately $1\ \mu\text{m}$ [17].

It is very important to note that these results are quite different than those obtained for room-temperature recrystallization studies of electroplated copper. As mentioned in the literature review, factors such as additive level, current density, and specimen dimensions influence not only the recrystallization kinetics but also the final grain size, texture, and sheet resistance of the recrystallized microstructure [20,21,23,29,30,31]. As mentioned earlier, the mechanisms generally cited to provide the driving forces for the self-annealing process include stored energy in the form of a high grain boundary energy density, the rejection of incorporated plating impurities, and crystalline defects such as dislocation loops or vacancies [17,23,25].

It has also been suggested that some of this stored energy remains in the film after room-temperature recrystallization, the degree of which is dictated by the initial electrodeposition conditions [20]. This implies that the final microstructure may be thermodynamically metastable, in that lower energy states can be achieved. Some studies have suggested that a fine-grained component may persist after self or low-temperature annealing [14]. Most recently, Brongersma has shown that the self-annealed state is only an intermediate state due to the presence of incorporated electroplating impurities remaining in the grain boundaries that inhibit further grain growth [29].

Based on the grain-sizing results presented in this study, it is apparent that low-resistivity, electroplated, blanket Cu films with a large-grained microstructure can be achieved by a high-temperature annealing treatment that follows the self-annealing

process. In effect, this process makes the final grain size and film resistivity of blanket Cu films independent of electrodeposition parameters such as the brightener level or current density.

These results are clearly in agreement with and complementary to the work of Brongersma, who showed that extensive annealing at high temperatures results in an additional considerable enlargement of the grain structure accompanied by an additional decrease in the sheet resistance and the desorption of impurities that were incorporated during electroplating [29]. In this study, Brongersma used a Cu film electroplated at a current density of 2.38 mA/cm^2 and a brightener level of 3.0 ml/l. The trends shown in this study show that Brongersma's results can be extended to a wide range of current densities and brightener levels using the equipment, chemistry, and methodology employed in this investigation. Apparently, the high-temperature, inert-gas annealing treatment used in this study lead to desorption of most, if not all, of the additives remaining in the grain boundaries after self-annealing. Secondary ion mass spectroscopy (SIMS) depth profiles of the copper films before and after the high-temperature annealing treatment would be required to validate this interpretation.

The grain structure of polycrystalline thin films of face-centered cubic metals such as copper is well represented by a lognormal distribution [43]. A representative histogram of grain sizes for experimental condition 5 is shown in Figure 91. The high degree of positive skewness and kurtosis seen in the shape of the distribution are typical of lognormal distributions. The probability density function (PDF) of a two-parameter lognormal distribution is given by

Figure 91: A representative histogram of grain sizes obtained for experimental condition 5. The shape of the distribution suggests a high degree of positive skewness and kurtosis, which is typical of lognormal distributions. The mean grain size (μ) and standard deviation (σ) are also shown.

$$f(x) = \frac{1}{xb\sqrt{2\pi}} e^{-(1/2b^2)[\ln(x)-a]^2} \quad (18)$$

where $f(x)$ is the probability density function, x is the grain size, and **a** and **b** are parameters that define the shape of the distribution [97]. The mean (μ) and variance (σ^2) of x are related to these shape parameters by [97]

$$\mu = e^{a+0.5b^2} \quad (19)$$

$$\sigma^2 = \mu^2(e^{b^2} - 1) \quad (20)$$

The simplest way to fit the distribution to a set of grain size data is to take the natural logarithms and set **a** and **b** equal to the mean and standard deviations of these transformed data. The data shown in Figure 91 was transformed accordingly to give values of 0.547 and 0.345 for the lognormal parameters **a** and **b**, respectively. The resulting probability density function for the data of condition 5 is shown in Figure 92. The values of **a** and **b** for all nine conditions are summarized in Table 25.

Logarithmically transforming the data as mentioned above should, in accordance with the Central Limit Theorem, result in a set of data that is normally distributed [97]. A simple test for any serious deviations from lognormality would then be to first logarithmically transform the data and then construct a normal probability plot of the resulting data. If the data is normally distributed, the points on a normal probability plot should fall close to a straight line. A normal probability plot for the data of condition 5 is shown in Figure 93. From this plot, it can easily be seen that the data are normally

Condition 5

Figure 92: The lognormal probability density function for the distribution of grain sizes from experimental condition 5. Areas under the curve correspond to probabilities.

Table 25: *The distribution parameters derived for the lognormal probability density function for all nine experimental conditions. The results suggest very similar grain size distributions.*

Condition	<i>a</i>	<i>b</i>
1	0.476	0.430
2	0.501	0.436
3	0.444	0.400
4	0.501	0.332
5	0.547	0.345
6	0.528	0.310
7	0.580	0.363
8	0.487	0.305
9	0.575	0.285

Figure 93: A normal probability plot of the logarithmically transformed grain size data from condition 5. The high degree of linearity indicates that the transformed data is normally distributed and therefore indicates a good fit to a lognormal distribution.

distributed ($R^2 = 0.998$) and only minor deviations from normality exist at the extreme ends of the data set. It can thus be inferred that the data for condition 5 are lognormally distributed and are an excellent fit to a lognormal distribution of grain sizes. Without exception, similar results were obtained for the remaining eight experimental conditions.

Based on the discussion above, it is evident that the grain size distributions of blanket electroplated copper films remain lognormal in character after a high-temperature annealing process. These results are consistent with a study by Beyer that reported a lognormal distribution of grain sizes for a 1.3- μm electroplated copper film that was annealed at 400°C using a rapid thermal processing (RTP) treatment immediately after electrodeposition [33]. A lognormal distribution of grain sizes is generally associated with abnormal or secondary grain growth, where certain thermodynamically favored grains grow at the expense of others. The results of this study, RTP studies [33], and self-annealing studies [34] suggest that the recrystallization and subsequent grain growth of electroplated copper films proceed by an abnormal grain growth mechanism. Any fine grains remaining in the matrix after room-temperature recrystallization will grow and coalesce, or be consumed by the growth of larger recrystallized grains after a high-temperature annealing treatment. Concurrent with these processes would be the removal of any remaining crystalline defects and the desorption of any remnant solute impurities trapped at the grain boundaries that would impede further grain growth after room-temperature recrystallization.

To conclude this discussion, the sequence of events after electrodeposition that led to the large-grained, low-resistivity blanket films seen for all conditions in this study will

be summarized. For simplicity, only the two extremes of high and low current density (conditions H and L, respectively) and a constant additive level will be considered. The reader is referred to Figure 94, which graphically summarizes these events. Immediately after electrodeposition ($t = T_0$), condition H will have a slight smaller grain size ($D_{Hi} < D_{Li}$) and more stored energy than condition L. In accordance with the literature on self-annealing, condition H will recrystallize faster ($T_1 < T_2$) and have a larger final self-annealed grain size ($D_{Hf} > D_{Lf}$) after the transient period [23]. At this stage recrystallization is complete and the primary reason for the difference in grain size, based on the work of Brongersma, would be different levels of impurity incorporation in the grain boundaries that would impede further grain growth and influence the final grain size distribution [20,21,29]. At the start of the high-temperature annealing treatment ($t = T_3$), additional post-recrystallization abnormal grain growth begins to occur for both films. The film for condition H, with fewer incorporated impurities at the grain boundaries, will recrystallize faster than that for condition L ($T_4 < T_5$). As the grains of film L grow under the conditions of prolonged thermal exposure, the impurities that impeded further grain growth after self-annealing percolate along the grain boundaries and eventually desorb from the film. In both cases a practical upper limit to grain size is reached (D_{HLf}) due to free-surface effects such as a reduction of the grain boundary curvature and thermal grooving [16].

5.2.3 Microstructure within Damascene Trench Features

The microstructure of the recrystallized Cu with 0.35 and 0.50- μm Damascene lines was also examined. Figure 95 illustrates representative FIB images for condition 5 taken

Figure 94: A graphical summary of the events leading to similar grain sizes in self-annealed, electroplated copper films, followed by a high-temperature thermal treatment.

Figure 95: Representative tilt-view FIB images taken at 35000× magnification for condition 5, showing the grain structure within 0.50-μm (top) and 0.35-μm (bottom) Damascene trench structures in cross section.

at a tilt angle of 52° relative to the surface normal at $35000\times$ magnification. Additional FIB images of the trench structures may be found in Appendix D. The large grains in these figures illustrate that the Cu within these fine trench features appears to be fully recrystallized, as there is no evidence of a fine-grained component or other defects that would tend to reduce the image clarity within select regions of the image. This observation complements the work of Ritzdorf, which showed that room-temperature annealing does not ensure the recrystallization of Cu in fine trench lines and that some type of thermal annealing is required [19]. His study also showed that annealing conditions are a function of trench line width, in that smaller lines require more thermal energy to achieve full recrystallization than wider lines. The annealing process implemented in this investigation provided enough thermal energy to achieve recrystallization down to line widths of $0.35\text{ }\mu\text{m}$.

The grains in the $0.5\text{-}\mu\text{m}$ lines are observed to be larger than those of the $0.35\text{-}\mu\text{m}$ lines, which is consistent with the observation that grain size within Damascene features decreases linearly with trench width [52]. Similar to the case of blanket films, the occurrence of twinning is also observed to be common within these features, especially in the larger grains. It is also evident that there is a tendency for some grains in the overlying copper to propagate into the trench structures during the grain growth process. This behavior has also been observed by Jiang [31]. Within these features, a variety of grain sizes were found, but occasionally very large grains which occupied the entire width and a large percentage of the trench cross-sectional area were observed. The semiconductor industry generally refers to this grain structure as a “bamboo”

microstructure. Similar occurrences of these very large grains were found in the 0.35- μm trenches. There are also some indications that grains nucleate and grow from the side and bottom walls of the trench, which, in addition to the trench corners, may serve as possible nucleation sites during the recrystallization process.

It has been reported by Dubin that large Cu grains occupying the entire trench have been achieved in Damascene structures after high-temperature annealing [34]. In Dubin's study a 400°C, 1-hour isothermal annealing process was used after room-temperature recrystallization. A 0.5- μm trench in cross section, using an FIB image taken at 35000 $\times$ magnification, was exhibited to support this claim. Upon close inspection of the image in Dubin's paper, it appears that this claim is not universally true [34]. In fact, 5-6 grains were evident in the image presented in his paper, although one grain clearly dominated the trench cross-section.

To better discern the grains within the trench features of the 0.35 and 0.50- μm trenches in this study, additional FIB cross sections were taken at 50000 $\times$ magnification. Representative images are shown in Figure 96, which were randomly chosen from experimental condition 5. From these images it is apparent that a wide variety of grain structures exist with these features. In some cases, large grains that occupy approximately 50 to 100% of the trench cross-sectional area can be seen. In other cases, it can be seen that several small grains occupy the trench, with a wide variety of shapes and sizes. Hence, it is apparent that even with a high-temperature annealing treatment, it is not universally true that large grains will occupy the entire, or even a significant portion of, the cross-sectional area encompassed by fine trench features. This suggests

Figure 96: Representative tilt-view FIB images taken at 50000 $\times$ magnification for condition 5, showing the grain structure within 0.50- μm (top) and 0.35- μm (bottom) Damascene trench structures in cross section.

that other factors, such as the nucleation and growth processes that occur during electrodeposition and lead to as-deposited structures with different amounts of stored energy could potentially influence not only the recrystallization kinetics but also the final microstructure within fine trench or via structures.

5.2.4 Grain Size within Damascene Trench Features

To gain further insights into the annealed copper microstructure within the Damascene lines, a grain size analysis was performed for all nine experimental conditions using the 0.35 and 0.50- μm trench features. The tilt-view FIB images taken at 35000 $\times$ magnification were employed for this purpose. In all cases, die 17 from each experimental wafer was utilized for the analysis, and the grains within ten (0.50- μm features) or fourteen (0.35- μm features) trenches were considered. Similar to the work of Ritzdorf, the grain size was quantified as the grain density, which is the number of grains per unit cross-sectional trench area [19]. Using this grain density index, a larger value is indicative of a smaller cross-sectional grain size. Image analysis software was utilized to calculate the cross-sectional area of each trench and to enhance the image as necessary to detect grains that were difficult to discern [112]. Tables 26 and 27, which summarize the results of this analysis for each condition, show that sufficient variability exists in the data to warrant further investigation of possible trends in the data with respect to the electroplating variables.

Figures 97 and 98 are plots of the grain density (expressed as grains/ μm^2) as a function of current density for each of the three additive levels used in this study, for both

Table 26: A summary of the grain density results for the 0.5- μm trench features. A smaller grain density implies a larger, average, cross-sectional grain size.

Condition	Number of Trenches	Average Grains per Trench	Average Trench Area (μm^2)	Average Grain Density (Grains/μm^2)
1	10	3.2	0.305	10.49
2	10	3.0	0.309	9.71
3	10	2.8	0.307	9.12
4	10	3.4	0.295	11.53
5	10	3.1	0.300	10.33
6	10	2.8	0.296	9.46
7	10	3.4	0.298	11.41
8	10	3.3	0.344	9.59
9	10	2.8	0.297	9.43

Table 27: A summary of grain density results for 0.35- μm trench features. A smaller grain density implies a larger, average, cross-sectional grain size.

Condition	Number of Trenches	Average Grains per Trench	Average Trench Area (μm^2)	Average Grain Density (Grains/μm^2)
1	14	3.43	0.180	19.05
2	14	3.57	0.187	19.10
3	14	2.57	0.206	12.48
4	14	4.00	0.180	22.22
5	14	3.86	0.189	20.41
6	14	2.86	0.207	13.80
7	14	4.14	0.170	24.37
8	14	4.07	0.185	23.95
9	14	2.43	0.189	12.85

Figure 97: A plot showing the trends in grain density within the 0.50- μm trenches for all nine experimental conditions. The small grain density obtained for experimental condition 8 (9.59 grains/ μm^2) may have been a consequence of the somewhat larger cross-sectional areas of the 0.50- μm trenches measured on this wafer.

Figure 98: A plot showing the trends in grain density within the 0.35- μm trenches for all nine experimental conditions. The data suggest a stronger tendency for the grain size to increase with current density as compared to the 0.50- μm trenches, which occurs in the current density range of 45 to 105 mA/cm^2 .

the 0.50- μm and 0.35- μm features, respectively. It is emphasized that the grain densities represented are perpendicular, and not parallel, to the current path. Consequently, no direct inferences can be made from this data about the grain size and grain structure parallel to the trenches. It is evident from Figure 97 that there exists a minor, but consistent, tendency for the grain density to decrease with current density after recrystallization in the 0.5- μm trenches, but no obvious trend with respect to the additive level. The smaller grain densities in the 0.50- μm trenches shown for experimental condition 8 are probably a consequence of the somewhat larger cross-sectional areas of the trenches measured on this wafer as compared to the other wafers

To determine the statistical relevance of these trends, analysis of variance (ANOVA) with replication was performed at the 95% confidence level ($\alpha = 0.05$) on the entire 0.50- μm data set. The results are presented in tabular form in Table 28. In this table, df represents the number of degrees of freedom, SS is the sum of the squares, MS is the mean square value, Fcalc is the calculated variance ratio, and Fcrit is the critical variance ratio at the assigned significance level, based on the degrees of freedom. The p-value is the probability of a value as extreme as the observed value. A calculated p-value less than 0.05 for a given variable implies statistical significance at the 95% confidence level. Table 28 shows neither the current density, additive level, or their interactions have a significant influence on grain size at the 95% confidence level. In fact, a p-value of 0.09 implies significance at only the 91% confidence level.

Table 28: ANOVA results at the 95% confidence level for the entire 0.50- μm grain density data set.

Source of Variation	df	SS	MS	F_{calc}	F_{crit}	p-value
Current Density	2	51.54	25.77	2.48	3.11	0.090
Additive Activity	2	6.67	3.34	0.32	3.11	0.727
Variable Interaction	4	3.61	0.90	0.09	2.48	0.986
Error	81	843.33	10.41			
Total	89	905.16				

In reviewing Figure 97, it was mentioned that condition 8 was generally incongruous with the other data shown, which was attributed to the larger trench areas for this condition (Table 26). To remove the effects of this data point and gain further insights, there are two methods that can be used to circumvent this problem and reanalyze the data. One method is to collapse the analysis into an experimental design in which only the extreme values of current density (15 and 105 mA/cm²) are considered at the three additive levels. Alternatively, a correction can be made to the cross-sectional area for condition 8, based on the average value for the remaining eight conditions. Both methods were considered and the ANOVA results are shown in Tables 29 and 30, respectively. With the former method (Table 29), it is clear that the current density becomes significant at the 95% confidence level. With the latter method (Table 30), however, there is only significance at the 89% confidence level. Since this method is more in general agreement with the original analysis, it appears that increasing current density only has a minor influence, at best, on the final grain size in the 0.50-μm features at a relatively low level of confidence, an exact value of which is difficult to determine without additional data for condition 8. Additive level, or the interaction of additive level with current density, are also shown to exert no significant influence at the 95% confidence level.

From Figure 98 it is evident that there is a stronger influence exerted by the current density in the 0.35-μm features, as compared to the 0.50-μm features. Furthermore, there is a subtle suggestion that the additive level might play a minor role with respect to the recrystallized grain size at low and intermediate current densities. Similar to the 0.50-μm

Table 29: Modified ANOVA results at the 95% confidence level for the 0.50- μm grain density data that considers only the low and high current density levels, for all three additive levels.

Source of Variation	df	SS	MS	Fcalc	Fcrit	p-value
Current Density	1	48.94	48.94	5.22	4.02	0.03
Additive Activity	2	5.68	2.84	0.30	3.17	0.74
Variable Interaction	2	1.44	0.72	0.08	3.17	0.93
Error	54	505.87	9.37			
Total	59	561.93				

Table 30: Modified ANOVA results at the 95% confidence level for the 0.50- μm grain density data that employs a trench area correction to experimental condition 8.

Source of Variation	df	SS	MS	Fcalc	Fcrit	p-value
Current Density	2	49.13	24.56	2.30	3.11	0.11
Additive Activity	2	11.52	5.76	0.54	3.11	0.58
Variable Interaction	4	3.46	0.87	0.08	2.48	0.99
Error	81	864.29	10.67			
Total	89	928.40				

results, it is also interesting to note that there is very little difference in the final grain size with respect to additive level at the highest current density level. ANOVA was performed on the entire data set and the results are shown in Table 31. The results of this analysis, which assume linearity in the responses over the entire range of conditions, reveal that increasing the current density or decreasing the additive level have a positive effect on grain size at the 95% confidence level, without any interactions. However, it should be obvious that current density is by far the dominant effect, as its p-value is several orders of magnitude smaller.

In reexamining the data trends shown in Figure 98, it appears that current density plays a much more dominant role in determining the final grain size in going from 45 to 105 mA/cm². Additive activity, on the other hand, appears to exert a significant influence in going from 15 to 45 mA/cm². To further understand these two trends, two separate ANOVA analyses were performed in this regard. The ANOVA analysis shown in Table 32 considers only the 15 and 45 mA/cm² current density levels for all three levels of additive activity. Similarly, Table 33 considers only the 45 and 105 mA/cm² current density levels for all three levels of additive activity. In examining these tables, it should be apparent that the trends mentioned above in relation to Figure 98 both have statistical significance at the 95% confidence level. In comparing the two analyses shown in Tables 32 and 33, however, it is clear that current density is a far more dominant effect.

In summary, the results of this study suggest that within 0.35- μ m trenches there is a strong tendency for the grain size to increase with current density over a current density

Table 31: ANOVA results at the 95% confidence level for the entire 0.35- μm grain density data set.

Source of Variation	df	SS	MS	Fcalc	Fcrit	p-value
Current Density	2	2020.35	1010.18	26.94	3.07	2.38E-10
Additive Activity	2	260.11	130.05	3.47	3.07	0.03
Variable Interaction	4	129.98	32.49	0.87	2.45	0.49
Error	117	4387.51	37.50			
Total	125	6797.95				

Table 32: Modified ANOVA results at the 95% confidence level for the 0.35- μm grain density data that consider only the low and medium current density levels, for all three additive levels.

Source of Variation	df	SS	MS	Fcalc	Fcrit	p-value
Current Density	1	11.12	11.12	0.33	3.96	0.57
Additive Activity	2	363.92	181.96	5.41	3.11	0.01
Variable Interaction	2	13.17	6.58	0.20	3.11	0.82
Error	78	2625.09	33.66			
Total	83	3013.30				

Table 33: Modified ANOVA results at the 95% confidence level for the 0.35- μm grain density data that consider only the medium and high current density levels, for all three additive levels.

Source of Variation	df	SS	MS	F_{calc}	F_{crit}	p-value
Current Density	1	1380.24	1380.24	34.42	3.96	1.02E-07
Additive Activity	2	95.30	47.65	1.19	3.11	0.31
Variable Interaction	2	94.05	47.03	1.17	3.11	0.31
Error	78	3128.14	40.10			
Total	83	4697.72				

range of 45 to 105 mA/cm² at the 95% confidence level. A similar, but much weaker, tendency is exhibited in the 0.50-μm trenches at approximately the 90% confidence level. Within the current density range of 15 to 45 mA/cm², increasing the brightener level tends to produce smaller grains in 0.35-μm trenches at the 95% confidence level. The mechanisms underlying these dependencies are unclear at this time, but the following discussion, which utilizes some information from the literature, proposes some possible explanations.

Based on studies presented earlier in the literature review, it has become clear that electroplated copper within Damascene trenches does not recrystallize as readily as the bulk film and that a larger thermal budget will be required as geometries continue to shrink [18,19,24,31,52]. Furthermore, it has been shown that annealing conditions are a function of trench line width, and smaller trench sizes generally require more thermal energy to achieve full recrystallization than larger trench sizes [19]. Even in blanket films, it has been shown that self-annealing will not occur when the film thickness becomes less than approximately 0.50 μm [17,18,21]. These facts suggest that the ability of electroplated films to recrystallize in fine features depends on geometrical factors that limit grain growth, the number of available sites for nucleation, as well as the amount of energy stored in the as-deposited films [18]. Implied with these tendencies would also be the possibility of a higher activation energy for recrystallization in these fine features, which, unlike blanket films, has yet to be explored in the literature

In the current study, it has been shown that current density is a significant factor affecting the final grain size in fine Damascene trenches after allowing sufficient time for

self-annealing, followed by a high-temperature annealing treatment. In both 0.35 and 0.50- μm features, the higher current densities tend to produce larger final grain sizes. However, this factor has been shown to also be line width dependent, in that the effect was far more pronounced for the smaller geometry. Considering the available information on copper recrystallization, it is proposed that after the self-annealing process, the small trench features were at best only partially recrystallized [19]. The 0.50- μm trenches, however, would be expected to have exhibited a much larger degree of recrystallization, based on the work of Ritzdorf [19].

The ensuing high-temperature annealing treatment then completed the recrystallization process within these features and possibly led to some post-recrystallization grain growth. The current density dependence can be understood by considering that higher current densities generally lead to higher defect densities and lower impurity levels in the as-deposited film [23,38]. The films deposited at higher current densities would thus be expected to exhibit faster recrystallization kinetics due to the presence of a higher driving force for recrystallization resulting from more stored energy in the film and less grain-growth inhibition from incorporated additives [17,23,25]. Thus, they would have more opportunity for post-recrystallization grain growth. Alternatively, with geometrical constraints and a limited number of nucleation sites, it is also possible that the ratio of the nucleation to growth rates during the recrystallization process may change as a function of current density within these fine features. Ultimately, either of these events could lead to a larger final grain size and the increased potential for a “bamboo” microstructure with an adequate thermal budget

within fine Damascene features. The dependence of grain size on current density in these fine features could thus merely be a manifestation of a similar phenomenon seen in self-annealed blanket films. The primary differences between the self-annealing of blanket films and the thermal recrystallization in small trench features would be faster kinetics arising from the high-temperature treatment and less opportunity for nucleation and growth due to the imposed geometrical constraints.

It should be reemphasized that annealing under high-energy conditions, even after recrystallization, will generally always result in some additional grain growth. However, unlike the blanket films, the grain growth in these fine features becomes limited by geometrical constraints. Hence, the additional post-recrystallization grain growth arising from the thermal treatment after the self-annealing process in the blanket films did not occur to the same degree in the 0.35 and 0.50- μm features due to the inherent geometrical restrictions on growth. Such restrictions also explain why the 0.50- μm feature size exhibits a somewhat larger final grain size as compared to the 0.35- μm feature size. Based on the results of this study, it is also clear that increasing the level of geometrical constraint makes the entire system more sensitive to the current density level. Even without a specific knowledge of the mechanisms leading to these results, it appears that the level of geometrical constraint, the number of available sites for nucleation, and the amount of stored energy in the film are factors to be considered.

In addition to the current density effect, it also appears that the additive level will become a more significant factor affecting the final grain size in Damascene features as geometries continue to shrink. It was shown in this study that the additive level was also

a significant factor affecting the final grain size, in going from low to medium current densities in 0.35- μm trenches. It should also be reemphasized that lower current density levels generally lead to more additive incorporation in the as-deposited film. Some studies that have addressed additive incorporation in Cu films have proposed that additives, which can inhibit grain growth, will diffuse along Cu grain boundaries during the self-annealing process after being rejected from the abnormally growing grains [25]. These grain boundaries form a percolation path by which incorporated additives can diffuse through the film, which eventually leads to surface desorption and a reduction in film stress. However, it has been shown that some additives remain in blanket films even after the self-annealing process, the depletion of which can be facilitated by an air/vacuum cycle or high-temperature treatments [27,29].

If it were assumed that the grains in the trenches were only partially recrystallized prior to the high-temperature annealing process, the microstructure would possess a substantial fine-grained component after one week [19]. These small grains would be expected to have a high defect density, a high grain boundary energy density, and a significant degree of additive incorporation. It would also be expected that the 0.35- μm trenches would be affected more than the larger 0.50- μm trenches. However, as compared to large-grained films, there would be much more grain boundary volume by which the additives could diffuse through the trench volume during the high-temperature treatment. The overlying large-grained microstructure, however, could pose rate limitations for this process, in that some incorporated additives remain trapped in the trench films after the high-temperature annealing treatment. These incorporated

additives, in turn, could impose grain growth inhibition by acting as pinning sites at the grain boundaries. Secondary ion mass spectroscopy (SIMS) depth profiles of the copper films before and after the annealing treatment would be required to validate this interpretation. It is important to note that many species have higher diffusion coefficients than copper atoms in copper grain boundaries, and the combination of their diffusion coefficients, segregation coefficients, and pinning characteristics ultimately determine their respective roles in initially pinning, then releasing, the grain boundaries [17].

5.2.5 Gap Filling within Damascene Trench Features

Since the success or failure of any semiconductor metallization process is predicated on the ability to adequately fill fine features with high aspect ratios (AR), the gap-filling capabilities were also examined. Electroplating defects are generally manifested as either vertical seams or voids in the trenches or vias. Such three-dimensional defects not only increase the effective resistance of the feature but also result in premature electromigration failures. It should be noted that a successful gap-filling process requires a significant amount of process development that is dependent on many variables. These include the type of electroplating cell, the current waveform used to electrodeposit, the additive formulation, the plating temperature, and step coverage of the copper seed layer in the feature prior to electrodeposition. It is not the intent of the author to evaluate the electroplating cell or processes employed, based on the gap-filling results obtained for this investigation. Cohen has demonstrated that this equipment, along with extensive process development, is capable of filling 0.05- μm features with aspect ratios of 28:1 [75]. The primary purpose of this section is to identify and discuss

any gap-filling defects occurring within the smallest trench features available on the experimental wafers for the entire range of electroplating conditions.

The vertical seams commonly seen in Damascene trenches are generally associated with a pinching off of the opening prior to a complete fill of the structure [10,11]. Such plating defects generally result from a conformal filling mechanism (i.e. the deposition rate at the trench top is essentially equal to that of the side wall), or from an excessive amount of copper seed at the feature opening [10,11]. Electroplating voids, which are generally found near the bottom of the feature, are associated with insufficient side wall coverage by the PVD or CVD copper seed layer [10]. Ideally, a minimum of approximately 10 nm of copper seed on the lower side walls of the trench is sufficient for a void-free electroplating fill [10]. Thin (< 5 nm) coverage on the side wall can result in the dissolution of the Cu seed layer by the acid copper sulfate plating solution [10]. Typically the wafer is immersed in the solution for a short period prior to deposition to remove any copper oxide from the surface of the seed layer. Voids are more likely to occur during electroplating as the aspect ratio becomes large ($AR > 6$), due to minimal step coverage of the seed layer[10,11].

In this study, the features used to evaluate the gap filling were the 0.35- μm and 0.50- μm Damascene trenches, which were the smallest feature sizes available on the experimental wafers. It has become customary to use electron images rather than ion images to examine gap-filling capabilities, as voids and seams are more readily identified. Hence, an SEM, or a dual-beam FIB-SEM imaging system, can be used for

such purposes. Table 34 summarizes the key geometrical features of the trenches that were used to examine the gap filling.

Representative cross-sectional electron images at 65000 $\times$ magnification of the filled 0.50- μm trench features are shown in Figure 99 for experimental conditions 1 and 7. The images show that no voids or seams exist in the trenches of condition 1 (top), while condition 7 exhibits a large void in the rightmost trench. Conditions 2 and 7 were the only cases where bottom voids were found in the 0.50- μm features.

Figure 100 shows two electron images of the 0.35- μm features for experimental conditions 1 and 7. The top image (condition 1) shows very good gap filling within this feature. The bottom image (condition 7), on the other hand, shows large voids in three of the four features near the trench bottom. In addition to condition 7, large bottom voids were observed for conditions 2, 6, and 8, and smaller crescent-shaped voids, which were also located at the trench bottom, were also noted for conditions 3 and 5. With the limited number of trenches surveyed at this magnification, no attempts were made to examine any statistical trends with respect to the occurrence of voids and the electroplating variables employed. However, it is clear that the only gap filling defect that occurred in this investigation was bottom voiding, as no central seams were observed for any of the nine conditions. It is also evident that this type of defect was far more prevalent in the 0.35- μm features as compared to the larger 0.50- μm features. Electron images for all nine experimental conditions may be found in Appendix E.

The shape and location of these voids would generally be associated with the voiding that tends to arise from poor step coverage of the seed layer near the bottom of

Table 34: Key geometrical features pertaining to the Damascene trenches used to observe gap filling.

<i>Feature Width</i>	<i>Feature Height</i>	<i>Aspect Ratio</i>	<i>Line Density</i>
<i>0.50 μm</i>	<i>0.8 μm</i>	<i>1.60</i>	<i>50%</i>
<i>0.35 μm</i>	<i>0.8 μm</i>	<i>2.28</i>	<i>50%</i>

Figure 99: Electron beam images of 0.50-μm trenches illustrating the gap filling for conditions 1 (top) and 7 (bottom). A large bottom void can be seen in the rightmost trench of the latter condition.

Figure 100: Electron beam images of 0.35-μm trenches illustrating the gap filling for conditions 1 (top) and 7 (bottom). Three large bottom voids can be seen in the latter condition.

the trench. In no case, however, were voids found in all the trenches for any of the nine conditions. Since the trench separation is approximately equal to the trench width for both feature sizes, it seems unlikely that the step coverage of the seed layer would be adequate in one trench and poor in an adjacent trench of very close proximity. A recent study, however, has shown that the dewetting or agglomeration of copper from the underlying barrier material during thermal processing can also lead to voiding at the bottom of Damascenes trenches [98]. Even though this study showed that Ta is one of the most resistant materials to copper agglomeration, it is still possible, with the prolonged heat exposure of the wafers during the annealing process, that this could still be a viable failure mechanism.

5.3 (111) Texture of Blanket Copper Films

5.3.1 General Approach for Texture Analysis

In an effort to obtain a general assessment of the quality of the (111) fiber texture for the films used in this investigation, x-ray diffraction (XRD) techniques were employed. As previously discussed, there are many significant influences on the quality of the (111) fiber texture in a Damascene materials system. Furthermore, there seems to be general disagreement as to whether the (111) fiber texture improves or degrades after high-temperature annealing. These observations highlight the complexity and the lack of a complete understanding of the underlying mechanisms that lead to the evolution of texture in this system. Nevertheless, the development of a strong (111) fiber texture in electroplated copper, and more generally any FCC metal, is generally attributed to the minimization of surface and interface energies at the free surface and film-substrate interface [17,28,44,53]. However, other texture components can develop due to the crystallographic anisotropy of copper, the most common of which is a (200) texture component [17,28,43,44,53]. Since the elastic constants of copper are highly anisotropic, grains of different orientations can develop from different levels of strain energy as the film is subjected to a biaxial stress [28]. Hence, a (200) preferred orientation could develop for conditions that favor strain energy minimization and a (111) orientation for conditions that favor surface and interface energy minimization [28,53].

In this investigation, fiber plots were generated using a novel method that allows relatively fast and accurate texture analysis and requires only an ordinary powder diffractometer [90,91]. This method was developed by Vaudin and has been used

extensively with ceramic thin films and was found to correlate well with both the pole figure and Rietveld methods for both textured and untextured films [90,103]. More recently, the method has also been extended to electroplated copper films [91]. With Vaudin's method, two XRD scans are recorded from the textured sample. First, a high-resolution θ - 2θ scan is obtained for the Bragg peak of interest whose diffracting planes are perpendicular to the preferred orientation direction. Second, an ω scan, or rocking curve, is obtained using this same Bragg peak.

The rocking curve contains the required texture information, as its width is a direct measure of the range of orientation present in the irradiated area of the crystal [88,90,91]. However, to generate an accurate texture profile, the intensities must be corrected for defocusing and absorption [41,90,91,103]. With Vaudin's method, the defocusing corrections can be made in conjunction with a standard θ - 2θ Bragg scan of the peak of interest. Absorption corrections, on the other hand, can be made using calculations based on first principles. To facilitate these corrections to the rocking curves, a software program designated as "Texture Plus" has been developed by Vaudin, which was used in this investigation [99]. These corrections can be viewed as dividing the measured rocking curve intensities by a "random" rocking curve calculated using the θ - 2θ scan of the Bragg peak of interest, which is very similar to the correction made to pole figures [90,91]. For further reading on the complex theoretical basis for these corrections to the rocking curves, the reader is directed to references [90] and [91]. From the corrected rocking curve, the program generates a fiber, or texture, plot that can be used to calculate the required figures of merit for texture.

5.3.2 Bragg Scans

As mentioned in the experimental section, Bragg scans of the Cu (111) peak were obtained for each of the nine experimental conditions. A scan, with the background intensity subtracted, is shown for experimental condition 4 in Figure 101. Since the scan was terminated at 100° in 2θ , the (400), (331), and (420) peaks are not present in the figure. Noticeably absent are any peaks from Si, SiO₂, or Ta, so peak overlap was not a problem in this study and no peak deconvolution was required. The figure also shows the (111) peak to be the dominant peak. To compare the relative integrated peak intensities of this sample to a random sample, the areas of each peak from condition 4 were normalized to that of the (111) peak. The peak areas were calculated by fitting the $K\alpha_1$ peak shape to a Pearson VII profile and integrating with the Scintag software package [92]. An example of such a fit will be discussed shortly. The peak positions, maximum peak intensities, and full-width, half-maximum (FWHM) values for each Bragg peak were also determined in this step. The relative intensity data were then compared to ICDD (International Center for Diffraction Data) card number 4-836 for untextured polycrystalline copper [94]. The results for condition 4 are shown in Figure 102. From this figure it is very evident that there is a distinct preferred orientation to the film, as the relative intensities have become severely distorted as compared to a random, untextured copper sample [89]. The relative intensity data for the entire experimental matrix may be found in Table 35.

Figure 103 shows the (111) Bragg peak for condition 4 in greater detail. Noticeably present is a smaller satellite peak that is superimposed on the primary (111) peak at a

Figure 101: A representative high-resolution, Bragg-Brentano θ - 2θ scan for experimental condition 4 with the background intensity removed.

Figure 102: A comparison of the relative intensity values between the ICDD database for Cu and those obtained for experimental condition 4.

Table 35: A summary of the relative intensity data for all nine experimental conditions, based on normalizing the peak areas taken from the Bragg scans to that of the Cu (111) peak. The relative intensity information for random, polycrystalline Cu (ICDD Card 4-386) is also shown for reference [94]. These data suggest a strong preferred orientation of a low-index component.

	Experimental Condition									
	1	2	3	4	5	6	7	8	9	ICDD
(111)	100	100	100	100	100	100	100	100	100	100
(200)	2.9	3.6	3.8	2.6	3.4	3.3	2.7	3.4	3.5	46
(220)	3.1	4.0	4.3	2.6	3.8	3.8	3.0	3.8	3.8	20
(311)	4.1	5.0	5.3	3.9	4.3	4.2	4.0	4.4	5.0	17
(222)	3.6	4.4	4.5	3.2	3.8	3.8	3.4	3.9	4.3	5

Figure 103: A detailed view of the Cu (111) peak obtained from a high-resolution, Bragg-Brentano θ - 2θ scan from experimental condition 4.

slightly higher 2θ angle. The origin of this satellite peak stems from the fact that the beam of the x-ray tube, when operated above the K excitation voltage, is not truly monochromatic [88]. Although there are several lines in the K set, the strongest characteristic emission line for most materials, and the one most useful for x-ray diffraction, is the $K\alpha$ line which for copper occurs at 0.154178 nm [100]. The $K\alpha$ line is composed of two components that are very closely spaced in wavelength. Individually, they are referred to as the $K\alpha_1$ and $K\alpha_2$ components and collectively as the $K\alpha$ doublet. The wavelength of Cu $K\alpha_1$ radiation is 0.154433 nm, while that of Cu $K\alpha_2$ radiation is 0.154051 nm [100]. If the two wavelengths are resolved in an x-ray scan, $K\alpha_1$ is always about twice as strong $K\alpha_2$ [88]. These two facts made identification of the $K\alpha$ doublet definitive in the Bragg scan of the (111) peak shown in Figure 103. $K\alpha$ doublets were resolved on all Bragg peaks for the entire experimental matrix. Further examination of Figure 103 shows the peak to be relatively narrow ($\cong 0.06^\circ$), which suggests the copper has recrystallized and that the receiving slit used on the diffractometer is narrow [100]. The long peak shoulders are emblematic of stacking faults (crystallographic twins), which were found to be abundant in the FIB images previously shown [100].

As mentioned previously, a Pearson VII function is commonly used to model x-ray diffraction intensity data for a specific Bragg peak [93]. Using this method, the peak positions, peak widths, and maximum peak heights can be derived. The area under the best-fit function can then be determined by integration and the d-spacing using Bragg's Law. Pearson VII functions are also commonly used to measure residual film stresses, but were not used in this study. This technique measures the changes in d-spacing with

different sample orientations to measure stress. Since the peak areas, based on Pearson VII fits to the diffraction peak data with the Scintag software package [92], were used to derive the relative intensity data presented above, a brief discussion is presented to familiarize the reader with this method.

A Pearson VII function takes on the general form

$$I(2\theta) = A \left(1 + \frac{B^2}{M} (2\theta - 2\theta_0)^2 \right)^{-M} \quad (21)$$

where A is the maximum intensity of the $K\alpha_1$ peak, B is a peak width parameter, M is a decay rate parameter, and $2\theta_0$ is the $K\alpha_1$ peak position [93]. M and B are related to the peak FWHM value by [93]

$$FWHM = \frac{2}{B} \sqrt{M \left(2^{\frac{1}{M}} - 1 \right)}. \quad (22)$$

A program called "Winfit" was used to perform a Pearson VII fit to the Intensity- 2θ data of the Cu (111) $K\alpha_1$ peak and establish the fitting parameters shown in Equation (21) [101]. This program, which was designed for powder diffraction data analysis, performs a least-squares fit to establish these fitting parameters, using multiple iterations until convergence is achieved. Figure 104 compares the results of this method to the fit obtained from the Scintag software for experimental condition 4. The results are in

Figure 104: A comparison of Pearson VII fits to the Cu (111) $K\alpha_1$ Bragg peak data obtained from experimental condition 4. The fitting parameters shown were obtained from the “Winfit” software program for powder diffraction data.

excellent agreement with the fit obtained from the Scintag software. The lack of full correlation to the raw data ($R^2 = 0.95$) is apparently due to the fact that the tails of the raw data decay somewhat less rapidly than those of the Pearson VII function.

5.3.3 Rocking Curves

In order to satisfy the requirements of the Texture Plus software program, rocking curves of the (111) peaks were also measured for all nine conditions. While the rocking curve technique does provide a direct measure of the shape of the texture distribution for a particular set of crystallographic planes, the range of orientation space that can be measured is experimentally limited by the value of θ_B for the particular Bragg reflection [90,91]. Typically such measurements cover a range of orientation space that is limited to tilt angles (ω) corresponding to $\pm \theta_B$ [90]. Low-index planes, such as the Cu (111) peak, therefore allow a much more limited range of orientation space to be sampled as compared to higher-index planes, making the method inherently more limited than the pole figure technique. However, this is generally of little importance for samples that exhibit a very strong texture, as the tilting distributions are generally less than 3° [34,35,40,].

A typical (111) rocking curve is shown in Figure 105 for condition 4. Typically a rocking curve will be symmetric and centered at $\omega = 0^\circ$. The figure shows the peak to be shifted in the negative direction by approximately 0.3° . Shifts of this magnitude were found to be present for all nine (111) rocking curves and ranged from 0.1° to 0.7° . The most likely cause of this displacement is a slight specimen misalignment [92,99]. Since

Figure 105: A representative Cu (111) rocking curve obtained for condition 4.

the specimen holder was designed for bulk one-inch square samples and not 20-mm square flat samples, sample preparation required the use of modeling clay as a spacer to elevate and center each sample with respect to the reference surface of the holder ($\theta = 0^\circ$ plane). Any slight misalignments with respect to this plane could then result in slight rocking curve displacements.

5.3.4 Texture (Fiber) Plots

In addition to Bragg scans and rocking curves of the Cu (111) peak, additional information was required to execute the Texture Plus program and make the necessary defocusing and absorption corrections to the (111) rocking curves. A list of this information, along with the values used for this investigation, is shown in Table 36. With the incident beam optics used in this experiment, the length of the specimen in the diffraction plane was calculated to be approximately 13.9 mm for the Cu (111) peak.

With all the aforementioned information, defocusing and absorption corrections were made to the (111) rocking curves using Texture Plus. Figure 106 shows the nature of the corrections to the rocking curve for condition 4. In comparing the FWHM value of 0.616° from the corrected scan to 0.625° from the raw scan, it is obvious that the defocusing and absorption corrections had almost no effect on the rocking curve data. Similarly, the maximum peak intensity also changed very little as compared to that of the raw data. The magnitude of these corrections is consistent with previous work done by Vaudin [91]. In that study, Vaudin showed that the absorption and defocusing corrections performed by using the Texture Plus program are essentially negligible for highly textured specimens whose textured fractions exceed approximately 70% [91]. For

Table 36: A list of the information required for the Texture Plus program, in addition to the Bragg and rocking curve intensity data for the peak of interest.

<i>Parameter</i>	<i>Value</i>
<i>Diffractometer Radius (mm)</i>	250
<i>Specimen Length (mm)</i>	13.91
<i>Incident Beam Divergence (Degrees)</i>	1.2
<i>Film Thickness (nm)</i>	1300
<i>Cu Mass Absorption Coefficient (μ^I)</i>	0.046

Figure 106: An example of the defocusing and absorption corrections made to the (111) rocking curve for experimental condition 4, using "Texture Plus" software [99].

untextured specimens, which represent the opposite extreme, such corrections will degenerate the rocking curve into a flat line of constant intensity [90].

After making the necessary corrections to the rocking curves, the Texture Plus program creates fiber plots, which Vaudin refers to as “overlay” plots, that represent the negative and positive sides of the corrected rocking curves. During this step, any angular shifts from specimen misorientation are also corrected. The program also creates a mean fiber plot, which averages the intensity values of both the negative and positive fiber plots. In this study, the mean fiber plot was used to determine the figures of merit for texture. These three texture plots are illustrated for condition 4 in Figure 107. The program then calculates the (111) textured fraction by first fitting the fiber plot to a single-parameter March-Dollase function [102]. The (111)-textured and untextured fractions are then determined using the appropriate limits of integration to this function (i.e. the point where the intensity levels off to a constant value).

The mean fiber plot data were then analyzed to determine the angular widths for the various volume fractions, as is customary in the literature on texture [43]. This method involved generating a cubic spline fit of the mean fiber plot data with the area corresponding to the untextured fraction removed and then performing successive integrations until the appropriate peak area ratio corresponding to the volume fraction of interest was determined. The angle corresponding to this volume fraction represents the angular width of the distribution for the volume fraction of interest. To be consistent with the literature, the angular widths of the 95 (ω_{95}), 90 (ω_{90}), and 50 (ω_{50}) percent volume fractions were determined in this investigation [40, 43].

Figure 107: The mean, negative, and positive (111) fiber plots obtained from “Texture Plus” software for experimental condition 4 [99]. The mean fiber plots were used to extract the figures of merit for texture in this investigation.

A summary of the data derived from the fiber plots for the entire experimental matrix is shown in Table 37. The figures of merit include the maximum (111) peak intensity ($I_{(111)}$), the (111) textured fraction, and the width of the (111) texture distribution in terms of the three volume fractions mentioned above. A highly (111)-fiber-textured material will exhibit a large (111) volume fraction, a narrow distribution, and a large $I_{(111)}$ intensity value, as compared to a less textured material [43]. Of these three figures of merit for texture, the widths of the distributions and the textured fractions are generally considered the most reliable and meaningful, as they are not as equipment and technique dependent [40,43].

From the data presented in Table 37, it is apparent that very little variability exists in the widths of the texture distributions in comparing the ω values at different volume fractions. The very narrow angular widths of these volume fractions, however, are emblematic of a highly textured material and are similar to those reported in other studies after a similar high-temperature annealing treatment with blanket ECD Cu films that employed a Ta barrier material [34,40]. With respect to the textured fractions and $I_{(111)}$ values, there was much more variability in the data. The $I_{(111)}$ values, which are sometimes used as an index of (111) texture, did correlate well ($R^2 = 0.90$) with the textured fractions, which is illustrated in Figure 108. This correlation is reasonable, as a sample with a higher (111) textured fraction would be expected to have a greater number of (111) planes aligned with the fiber axis, given the limited variability in the widths of the distributions. Experimental condition 4 ($j = 15 \text{ mA/cm}^2$, $A_B = 4.94$), which had a 91% (111) volume fraction, exhibited the best (111) texture for all nine conditions.

Table 37: A summary of the data obtained from fiber plots used to evaluate the (111) fiber texture for all nine experimental conditions.

Condition	$I_{(111)}$ (CPS)	(111) Volume Fraction	Width of (111) Distribution (degrees)		
			ω_{50}	ω_{70}	ω_{95}
1	15040	0.86	0.28	0.84	1.10
2	7438	0.75	0.34	0.91	1.15
3	7205	0.74	0.29	0.90	1.17
4	24654	0.91	0.33	0.96	1.19
5	10310	0.82	0.28	0.83	1.04
6	10100	0.81	0.31	0.88	1.09
7	19324	0.89	0.35	0.87	1.13
8	9347	0.79	0.33	0.93	1.12
9	8945	0.78	0.36	0.97	1.15

Figure 108: A plot of the maximum (111) peak intensity as a function of the (111) textured fraction for all nine experimental conditions. The Pearson Correlation Coefficient suggests a good correlation between these two metrics of texture.

Given the limited variability in ω_1 and the good correlation between the maximum intensity and textured fraction data, the (111)-textured fractions were further examined with respect to the electroplating variables used in this study. A plot of the (111) textured fraction as a function of current density for the three additive levels is shown in Figure 109. From this figure, it appears that increasing the current density between the low and medium levels results in a significant degradation in the (111) textured fraction. In going from the medium to high current density levels, on the other hand, there appears to be no significant effect. In examining the trends with respect to additive level, it is interesting to note that the medium additive level consistently showed the largest (111) textured fraction and the low additive level the smallest for all current density levels. Further examination of this figure also shows that very little difference (2-3%) exists between the medium and high additive levels for all three current densities. The fiber plots for experimental conditions 1, 4, and 5 were chosen to further illustrate some of these key trends and are shown in Figure 110. The shapes of these curves and the associated tilting ranges are generally consistent with those reported in other similar texture studies [45].

With these trends in mind, the data were further analyzed using one-way analysis of variance (ANOVA) without replication to determine if any of these trends show possible statistical significance at the 95% confidence level. In accordance with these trends, the analysis was collapsed into a 2^2 factorial design experiment, in which only the low and medium levels were considered for each of the two electroplating variables of interest. A summary of these results is shown in Table 38, which suggests that neither the current density nor the brightener activity have a significant effect on the (111) textured fraction

Figure 109: The (111) textured fraction as a function of current density for all three brightener activity levels.

Figure 110: Three fiber plots for experimental conditions 1, 4, and 5 that illustrate some of the key trends with respect to the electroplating variables used in this study.

Table 38: ANOVA results at the 95% confidence level to assess the statistical significance of the impact electroplating variables have on the (111) textured fraction.

Source of Variation	df	SS	MS	Fcalc	Fcrit	p-value
Current Density	1	0.01	0.01	100	161.4	0.06
Additive Activity	1	0.0036	0.0036	36	161.4	0.11
Error	1	1E-04	1E-04			
Total	3	0.0137				

at the 95% confidence level, since both p-values are greater than 0.5. However, the results do intimate that increasing current density, which is the dominant affect, does have a negative influence on the textured fraction within this range at the 94% confidence level. Increasing the brightener level, on the other hand, has a positive influence on the textured fraction at only approximately the 90% confidence level. It is emphasized that these conclusions are based on only one set measurements for each experimental condition, and additional experimentation and metrology would certainly be justified.

In consideration of the work of Brongersma [29] and Lee [28], the trends illustrated above do suggest the possibility that a (200) texture component exists in these films. Brongersma illustrated that increasing the current density in the range of 2.38 to 19 mA/cm² resulted in consistently higher residual tensile film stresses, after thermal cycling the films between 20 and 400°C at a rate of 3°C per minute [29]. The residual stresses corresponding to these current densities ranged between 75 and 150 MPa and were previously shown in Figure 16. After exceeding a critical tensile stress level of 70 MPa for Cu films that are approximately 1-μm thick, it has been shown by Lee that the state of film stress correlates well with texture [28]. In particular, the (111) texture starts to degrade and a (200) texture component develops for blanket films that exceed this critical stress (Figure 15). A likely source of this stress development would be the additional grain growth that accompanies the high-temperature annealing process [29].

In consideration of these two studies [28,29], the trends shown in this study suggest that increasing the current density within the range of 15-45 mA/cm² might result in an increased residual tensile stress in the copper films after a high-temperature annealing

treatment. This additional stress, in turn, would be expected to degrade the (111) texture as a stress-induced (200) texture component begins to develop, which would be manifested as a reduced (111) textured fraction [28,53]. This was evidenced by a decrease in the (111) textured fraction that ranged between 10-13% for all three additive levels while increasing the current density within this range. Decreasing the brightener activity between 4.94 (1.50 ml/l) and 2.78 (0.75 ml/l) appears to have a similar affect on the textured fraction, but to a much lesser extent and at a correspondingly lower confidence level. Validation of these interpretations would require initial and final stress measurements, as well as a (200) texture analysis for all nine conditions.

CHAPTER 6

CONCLUSIONS

The results of this study have shown that a large-grained microstructure can be achieved in unpatterned Damascene copper thin films for a wide variety of DC jet electroplating conditions, with a high-temperature treatment that follows the self-annealing process. In all cases the blanket copper films exhibited equivalent sheet resistance values at the 95% confidence level and resistivities that approach the bulk value of $1.67 \mu\Omega\text{-cm}$ for copper. For all nine experimental conditions, the blanket film microstructure consisted of large columnar grains that spanned the entire film thickness of $1.3 \mu\text{m}$ and exhibited a high degree of crystallographic twinning.

The average, in-plane grain diameters in these blanket copper films ranged between 1.7 and $1.9 \mu\text{m}$, with large standard deviations ranging from 0.5 to $0.8 \mu\text{m}$. Within a current density range of 15 to 105 mA/cm^2 and brightener level range of 0.75 to 2.25 ml/l , there was no statistically significant difference in the mean grain size at the 95% confidence level after the post-self-annealing, high-temperature treatment. These results suggest that any grain growth inhibition factors, such as remnant electroplating impurities incorporated in the blanket film microstructure after the self-annealing process, can be effectively be removed from these films with a sufficient thermal budget. For all nine conditions the grain-size distributions were found to have similar lognormal characteristics, which suggests abnormal grain growth during both the recrystallization and subsequent grain growth processes. The largest grain sizes in these distributions

were found to be four to five times the blanket film thickness, which is characteristic of abnormal grain growth.

The recrystallized cross-sectional microstructure within 0.50 and 0.35- μm Damascene trench features of was also examined for all nine conditions. In both feature sizes recrystallization was complete, as no evidence of a fine-grained component was observed. Within these features a "bamboo" microstructure, in which large grains occupy the entire trench width and a significant portion of its volume, was frequently observed. Such grains also exhibited a high degree of crystallographic twinning and often appeared to have propagated into the trench structures from the overlying copper film during the recrystallization process. In many instances, however, several small grains occupied the trench volume, many of which appeared to have nucleated along the trench bottoms or sidewalls during the recrystallization process.

To investigate any possible remnant effects of current density or brightener level within these trench features, the cross-sectional grain densities ($\text{grains}/\mu\text{m}^2$) were analyzed within both feature sizes for all nine experimental conditions. Using this index of grain size, a larger grain density implies a smaller cross-sectional grain size, which is perpendicular to the direction of electrical current within these interconnect features. Within the 0.5- μm trenches, it was found that increasing the current density within a range of 15 to 105 mA/cm^2 resulted in somewhat smaller grain densities. Due to experimental difficulties with one of the nine data points, the exact statistical significance of this trend with respect to the entire experimental matrix was indeterminate. A modified statistical analysis, which considered only the extreme values of current density

for all three additive levels, did suggest the possibility that this trend could be significant at the 95% confidence level. At the highest current density level of 105 mA/cm^2 , similar grain densities were observed for all three additive levels within this feature size. No statistically significant trends on grain density were observed in the $0.5\text{-}\mu\text{m}$ lines with respect to additive level or the interaction of additive level with current density.

A grain density analysis with the $0.35\text{-}\mu\text{m}$ features revealed that both current density and additive level had a significant effect on the grain density at the 95% confidence level, when considering the entire data set. The trends revealed that increasing the current density or decreasing the brightener level had a positive influence on grain size. The current density was found, however, to be the dominant effect in producing larger cross-sectional grain sizes in this phase of the analysis. Generally speaking, this current density dependence was found to be much stronger in $0.35\text{-}\mu\text{m}$ trenches, as compared to the $0.50\text{-}\mu\text{m}$ trenches. In considering the entire data set, no statistically significant variable interactions were observed between current density and additive level.

Further examination of the $0.35\text{-}\mu\text{m}$ grain density data revealed two distinctly different behaviors with respect to these two electroplating variables. Within a current density range of 15 to 45 mA/cm^2 , the additive level was found to be the dominant effect in producing larger grain sizes within this feature size. The current density, on the other hand, was found to be the dominant effect in producing larger grain sizes within a current density range 45 to 105 mA/cm^2 . These two dependencies were both found to be statistically significant at the 95% confidence level. Similar to the analysis of the $0.5\text{-}\mu\text{m}$

trenches, it is also interesting to note that a current density level of 105 mA/cm^2 resulted in similar grain densities irrespective of the additive level and produced the smallest grain densities, or largest cross-sectional grain sizes, for the entire data set. In considering both the 0.35 and $0.50\text{-}\mu\text{m}$ grain density results, it appears that current density, and to a lesser extent additive level, will play a much more dominant role in determining the final grain size in Damascene trenches, as interconnect geometries become smaller in conjunction with increasing aspect ratios. Even without a specific knowledge of the mechanisms leading to these dependencies in the trench features, it appears that the level of geometrical constraint, the number of available nucleation sites, the amount of stored energy in the microstructure, and degree of additive incorporation in these interconnect films are factors to be considered.

The last phase of the microstructural analysis included a texture analysis of the (111) crystallographic component for all nine experimental conditions in the blanket film regions, using fiber plots derived from x-ray diffraction scans. In all cases a strong (111) fiber texture was observed to be the dominant texture component, with (111) textured fractions ranging between 0.74 and 0.91 and similar tilting distributions.

There were, however, some differences noted between the nine conditions with respect to the (111) textured fractions. In particular, it was found that the highest (111) textured fractions were produced at the lowest current density level of 15 mA/cm^2 for all three additive levels, which ranged between 0.86 and 0.91 . Furthermore, increasing the current density from 15 to 45 mA/cm^2 resulted in a significant degradation of the (111) textured fraction, whereas increasing the current density from 45 to 105 mA/cm^2 resulted

in no further degradation. In examining the trends with respect to additive level, it was noted that the medium additive level (1.50 ml/l) consistently exhibited the highest (111) textured fraction and the low additive level (0.75 ml/l) the lowest for all three current density levels.

In consideration of these trends, a subset of the data was statistically analyzed that considered only the low and medium levels for both electroplating variables employed in this study. This analysis suggested that neither the current density nor the additive level had a significant affect on the (111) textured fraction at the 95% confidence level. However, the results do intimate that increasing the current density within this range does have a negative influence on the (111) textured fraction at the 94% confidence level. Increasing the brightener level, on the other hand, had a positive influence on the (111) textured fraction at approximately only the 90% confidence level. Based on results reported in the literature, the current density trend does raise the possibility of higher tensile stresses in the films and the evolution of a (200) textured fraction as a result of increasing the current density [28,29]. As mentioned earlier, a (200) texture component was shown to exist in these blanket copper films, based on the 90° angle between intersecting twin boundaries found in the FIB images. It should be reemphasized that these conclusions only pertain to the data subset encompassed by the low and medium levels of both the electroplating variables used in this investigation.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE WORK

The following studies are recommended to further improve an understanding of the evolution of microstructure in Damascene copper interconnect films and expand on the results of this investigation. A characterization of the grain structure, grain size, film stress, and texture in both the blanket films and trench features prior to the high-temperature annealing treatment would be instructive. Such an analysis would allow one to differentiate between the effects of room-temperature recrystallization and high-temperature annealing, in relation to the variables used in this study. The sources of the processing defects observed in this investigation should be further explored and understood in terms of the methodology used. These include the macroscopic blisters observed in the patterned regions, the small circular voids observed at the grain boundaries, and the gap-filling voids observed at the bottoms of the trench features.

An additional matrix element to investigate the minimum thermal budget required to achieve a stable microstructure with a high degree of (111) texture is also recommended. This would include reducing the temperature or annealing time with the inert-gas sweep method, or attempting to use other methods such as rapid thermal processing (RTP).

Secondary ion mass spectroscopy (SIMS) depth profiling should be performed on the blanket films used in this study to confirm the contention that all the incorporated plating additives were desorbed from the low-resistivity, large-grained films. A similar analysis should also be performed in the 0.35 and 0.50- μm trench features. Such an

analysis might help explain the grain density dependencies on the electroplating variables used in this study. Other brightening additive formulations should also be tested and the results compared to those of this investigation.

With respect to the Damascene trench features, there are several additional areas that would expand on the results of this investigation. A study of the longitudinal grain size and grain structure in the 0.35 and 0.50- μm trenches would afford a more comprehensive understanding of the microstructure in these features. Such an analysis could also be used to determine if the electroplating variables of current density and brightener level influence the longitudinal grain size within these fine Damascene features. Electromigration lifetime tests should also be performed on the 0.35 and 0.50- μm trench features to determine if these electroplating variables should be considered in semiconductor processes for future technology generations.

Using a technique such as electron backscattering diffraction (EBSD), a thorough microtextural analysis should also be performed within these same trench features. This would include an analysis of both the (111) and (200) fiber texture components, as well as testing for the possibility of other texture components. The results of such a study could then be compared to those of this study, in relation to the electroplating variables of interest and the degradation of the (111) texture component. The analysis of the (200) component, in conjunction with residual stress measurements, could be used to determine if film stress becomes more predominant within such features as a result of using different current densities or brightener levels. Using different thermal budgets would

also allow one to determine if any interrelationships exist between these electroplating variables and the annealing methodology.

An analysis of the film stress and (200) texture component in the blanket film regions for the conditions of this study would provide further insights on the interrelationships between stress and texture. Such a study could help explain the origins of the (111) texture component degradation reported in this investigation. Additional texture measurements of the (111) fiber component are also recommended for statistical purposes and the results compared to the pole figure technique to determine the level of agreement between the two methods. Chemical mechanical planarization (CMP) tests should be performed on the blanket films to determine if any significant differences exist in the removal rates or uniformities over the wafer surface, for conditions having significantly different (111) textured fractions. These results can be used to determine if the electroplating variables used in this study should be considered in future CMP processes.

CHAPTER 8

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APPENDIX A

SHEET RESISTANCE STATISTICS

Table 39: Sheet resistance summary statistics for low brightener level.

Condition	1		2		3	
Current Density	15 mA/cm ²		45 mA/cm ²		105 mA/cm ²	
Count	69	69	69	69	69	69
Sum	0.8165	0.8135	0.8433	0.8195	0.8459	0.8740
Average	0.01183	0.01179	0.01222	0.01188	0.01226	0.01267
Median	0.01155	0.01159	0.01174	0.01144	0.01177	0.01191
Trimmed Mean	0.01128	0.01143	0.01145	0.01115	0.01151	0.01171
Minimum	0.00912	0.00987	0.00905	0.00887	0.00907	0.00923
Maximum	0.04984	0.03813	0.05932	0.05292	0.05784	0.07161
Range	0.04072	0.02826	0.05027	0.04405	0.04877	0.06239
Standard Deviation	0.00480	0.00331	0.00604	0.00532	0.00585	0.00743
Variance	2.303E-05	1.094E-05	3.648E-05	2.827E-05	3.428E-05	5.527E-05
Standard Error	0.00058	0.00040	0.00073	0.00064	0.00070	0.00090
Skewness	7.512	7.626	7.209	7.002	7.180	7.563
Kurtosis	60.11	61.46	56.36	53.99	55.98	60.38

Table 40: Sheet resistance summary statistics for medium brightener level.

Condition	4		5		6	
Current Density	15 mA/cm ²		45 mA/cm ²		105 mA/cm ²	
Count	69	69	69	69	69	69
Sum	0.7901	0.8059	0.8502	0.8487	0.8108	0.8808
Average	0.01145	0.01168	0.01232	0.01230	0.01175	0.01277
Median	0.01150	0.01163	0.01177	0.01181	0.01166	0.01164
Trimmed Mean	0.01123	0.01147	0.01143	0.01144	0.01137	0.01147
Minimum	0.00946	0.00989	0.00906	0.00913	0.00888	0.00897
Maximum	0.03013	0.02796	0.06705	0.06544	0.03988	0.08373
Range	0.02068	0.01807	0.05799	0.05631	0.03100	0.07476
Standard Deviation	0.00247	0.00213	0.00689	0.00672	0.00369	0.00917
Variance	6.084E-06	4.529E-06	4.753E-05	4.512E-05	1.358E-05	8.411E-05
Standard Error	0.00030	0.00026	0.00083	0.00081	0.00044	0.00110
Skewness	6.510	6.730	7.589	7.519	6.686	7.177
Kurtosis	49.74	51.93	60.70	59.85	51.44	54.87

Table 41: Sheet resistance summary statistics for high brightener level.

Condition	5		6		7	
Current Density	15 mA/cm²		45 mA/cm²		105 mA/cm²	
Count	69	69	69	69	69	69
Sum	0.8309	0.8055	0.8365	0.8416	0.8456	0.8553
Average	0.01204	0.01167	0.01212	0.01220	0.01226	0.01240
Median	0.01187	0.01160	0.01189	0.01180	0.01157	0.01180
Trimmed Mean	0.01175	0.01148	0.01151	0.01153	0.01159	0.01163
Minimum	0.00987	0.00954	0.00920	0.00928	0.00908	0.00908
Maximum	0.03427	0.02932	0.05205	0.05347	0.05172	0.06314
Range	0.02440	0.01978	0.04285	0.04419	0.04264	0.05406
Standard Deviation	0.00291	0.00239	0.00509	0.00526	0.00508	0.00638
Variance	8.476E-06	5.730E-06	2.588E-05	2.771E-05	2.584E-05	4.070E-05
Standard Error	0.00035	0.00029	0.00061	0.00063	0.00061	0.00077
Skewness	6.689	5.976	7.322	7.303	7.102	7.615
Kurtosis	51.48	44.39	57.87	57.62	55.28	61.17

APPENDIX B

PLAN-VIEW FIB IMAGES OF BLANKET COPPER FILMS

Figure 111: Representative plan-view FIB images for experimental conditions 1 (top) and 2(bottom).

Figure 112: Representative plan-view FIB images from experimental conditions 3 (top) and 4 (bottom).

Figure 113: Representative plan-view FIB images from experimental conditions 5 (top) and 6 (bottom).

Figure 114: Representative plan-view FIB images from experimental conditions 7 (top) and 8 (bottom).

Figure 115: Representative plan-view FIB image from experimental condition 9.

APPENDIX C

TILT-VIEW FIB IMAGES OF BLANKET COPPER FILMS

Figure 116: Representative tilt-view FIB images for experimental condition 1 (top) and 2 (bottom) showing the blanket copper films in cross section.

Figure 117: Representative tilt-view FIB images for experimental condition 3 (top) and 4 (bottom) showing the blanket copper films in cross section.

Figure 118: Representative tilt-view FIB images for experimental condition 5 (top) and 6 (bottom) showing the blanket copper films in cross section.

Figure 119: Representative tilt-view FIB images for experimental condition 7 (top) and 8 (bottom) showing the blanket copper films in cross section.

Figure 120: Representative tilt-view FIB image for experimental condition 9.

APPENDIX D

TILT-VIEW FIB IMAGES OF TRENCH FEATURES

Figure 121: Representative tilt-view images of 0.50 and 0.35- μm trench features for experimental conditions 1 (top), 2 (middle), and 3 (bottom).

Figure 122: Representative tilt-view images of 0.50 and 0.35- μm trench features for experimental conditions 4 (top), 5 (middle), and 6 (bottom).

Figure 123: Representative tilt-view images of 0.50 and 0.35- μm trench features for experimental conditions 7 (top), 8 (middle), and 9 (bottom).

APPENDIX E

TILT-VIEW ELECTRON IMAGES OF TRENCH FEATURES

Figure 124: Representative tilt-view electron images of 0.50 and 0.35- μm trenches for experimental condition 1 (top), 2 (middle), and 3 (bottom).

Figure 125: Representative tilt-view electron images of 0.50 and 0.35- μm trenches for experimental condition 4 (top), 5 (middle), and 6 (bottom).

Figure 126: Representative tilt-view electron images of 0.50 and 0.35- μm trenches for experimental condition 7 (top), 8 (middle), and 9 (bottom).