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The characterization of residual gases in a production sputtering system

Thomas Arthur Quinn
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THE CHARACTERIZATION OF RESIDUAL GASES
IN A PRODUCTION SPUTTERING SYSTEM

A Thesis

Presented to

The Faculty of the Department of Materials Engineering
SAN JOSE STATE UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Thomas Arthur Quinn
December, 1994

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ABSTRACT

THE CHARACTERIZATION OF RESIDUAL GASES IN A PRODUCTION SPUTTERING SYSTEM

by Thomas Arthur Quinn

The relative impact of gaseous impurity elements on aluminum-copper thin film morphology and electromigration is modeled in terms of differences in atomic parameter values between the impurity element and aluminum. The parameters representing impurity solute size and electronegativity differences from the aluminum host are discussed in terms of their effects on the resulting film morphology and the grain boundary diffusivity. The relative impact of four gaseous impurity elements, O, C, N, and H, are predicted by this model. The model is tested with data from the literature and is substantiated in most cases.

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1. INTRODUCTION

Thin film metal conductor failure in semiconductor devices due to electromigration continues to be a primary topic of research. Past efforts to characterize the mechanisms leading to electromigration failure and to extend the life of thin film metal conductors resulted in thin film deposition process and materials changes. The addition of certain solutes to aluminum metallization extends lifetimes prior to electromigration failure.³⁰ Past research shows that contaminant gas partial pressures $\geq 10^{-7}$ Torr in the metal film deposition environment has a direct impact on the film morphology^{2,4} and is related to electromigration performance.^{8,12,17} The result has been a continuous drive to improve film deposition ambient purity to parts per billion (ppb) contamination levels in order to achieve yield and reliability gains in semiconductor devices.

Due to the cost and difficulty associated with achieving higher vacuum integrity, this study attempts to identify the controlling mechanisms by which impurities affect electromigration performance of metal thin film conductors. The relative effects of different gaseous and atomic species on the film morphology and hence the electromigration behavior are predicted. These predictions are tested with existing data from the literature. Efforts may then be focused on elimination of deposition ambient impurities that truly impact electromigration.

2. BACKGROUND

2.1 Gases in a Physical Vapor Deposition Chamber

Gaseous contamination levels in a semiconductor device thin film sputter deposition system are but one component of a complex series of process variables that can have a significant effect on the nucleation, growth, microstructure, and physical properties of the deposited film.² The nature and concentration of the gas contamination will affect the deposition rate and structure of the film and can alter the intended performance of the semiconductor device.³⁵

Contaminant Gas sources

The primary sources of contaminants in a sputter deposition system are the surface and bulk of chamber walls and sputtering targets, process gas impurities, vacuum system leaks, and the device wafers themselves. The sources and concentrations of contamination are unique to each deposition system. Trace contaminants of water vapor and oxygen are common on most and are likely to come from the targets, prior venting of the chamber during maintenance, or from possible leaks in the system. Ultra-pure argon process gases are not a likely source of water vapor or oxygen, since reported levels of these contaminants are no greater than 2 - 5 parts per billion (ppb).⁴⁸ At a process chamber pressure of 7×10^{-3} Torr, this equates to a maximum water vapor or oxygen partial pressure of 3.5×10^{-11} Torr in Argon. Metal targets are fabricated by melting in vacuum or protective atmospheres. Even under these manufacturing conditions, oxygen and hydrogen concentration levels in aluminum-copper targets range from 30 - 250 ppm.⁴⁷ These levels pose more of a threat than those of the process gases. Physisorbed gases are typically sputtered from the target prior to film deposition. Chemisorbed gases

are sputtered from the target during deposition. Desorption of gases occurs even for very dense target materials. Significant gas desorption contaminates the sputtering gas and hence the deposited film.

Method of residual gas measurement

Residual Gas Analysis (RGA) is used extensively to determine the concentrations of gaseous contaminants in vacuum process equipment.^{1,2,3,4,7,9} Sputter deposition equipment is among these. RGA is mass spectrometry. Analyzers consist of an ion source, mass filter, and an ion detector. There are two types of ion sources in use. These are the open source and the closed source. The design differences between these two systems are shown in Figure 1.

Fig. 1. (a) Closed and (b) Open Ion Source RGA designs.⁶

The primary advantage of the closed source RGA is the ability to get accurate, sub-parts per million (ppm) detection sensitivity while sampling a sputtering chamber in the millitorr pressure range during the deposition process. The pressure of the separate ionization chamber is controlled approximately one order of magnitude below the process chamber pressure through the use of an orifice. At process pressures, the RGA sampling chamber pressure is maintained at or below 10^{-6} Torr for proper quadrupole filter operation. The sampler chamber background contamination levels are thereby maintained well below the levels in the ionization chamber because of the isolation between the two chambers. The open ion source RGA is useful for monitoring contamination in high and ultra-high vacuum environments ($\leq 10^{-5}$ Torr). The analyzer's ionization probe is placed directly in the vacuum environment in these cases since there is no effect on the performance of the detector at these pressures.

RGA's analyze ions according to their mass-to-charge ratio (m/q). Each molecular gas species, when ionized, has a characteristic set of detectable peaks due to the different molecular ions and charge states that may be present. This set of m/q peaks is the "cracking pattern" of the gas. See Table 1 for quadrupole mass analyzer cracking patterns for several species of interest. This table shows that ions of different molecular gases may display RGA peaks having mass-to-charge ratios at the same atomic mass unit (AMU). The use of peaks of alternate ions may be necessary to identify and quantify a particular gas. Monitoring other than the primary peak also provides for more sensitive detection of the gas.

Residual Gas Equilibrium Partial Pressures

Equilibrium in a gas system containing different molecular species is achieved when the Gibb's free energy,

$$G = G^o + RT \ln P_{Total} ,$$

is minimized. According to Dalton's law of partial pressures, $P_{Total} = \sum_i p_i$. In a system controlled at constant temperature and total pressure, changes in p_i of one species in the system will temporarily push the system away from equilibrium. To re-establish equilibrium, the p_i of other species in the system must change to compensate. Therefore, the concentration of a given species may depend on the amounts of other species present in the chamber. The calculation of the equilibrium partial pressures of all species when the initial partial pressure of one species is changed makes it possible to model which gas species will have the greatest impact on the amounts of other species in the chamber.

Equilibrium conditions change as temperature changes. Gas species incorporated into the film under the equilibrium conditions during deposition may either exceed or be less than the calculated equilibrium partial pressures at the annealing temperature. The behavior of the gas may be determined by these comparisons.

2.2 Interaction of Gas Species with the Film Surface

The kinetics of adsorption are controlled by temperature, pressure, and relative concentrations of reactants. The time for complete monolayer coverage of 10^{15} atoms/cm² is given by

$$\tau_c = \frac{10^{15}}{3.513 \times 10^{22}} \frac{\sqrt{MT}}{P} \text{ sec.} \quad (1)$$

This is the inverse of the impingement flux, discussed below, multiplied by the monolayer concentration. If a solid is in thermal equilibrium with an ambient gas, two possible scenarios exist. High kinetic energy mobile gas particles impinging on the surface most likely scatter back into the gas phase. Lower energy gas particles may even behave in the same way if there is a potential barrier in front of the adsorption well. The ratio of the adsorption rate to impingement rate is the sticking coefficient.³⁸

Sputtered atom impingement flux at the wafer surface

The impingement flux (Φ) of the sputtered species at the film surface controls the film growth rate. Alternatively, if the growth rate and final thickness of the film is known, the sputtered atom flux at the surface can be estimated. In this case, the following relationship is used:

$$\Phi = \frac{\dot{G} \rho N_A}{\text{g. m. w.}} \quad (2)$$

where $\dot{G}$ is the film growth rate in cm/sec, ρ is the density of the thin film material in g/cm³, and g.m.w. is the gram-molecular weight of the thin film material.

Residual Gas Impingement at the Film Surface

An important consideration in this study is the determination of the gas impingement flux at surfaces within the deposition chamber, particularly the wafer surface. The impingement flux relationship as derived by Ohring¹³ is discussed below.

The number of gas molecules that strike a surface per unit time and area is given by

$$\Phi = \int_0^{\infty} v_x dn_x . \quad (3)$$

The velocity distribution function is given by

$$f(v_x) = \frac{1}{n} \frac{dn_x}{dv_x} = \left| \frac{M}{2\pi RT} \right|^{1/2} \exp - \frac{M v_x^2}{2RT} . \quad (4)$$

Upon substitution into equation 3, the following relationship is obtained:

$$\Phi = \frac{n}{(2\pi)^{1/2}} \left| \frac{M}{RT} \right|^{1/2} \int_0^{\infty} v_x \exp - \frac{M v_x^2}{2RT} dv_x = n \sqrt{\frac{RT}{2\pi M}} . \quad (5)$$

Substitution of the perfect gas law $P = \frac{1}{3} \frac{nM}{N_A} \overline{v^2} = \frac{nRT}{N_A}$ into equation (5) yields the final form of the impingement flux relationship:

$$\Phi = 3.513 \times 10^{22} \frac{P}{\sqrt{MT}} \text{ molecules/cm}^2 \cdot \text{sec} , \quad (6)$$

where P is the gas pressure expressed in Torr, M is the gas molecular weight, and T is the absolute temperature.

Collision probability between sputtered metal atoms and residual gases.

In addition to the impingement at the film surface due to their partial pressures in the chamber, residual gases may also arrive at the film surface due to collisions with

sputtered metal atoms during deposition. For these collisions to effectively contribute to the impingement at the surface, they must occur within one mean free path length from the surface at the sputtering pressure. Molecular collision probability calculations²² are adapted to this application to estimate the number of collisions that take place.

A thin horizontal cross section of the sputtering area is shown in Figure 2. The wafer area is selected as the sputtering area. The thickness of this layer (dx) is estimated from calculation of the mean free path length, λ_{mfp} , of molecules at the sputtering process pressure given by:

$$dx = \lambda_{mfp} = \frac{5 \times 10^{-3}}{P} \quad (7)$$

where λ_{mfp} is in cm and P is in Torr.

The ratio of the number of collisions, dN , to the total number of sputtered atoms, N , is equal to the ratio of the area presented by the residual gas atoms/molecules (target atom area) to the total area (wafer area) presented by the layer.

$$\frac{dN}{N} = \frac{\text{target atom area}}{\text{wafer area}} \quad (8)$$

Fig. 2. Sputtered atom/residual gas atom collision cross section above the wafer surface.

The target area σ of a single (equivalent) collision is given by

$$\sigma = \pi(r_t + r_b)^2, \quad (9)$$

where r_t and r_b are defined as in Figure 3.

Fig. 3. Equivalent molecule used for determination of collision cross section.

This area is called the microscopic collision cross section of one (equivalent) molecule. The target molecule area is this microscopic cross section multiplied by the number of molecules in the layer. If there are n target gas molecules per unit volume, the number of molecules in the layer is $n\pi r^2 dx$. The total target atom area is $n\sigma\pi r^2 dx$. Substituting into the original equation, the following relationship is achieved:

$$\frac{dN}{N} = \frac{n\sigma\pi r^2 dx}{\pi r^2} = n\sigma dx \quad (10)$$

The flux of sputtered atoms through the area of interest must be determined in order to calculate the number of collisions.

2.3 Overview of Electromigration Phenomenon

Electromigration involves the movement (i.e. diffusion) of metal atoms in the thin film along the length of metallic conductors carrying large direct current densities. Thin film conductors can withstand current densities upwards of 10^6 A/cm² without immediate failure because there is sufficient removal, by the substrate, of joule heating in the conductor. Bulk metals rapidly approach their melting temperature at current densities two orders of magnitude lower than this.

There is a measurable degree of momentum transfer between the electrons and the vibrating lattice atoms of the conductor. Increasing inelastic scattering of electrons in the conductor will enhance the diffusion rate of the metal atoms in the direction of electron current flow.²⁹

Electromigration failures in thin film conductors manifest themselves in a number of ways. The conductor can fail by shorting with an adjacent conductor, formation of

large voids leading to an open circuit, or formation of hillocks on the surface of the conductor that crack dielectric passivation overlayers.¹³

As a result of the significant amount of study of electromigration phenomena, a well known empirical relationship for the log normal distribution of the Mean-Time-To-Failure (MTTF) as a function of the current density (j) and temperature has been formulated. The relationship, first proposed by Black¹⁶ is given by:

$$\text{MTTF} = A j^{-n} \exp(E_a/kT) \quad (11)$$

The pre-exponential constant (A) and exponent (n), and the activation energy (E_a) are empirically determined and k is Boltzman's constant. The pre-exponential constant (A) is characteristic of a given set of conductors. It is a function of the statistical distribution of inhomogeneities (which cause flux divergence), of the structure of the films, and of the geometry of the conductors (i.e. line width, length, and film thickness).³⁰ This relationship takes the Arrhenius form since electromigration is a thermally activated diffusion phenomenon under a driving force of current density. The atomic motion depends on the direction of motion of the charge carriers. The driving force depends on the type of lattice structural defects and the atomic configuration of the jumping path.²⁵ A significant source of electron scattering is the grain boundaries of a film because of the crystal orientation change across the boundary. As the crystallite size becomes smaller than the electron mean-free path, the contribution to the film resistivity from GB scattering arises.^{13,39}

The mass transport phenomena can be looked at in terms of a flux, J , which is dependent upon temperature, current density and grain structure. The temperature

dependence is due to EM being a diffusion process, the current density dependence is another driving force, and the grain structure is a third aspect defining the paths for diffusion.²⁹

Electromigration has been demonstrated to be a diffusion process.²⁵ It is clear from several studies that there are many process, geometry/structure, and materials variables that contribute to the resulting electromigration performance of a given metal conductor.^{41, 42, 43, 44} Under the driving force of electric current, the atomic flux can be through either lattice or grain boundary diffusion. At the electromigration test temperatures in question, ~150 - 200° C, the contribution of lattice diffusion is negligible. Many theoretical and experimental electromigration studies of metallic thin films have identified grain boundary diffusion as the dominant mass transport process.^{20, 25} Mass transport at grain boundaries in most metals is through vacancy diffusion. Grain boundaries are rich in atom size voids.²⁹ Many of these studies have demonstrated electron flux divergence at regions of variation in the grain morphology (grain size and distribution). Voids nucleate usually at grain boundaries or existing pinholes and grow into adjacent grains. Compared with large grained conductors, many more voids were seen in the fine-grained Al conductors. The number of diffusion paths along the direction of the current plays a direct role in the EM failure rate.²⁶ Therefore, it is reasonable to assume that larger grain sizes will minimize the total grain boundary area and decrease the number of available diffusion paths. This has been demonstrated through improved MTTF rates with increasing grain size.^{26,40}

However, with increasing grain size also comes the potential for higher variation in grain growth characteristics. Non-uniformity in the grain size of the metal film can cause atomic flux divergence at junctions across which there are a different number of

grain boundaries. Fewer ions leave the coarse grained area by grain boundary diffusion than are entering it from the fine grained areas because the number of available paths for mass transport changes abruptly. There will be a pile up or depletion of conductor material.²⁹ The increase of the Deviation of Time To Failure (DTTF) with increasing grain size may be related to the failure mode. For conductors with large grain size distributions and hyper-bamboo structures, as shown in Figure 4, each individual site of an atomic flux divergence becomes potentially more damaging.¹² In lines with hyper-bamboo structures each grain boundary may have different failure time characteristics due to the different nature of the grain boundaries. As the angle of the grain boundary gets further from perpendicular to the current direction, the time to failure decreases while the distribution of failure times remain constant irrespective of grain boundary angle.⁸ Since atomic flux at the grain boundaries plays the dominant role in the electromigration

Fig. 4. Hyper-bamboo grain structure with large grain size distribution.

process, this flux is defined by several film properties in equation (12) below.

$$J_b = \frac{1}{kT} \frac{N_b \delta}{d} D_b \cdot j \rho e Z_b^* \quad (12)$$

N_b = atomic density at the grain boundary

ρ = resistivity

d = average grain size

eZ^* = effective charge

D_b = diffusivity at the grain boundary

k = Boltzman's constant

δ = effective boundary width

j = current density

Minimizing J_b is essential to increasing the electromigration time to failure. It is apparent that variations in a number of the parameters in this flux equation can either reduce or increase the atomic flux at the grain boundary. It should be pointed out that the average grain size and the diffusivity at the grain boundary are separate, individual terms. This difference is significant and will be discussed in more detail below. It has also been demonstrated that grain boundary diffusion occurs by a defect mechanism which allows a net diffusion flux of atoms to occur.¹⁹ The atom flux is primarily through vacancy diffusion, rather than interstitial diffusion, because the vacancy formation energy at the grain boundary is lower than that for interstitials at the grain boundary. Sources and sinks for vacancies must be present at the boundaries to support the flux divergence.¹⁹

2.4 Thin Film Materials Characteristics Related to Electromigration

Atomic flux divergence within the conductor can be a result of inhomogenieties in local structure and temperature. Structural imperfections including point defects, dislocations, grain boundaries, and grain boundary triple points all play a role in lowering the resistance of the conductor to electromigration failure. A flux divergence can also be

caused by other structural discontinuities such as second phase particles, positions of deviation in chemical composition, variation in atomic structure, or variations in defect concentrations at the grain boundary (i.e., segregation of solute atoms).²⁵

Crystal Structure

Solvent diffusion dependence on crystal structure is highly variable. Lattice diffusion of solvent atoms by either interstitialcy or vacancy-atom exchange processes is expected to be higher in less densely packed crystals. Interstitialcy in a less dense lattice has a lower activation energy. Exchange by the vacancy mechanism is faster in lattices with lower coordination numbers.

Chemical Composition

Different elements added as solutes to a matrix will have different effects on the overall solvent diffusivity depending on atomic size differences, attraction between the solute and solvent atoms, and the ability to form compounds with the solvent. In a solution, the relative size of solute to the solvent atom will determine the solid solubility. Size differences also determine the mutual impact on diffusion of both atoms in the lattice. Formation of compounds serves to trap solute and solvent atoms so they cannot migrate freely within the lattice or at grain boundaries.

The electromigration mean time to failure of different aluminum alloy thin film conductors studied under equivalent deposition and testing conditions³⁰ are presented in Table 2.

TABLE 2
EFFECTS OF ALLOY SOLUTES ON
ELECTROMIGRATION MTTF²³

Alloy	MTTF (hours)
Pure Al	30
Al-2 wt%Ag	45
Al-2 wt%Au	55
Al-1.8 wt%Si	150
Al-2 wt %Mg	1000
Al-4 wt%Cu	2500
Al-1 wt%Ni	3000
Al-2 wt%Cr	8300

Point Defects

The presence of vacancies enhances atomic diffusion in the lattice and at the grain boundary by their own diffusion rate. Diffusion by a vacancy-atom exchange mechanism depends heavily on the vacancy concentration and vacancy migration rate. Both the vacancy concentration and diffusivity increase with increasing temperature. Interstitial solutes depress substitutional solute and solvent atom diffusion rates. Interstitials place a spherical strain on the lattice that increases the activation energy for atomic exchange in the vicinity of the interstitial.

Line Defects

Dislocations provide a conduit or pipe for diffusion. The diffusion rate is much higher along dislocations than for bulk diffusion.¹⁸ The impact of dislocations on the overall diffusion of a solute may be more critical in the case of low solute concentrations, such as with impurity diffusion.

Surface Defects

Free surface and grain boundary diffusion rates are significantly higher than bulk diffusion rates because of the more open structure than in the lattice. The structure of free surfaces is even more open than that of grain boundaries, but grain boundary diffusion rates in a polycrystalline sample often plays a more significant role in atomic transport because the total grain boundary area exceeds that of the free surface. The crystal lattice mismatch making up the grain boundary, consists of a two dimensional array of line and point defects that contribute to the diffusion coefficient along the grain boundary.

Volume Defects

Voids in a thin metal film contribute to electromigration failures by creating an atomic flux divergence. Voids also provide interior free surfaces that enhance diffusion rates. Precipitates can have a detrimental effect on the electromigration of a metal film depending on the nature and location of the precipitate. If the precipitate has a coherent interface with the solvent lattice, solvent diffusion enhancement is not expected. In fact, diffusion in the region of the coherent precipitate is expected to be depressed due to the lattice strain. However, if a non-coherent interface is formed in the lattice, the interface diffusion will be higher than if no precipitate were present. Precipitates at the grain boundary can have an altogether different effect and are discussed below.

Interaction of Defects

Defects have an energy associated with them. Different defects will interact with each other due to their individual energies. Substitutional and interstitial solutes will interact in a manner that causes mutual retardation of diffusion. This is due to the increased lattice strain around solutes. Vacancies enhance both substitutional and interstitial solute diffusivity by interacting with the solute and causing it to diffuse along with the vacancy.

With higher surface mobile sputtered adatoms, comes a higher dependence of grain size on film thickness.²⁹ Alternatively, if sputtered atoms are deposited in the presence of increasing concentrations of mobility limiting impurities, we would expect the grain structure to be progressively finer. The effect of residual gas atmospheres on the growth and structural development of vacuum deposited films has been investigated by several researchers.^{2, 29} Impurities which exceed the solubility limit of the film material find their way to growth steps, surfaces of the crystals or at grain boundaries and may have a limiting effect on grain growth.

Foreign atoms in the lattice can interact with migrating grain boundaries at earlier stages of grain growth and have a significant impact on the grain growth kinetics. Interstitial or substitutional incorporation of foreign atoms into the lattice will both have a similar effect. Interstitial atoms always cause an expansion of the surrounding lattice whereas substitutional solutes may cause either an expansion or contraction depending on relative size. There is a lattice strain energy associated with each of these cases. Since grain boundaries are regions of lattice misfit, they too produce strain on the lattice. Foreign atoms in the lattice will interact with the grain boundaries in a manner which lowers the total strain energy of the lattice. To achieve the lowest total strain energy,

atmospheres of solutes form around the grain boundary. In order for these atmospheres to maintain the lowest strain energy, they will tend to move with the grain boundary, producing a drag on the boundary migration. The impact of this interaction on grain growth is determined by the relative lattice strain, a function of lattice distortion and concentration, produced by the different solutes.¹⁴

Mean time to failure and the deviation of the time to failure has been linked to the degree of grain misorientation from the preferred [111] direction.^{4, 8} An aluminum film with a stronger (111) texture than an equivalent film exhibits better electromigration performance. As grain size gets larger, the preferred (111) texture also becomes more pronounced.⁸

The overall atomic flux increases as a function of the degree of misorientation between grains up to a point where the tilt angle of the grain boundary is 45°. It has been shown that grain boundary diffusivity is anisotropic and the degree of anisotropy is a function of the tilt angle of the grain boundary between two adjacent grains.²⁰ The popular explanation for this is that dislocation pipes are responsible for the atomic flux. For low angle grain boundaries the density of dislocations is lower because the equilibrium dislocation spacing is larger as shown in Figure 5. As the tilt angle increases, the equilibrium dislocation spacing at the boundary decreases to a point where the density of dislocations is much higher and the degree of anisotropy decreases, but never disappears completely.

In sub-micron width conductors, where the grain spans the width of the conductor, the actual grain size is less important than the uniformity in grain orientation. It is clear that a reduction in the mismatch in grain orientation will have a more significant impact on the available paths for the diffusion than increasing grain size. With higher thin film

deposition rates, more disorder occurs in the crystal structure with or without impurities. The resulting crystal orientations will be diverse. The specific effect of impurities is to further increase the disorder and broaden the $\{111\}$ crystal orientation peak.^{2, 13}

Fig. 5. Low angle grain boundary dislocation spacing.

Solutes added to the film in excess of the solubility limit diffuse to the grain boundaries. Depending on the nature of the solute, the formation of second phases at the grain boundaries also hinders the grain boundary diffusion. Heterogeneous nucleation of impurity solutes is limited by the number of available nucleation sites. The number of preferred heterogeneous nucleation sites follows the relationship below:

1. Increases at grain boundaries with decreasing grain size.
2. Increases at dislocations with increasing dislocation density.
3. Increases at vacancies with increasing vacancy concentration.

If the interstitial impurities that segregate to the grain boundary reduce the interfacial tension of a grain boundary, then the solute will occupy the high energy sites which were previously available for trapping vacancies and involved in grain boundary mass transfer. Thus, high energy grain boundaries are expected to show stronger segregation effects. The effect of impurities on the vacancy binding energy at the grain boundary could be significant if there is the formation of stable compounds at the grain boundary. This decreases the binding energy of vacancies at the grain boundary and the driving force for vacancy migration to the grain boundary from within the lattice. In this manner, impurity solutes will decrease the grain boundary self diffusion coefficient of the solvent.²¹ This is ironic since the impurities appear to be one of the possible sources of increased grain misorientation during deposition. High angle grain boundaries are expected to show more segregation since these have a larger number of high energy sites.

Geometrical Considerations

In addition to the film's microstructural effects on electromigration performance, the geometry of the conducting line also plays a significant role in the electromigration time to failure. It is seen that the geometry effects are not completely isolated from the microstructure.

A number of researchers investigated the effects of the physical geometry on the electromigration resistance of different metal thin film conductors. The first studies appeared in the early 70's on Al and Al-Si conductors. Learn ⁴¹ shows that the MTTF increases as the line length decreases for a conductor of given width. Schafft, et. al.,⁴² confirm this in Al-1%Si conductors. Agarwala, et. al.,⁴³ demonstrated that MTTF

increases as the Al line length decreases below a critical length. It is shown that the critical line length decreases as the line width decreases. The increases in MTTF at shorter line lengths also exhibit a larger standard deviation of the log normal failure distribution.

It is apparent from the above studies that the line length and width were inter-related. The MTTF decrease as the line width decreases for a given length. However, line widths eventually decrease to a point where the relationship between MTTF and line width is reversed. Scoggan, et. al.,⁴⁴ demonstrate this critical width to be on the order of 3 microns for Al-Cu conductors. This critical width is approximated by the grain size of the metallization. As the grain size and the conductor width approach each other, the number of triple points of intersecting grains is significantly reduced. As line width continues to decrease below this point, the MTTF increases, as shown by Kwok, et. al., in Al-Cu conductors of submicron width.

Electromigration lifetime also increases with decreasing film thickness. This is actually a function of the formation of more columnar grains that span the thickness of the film.

2.5 Gas Contaminant Effects on Film Structure

Assuming a sticking coefficient of unity, the ratio of the residual gas molecule impingement rate to the sputtered adatom impingement rate will provide us with an estimate of the impurity concentration in the film. If we assume that different gas species are incorporated into the film, we must answer the question as to what the interaction between the different components is. The thermodynamics of the system will tell us which compounds are the most stable.

Gas contamination of the film surface affects condensation considerably, but the role of contaminants depends on whether the binding energy of the surface is increased or decreased. Based on the results of several researchers, significant partial pressures of O_2 and H_2O present during deposition have been proven to have the greatest effects on film morphology.^{2,23,24,39} Chopra³⁹ reports that approximately 10^{-4} to 10^{-5} Torr of O_2 decreases the mobility of oxidizable vapor materials. This is consistent with results reported by d'Heurle, et al.,¹⁷ which demonstrated visible effects of O_2 partial pressures of $\sim 10^{-5}$ Torr on the grain size of aluminum films. At high partial pressures such as these, clusters formed during the condensation process may be covered with an oxide layer which prevents further coalescence and grain growth.³⁹

Chamber vacuum levels on the order of 7.5×10^{-8} Torr enhances the surface mobility effects of aluminum atoms.²⁹ The aluminum mobility is severely restricted (diffusion distances are negligible compared to a 1 μm feature size) if the partial pressure of water vapor and oxygen in the chamber exceeds approximately 7.5×10^{-8} Torr. Aluminum is a very reactive material. O_2 and H_2O can have a strong influence on its optical and morphological properties. Verkerk and Brankaert² found a well developed faceted aluminum microstructure at low water partial pressures ($\leq 2.3 \times 10^{-8}$ Torr). No pinning holes with bunches of growth steps and secondary nuclei were seen. This water partial pressure is apparently too low to affect film growth. At greater than 2.2×10^{-7} Torr, they found very rough surfaces and a decrease in preferred {111} orientation.

In vapor deposition systems using different deposition rates, it is possible to estimate the partial pressures of water necessary to cause the same effects as shown by Verkerk and Brankaert. This is achieved by establishing the partial pressure of water vapor to maintain the same ratio of aluminum atoms to water molecules striking the

growing film surface. The partial pressure of water vapor required to produce the same effects will increase as the growth rate of the film increases beyond what Verkerk and Brankaert used. The crystallite size of vapor deposited polycrystalline films increases with increasing surface mobility of adatoms and clusters during deposition. This is dependent on substrate temperature, rate of deposition, inertness of the surface and velocity of the vapor atoms parallel to surface. At low substrate temperature, grain size is not dependent on deposition rate. Contaminants and residual gases can influence grain size considerably. At higher deposition rates, adatoms interact more strongly and chemisorb with little surface migration. A fine columnar grain structure is obtained. This is the case for aluminum.³⁹ Specimen dimensions, discussed later, can also play a role in limiting the post-anneal grain growth rate and the maximum grain size.

Data from Frear, et al.²³ presented in Table 3 also demonstrates the inverse relationship between contamination partial pressure and grain size of as-deposited aluminum films.

Queirolo, et al.,⁴ show the effects of different residual gases on the as-deposited and post-annealed crystal orientation. This data for various pressures of O₂, CO₂, and N₂ presented in Table 4.

TABLE 3
EFFECT OF SPUTTERING AMBIENT ON GRAIN SIZE.²³

Sample	Partial Pressure of Gases (Torr)			Grain Size* (um)	Std. Dev.
	H ₂ O	N ₂	O ₂		
C1	4.7 E-06	1.4 E-07	3.7 E-08	0.673	0.085
C2	4.7 E-06	1.4 E-07	3.7 E-08	0.863	0.067
B	1.8 E-07	6.5 E-08	6.0 E-09	0.934	0.055
D	1.3 E-09	1.7 E-10	N/D**	1.012	0.092
E	6.8 E-08	2.7 E-08	N/D**	1.061	0.096

* 300° C Deposition Temperature, As-deposited films

** Not Detected

TABLE 4
EFFECT OF SPUTTERING AMBIENT ON CRYSTAL ORIENTATION.⁴

Ambient	Partial Pressure (Torr)	R_{cr}^+ As-Deposited	R_{cr} Post-Anneal [×]	MEF* (mJ/cm)
Reference	9.8 E-08	1850	∞	170
O ₂	9.0 E-07	390	∞	166
O ₂	3.2 E-06	67	1570	159
O ₂	1.8 E-05	92	190	115
CO ₂	1.2 E-06	51	210	141
CO ₂	3.8 E-06	6	13	93
CO ₂	2.1 E-05	4	0.8	36
N ₂	6.0 E-06	87	160	144
N ₂	1.0 E-05	17	18	37
N ₂	4.1 E-05	9	9	9

⁺ X-ray diffraction rocking curve relative peak intensity ($R_{cr} = I(111)/I(200)$).

[×] Annealed 450° C in H₂ for 30 min.

* Mean Energy to Failure.

3. OBJECTIVE

The original objective of this study was to characterize the gases present in a production Al-Cu thin film sputtering system and determine the effects of residual gas contaminant variations on the resulting film properties. It later became unfeasible to purposely contaminate the production sputtering system to process films under these conditions. Given this limitation, the objective was modified to theoretically model the effects of measured gas contaminant partial pressures on the electromigration performance of the film. The objective consists of three parts:

1. Determine, using residual gas analysis, the partial pressures of impurity gases in a production aluminum-copper film sputtering chamber.
2. Theoretically model the gas contaminant incorporation into the aluminum-copper film.
3. Estimate the expected impact on the electromigration performance of the film.

As discussed in the background, the literature contains studies relating residual gas contamination partial pressures $\geq 10^{-7}$ Torr to film properties relevant to electromigration, such as grain size, crystal orientation, and film resistance.^{2,4} The question that arises from these studies is whether or not contaminant partial pressures lower than those in the literature remain detrimental to the film properties related to electromigration performance.

4. PROCEDURE

This study applies actual residual gas measurements as the input for calculations estimating gas incorporation in the thin film. Studies in the literature identify specific gaseous contaminants to modulate physical film properties.^{2,4} These properties in turn affect electromigration performance.^{8,12,17} The procedure used to generate a model for estimating the relative impact of the different contamination species on electromigration is described below. Data from the literature is also used to test the model.

4.1 Residual Gas Measurement

The gaseous contamination levels in the sputtering chamber have been measured using a closed source residual gas analyzer with static scans (i.e. one-time sample) for atomic mass units (AMU) ranging from 1 to 200. The species selected for continuous tracking during the sputtering process were Ar, H₂, CH₄, N₂, NH₃, H₂O, CO₂, O₂, and CO. Appropriate AMU values were selected to avoid masking one species by another or to improve measurement sensitivity for that species. These AMU values and the closed source RGA detection limits of five of the contaminants at an argon deposition sputtering gas pressure of 4×10^{-3} Torr are reported in Table 5 below. The dynamic RGA measurement scans were taken during the sputter deposition processes of monitor films used to monitor equipment control. These films were deposited under exactly the same conditions as device wafers. The equipment available for RGA measurements was in a production environment and did not allow for intentional changes in the different impurity gas partial pressures.

TABLE 5
REPORTED RGA DETECTION LIMITS AND AMU TRACKED
FOR SELECT GAS SPECIES

Species	Detection Limit (Torr)	AMU Tracked
H ₂	5 - 7 x 10 ⁻⁸	2
H ₂ O	5 - 6 x 10 ⁻⁹	17
CO ₂	5 - 6 x 10 ⁻¹⁰	44
O ₂	1 x 10 ⁻¹⁰	32
N ₂	7 x 10 ⁻¹⁰	14
NO		30
CO		28
CH ₄		15
Ar		20, 40

4.2 Generation of the Models

Equilibrium Partial Pressure Calculations

Equilibrium concentrations in a complex system are determined through use of the free energy minimization method employed in a software program entitled STEPSOL, Version 4.20.²⁷ designed for this type of application. This software utilizes a well known chemical equilibrium program, SOLGASMIX.²⁸ By varying the initial amounts of different species, it is possible to model which species cause the most significant changes in equilibrium concentrations of other species in the system and hence, provide the most sensitive monitor of variations within the chamber.

Based on gas species found to actually reside in the sputtering chamber and those that can potentially exist in the same system, the following species are included in the calculations: Ar, H₂, H₂O, N₂, CH₄, CO₂, CO, NH₃, NO, O₂, and NO₂. The

equilibrium calculations are carried out at 323°K and 673°K, which represent the estimated sputtering chamber and annealing temperatures, respectively. The anneal temperature is selected to understand the chemical potential of the different atomic species during follow on thermal anneal processing if indeed they were incorporated into the film. The initial partial pressures of H₂, O₂, CO₂, and N₂, selected as primary H, O, C, and N containing species, are varied independently of each other in the calculations to assess which species has the largest impact on the equilibrium partial pressures of all other gas species. The initial amounts for each of the four species mentioned above are varied between concentrations lower than and significantly higher than those actually measured in the sputtering system with the RGA.

Residual Gas Incorporation into the Film

The total flux of residual gases impinging on a surface in the vacuum chamber during deposition is assumed to be comprised of both the impingement of residual gases in equilibrium with the surface due to pressure and those from collisions with sputtered atoms. These are determined from the summation of results of equations (6) and (10). The contribution of the collisions to the total gas impingement flux is determined for the region above the wafer surface equivalent to the mean free path of impurity gases at the sputtering pressure as determined by equation (7).

Film Bulk Impurity Concentration

The residual gas and Al-Cu sputtered atom impingement rates are used to calculate surface and bulk impurity concentrations under assumption of a sticking coefficient for the various species. The metal film thickness considered in this study is

3500 angstroms Al-0.5 wt% Cu. The estimated impurity concentrations are compared with the solubility limits for the impurity element in aluminum to predict the behavior of the impurity within the film.

Prediction of Impurity Effects on Electromigration

Available data from which to generate a quantitative correlation between the residual gas partial pressure measurements in metal thin film sputtering chambers and the resulting electromigration mean time to failure is limited. Any quantitative correlation that might exist is thought to be relevant only to the specific deposition system used and only qualitative for all other systems. The vast array of deposition systems and RGA configurations, deposition processing, electromigration test structures and test conditions required a more general approach to the question of how different impurity gases are expected to impact electromigration. This effort is focused on taking an atomistic approach to qualitatively modeling the relationship between electromigration behavior and the presence of specific impurities in the film.

The selection of appropriate parameters to model the expected behavior of impurity elements in an Al-Cu film is based on the work of Villars.³¹⁻³⁴ Villars generated phase diagrams of specific atomic properties for thousands of binary alloy systems predicting the compound formation and structure types of the different alloys. Of the atomic properties investigated by Villars to most accurately predict alloy behavior,

two are selected for review of their effects on electromigration behavior. These are:

1. $|\Delta(r_s + r_p)_{AB}^Z|$ - the magnitude of the Zunger potential radii difference of the two components represents properties related to the relative size of the atoms. This atomic property is used to describe various diffusion phenomena.
2. $|\Delta X_{AB}^{MB}|$ - the magnitude of the difference in electronegativity of two components. A larger value of this property indicates a greater attraction between the elements involved.

A model that describes the relative effects of contaminants on the film properties that modulate electromigration behavior is proposed. Literature reports of impurity gas partial pressure effects on as-deposited and post annealed grain size and crystal orientation are used to test the model.

5. RESULTS

5.1 Residual Gas Measurements - Species Detected

Examples of RGA static scans of the sputtering chamber are presented in Figure 6. These scans don't reveal significant levels of species other than H₂, CH₄, N₂, NH₃, H₂O, Ar, CO₂, CO, and O₂. Representative partial pressure trends of these species monitored with dynamic scans during chamber plasma strike are presented in Figure 7. An example of a dynamic scan taken during the sputtering process is presented in Figure 8.

From a sampling of dynamic scan data, the partial pressure levels of different detected species are presented in Table 6. To demonstrate the means used to determine the actual partial pressures, H₂O will be used as an example. The H₂O partial pressure in Figure 8 is shown at approximately 1×10^{-8} Torr. This represents the AMU 17 peak intensity which is 27% of the primary AMU 18 peak intensity. The AMU 17 partial pressure is multiplied by 4X to arrive at the typical value of 4×10^{-8} Torr reported. The partial pressure values of O₂ (100% peak intensity at AMU 32) range from 6×10^{-10} Torr to no larger than 5×10^{-9} Torr. The remaining partial pressure values were determined in the same manner as above.

Fig. 6 (a). Sample Static RGA Scan of Al-Cu Deposition Chamber.

Fig. 6 (b). Sample Static RGA Scans of Al-Cu Deposition Chamber.

Fig. 7 (a) Sample Dynamic Scan of Al-Cu Deposition Chamber under plasma conditions.

Fig. 7 (b) Sample Dynamic Scan of Al-Cu Deposition Chamber under plasma conditions.

Fig. 8. Sample Dynamic Scans of Al-Cu Deposition Chamber under plasma conditions.

TABLE 6

MEASURED RESIDUAL GAS PARTIAL PRESSURE LEVELS

Species	AMU	Relative Intensity of Primary Peak	Base Partial Pressure*	Sputtering Partial Pressure*	Detection Limit*
H ₂	2	100%	2.0 E-08	2.0 E-07	6.0 E-08
CH ₄	15	85%	2.3 E-09	2.3 E-09	
H ₂ O	17	27%	4.0 E-08	4.0 E-08	6.0 E-09
N ₂	14	9%	2.9 E-08	2.9 E-08	7.0 E-10
CO ₂	44	100%	5.0 E-09	5.0 E-09	6.0 E-10
O ₂	32	100%	5.0 E-09	5.0 E-09	1.0 E-10
CO	28	100%	5.0 E-09	5.0 E-09	
Ar	20, 40	6%, 100%	5.0 E-09	4.0 E-03	

* All pressures in torr.

5.2 Residual Gas Equilibrium Partial Pressure Calculations

Gas species made up of carbon, oxygen, hydrogen, and nitrogen are considered in the equilibrium calculations. The effects of varying the initial concentrations of the H₂, O₂, and N₂ species on the calculated equilibrium partial pressures of the other potential species in the system are presented in Figures 9 - 11, respectively. The different effects of deposition and annealing temperatures on the calculated equilibrium partial pressures of O₂, H₂, and H₂O as a function of changing H₂ initial partial pressure are shown in Figure 12.

Fig. 9. Effects of varying H₂ partial pressure on equilibrium partial pressures of other species in the sputtering chamber.

Fig. 10. Effects of varying O_2 partial pressure on equilibrium partial pressures of other species in the sputtering chamber.

Fig. 11. Effects of varying N₂ partial pressure on equilibrium partial pressures of other species in the sputtering chamber.

Fig. 12. Effects of deposition and annealing temperature on equilibrium partial pressures of select species.

Independent variation of the N_2 initial partial pressures, as shown in Figure 11, does not have a significant effect on the equilibrium partial pressures of other species in the system. The N_2 equilibrium partial pressures, as well as those of certain other species in the chamber, increase linearly with the increasing input amounts of nitrogen. Interesting effects are noted, however, when the initial amount of H_2 is varied. There is an initial concentration of H_2 above which the equilibrium partial pressure of O_2 drops significantly. While the input amount of hydrogen increases slowly, the oxygen decreases rapidly and the water vapor equilibrium partial pressure remains relatively constant. The equilibrium partial pressures of other oxygen containing species (NO and NO_2) also decrease to insignificant levels. The available hydrogen contributes to increases in CH_4 and NH_3 . The three oxygen species displaying a reduction in equilibrium partial pressure donate oxygen to CO . The resulting CO partial pressure is still well below the reported detection limit of the RGA unit. A similar effect is encountered with increasing initial partial pressure of O_2 , however, the resulting effects on other species is exactly opposite that of increasing the initial H_2 pressure.

Figure 12 demonstrates that the chemical potential of oxygen or hydrogen incorporated in the film and at equilibrium is significantly higher at the annealing temperature than at the lower deposition temperature.

5.3 Impingement Flux Calculations

The calculated impingement fluxes for the different gas species both measured and assumed to be in the system during deposition are presented in Table 7. These fluxes are calculated from the summation of the residual gas molecule impingement rate (equation 6) and the impingement of gas atoms due to collisions with sputtered adatoms approaching the surface (equation 10).

TABLE 7.--Calculated Impingement Fluxes of Gaseous Contaminant Molecules and atoms at 323 °K.

Molecular Species	Partial Pressure		Atom Species	Partial Pressure		Total Impingement Flux (cm ⁻² -sec ⁻¹)
	Measured Partial Pressure (Torr)	Induced Molecular Impingement Flux (cm ⁻² -sec ⁻¹)		Induced Atomic Impingement Flux (cm ⁻² -sec ⁻¹)	Atomic Collision Impingement Flux* (cm ⁻² -sec ⁻¹)	
H ₂ O	4 x 10 ⁻⁸	1.84 x 10 ¹³	H	1.14 x 10 ¹⁵	3.59 x 10 ¹²	1.14 x 10 ¹⁵
O ₂	5 x 10 ⁻⁹	1.73 x 10 ¹²	O	2.66 x 10 ¹³	4.37 x 10 ¹¹	2.70 x 10 ¹³
H ₂	4 x 10 ⁻⁷	5.5 x 10 ¹⁴	N	2.14 x 10 ¹³	6.84 x 10 ¹⁰	2.15 x 10 ¹³
CO	5 x 10 ⁻⁹	1.85 x 10 ¹²	C	4.44 x 10 ¹²	6.77 x 10 ¹⁰	4.44 x 10 ¹²
CO ₂	5 x 10 ⁻⁹	1.473 x 10 ¹²				
N ₂	3 x 10 ⁻⁸	1.07 x 10 ¹³				
CH ₄		1.12 x 10 ¹³				

* Calculations per equation (10) with $dx = 1.25 \text{ cm} = \text{mean free path length at } 4 \times 10^{-3} \text{ Torr.}$

The total impingement fluxes calculated above are used to calculate bulk film contamination concentrations. This bulk concentration is determined under the assumption of a sticking coefficient of 1. While this sticking coefficient may be an over estimate, it certainly provided a worst case scenario. The calculated estimates of the impurity concentrations compared with solubility limits in aluminum are summarized in Table 8.

TABLE 8
ESTIMATED ATOMIC IMPURITY CONCENTRATION IN THE
AL-CU FILM COMPARED WITH SOLUBILITY LIMITS.

Atom Species	Impingement Flux per Monolayer Al	Concentration (ppm)	Solubility Limit (ppm)
H	1.4 E13	9300	1.5 E-04
O	3.3 E11	220	0.02 - 0.05
N	2.7 E11	179	0.02
C	5.6 E10	37	

5.4 Model of Impurity Effects on Electromigration

A model relating impurity atomic parameters, selected from Villars' work, to electromigration behavior of an aluminum film is proposed below. The model describes the effects of residual gases adsorbed at the growing film surface on the resulting film morphology. The film properties defining morphology include grain size and preferred crystal orientation. Film morphology and grain boundary diffusivity are directly related to the electromigration performance of the film.

Grain Size

One of the parameters in the grain boundary flux equation (12) is the grain size. The grain size of the metal film must be considered in terms of both the as-deposited and annealed film. A reduction in metal adatom surface mobility will cause finer grains to form. Of the atomic properties representing the characteristics of impurity elements, the size and electronegativity of the impurity can be used to assess relative effects on grain size.

Two of the controlling factors of the as-deposited grain size are the physical and energy barriers to metal adatom mobility presented by impurities adsorbed at the surface. With increasing impurity size comes a greater activation energy for adatom surface diffusion. Impurities at the film surface either in molecular or atomic form present a physical barrier to the sputtered metal adatoms. Impurity species may initially be adsorbed on the film surface as demonstrated in Figure 13.

Fig. 13. Adsorbed impurity molecule effects on sputtered adatom mobility.

The activation energy required for the sputtered adatoms to diffuse along the surface to the high energy sites at kinks and jogs increases with the presence of these molecular impurities. At the surface of the growing film, atomic impurities like O, N, H, and C fill interstitial sites as illustrated in Figure 14 or inhabit sites at kinks and jogs. Sputtered metal adatoms without enough energy to overcome the physical barrier will have a shorter net diffusion length. Atomic hydrogen has the largest Zunger radii sum, $(r_s + r_p)^Z$, of the four impurities, as reported by Villars, with an estimated value of 1.25, followed by carbon at 0.64, nitrogen at 0.54, and finally oxygen at 0.465. Hydrogen's electronic shell is balanced by only a single proton, whereas the other atomic impurities have more protons in their nuclei. Strictly considering impurity size, hydrogen and carbon should have the largest impact on inhibiting metal adatom mobility and modulating as-deposited grain size.

Fig. 14. Effect of interstitial impurity on surface mobility of deposited adatom.

Atomic impurities having larger electronegativity differences from the metal atoms will react more strongly at free surfaces. It is proposed that the electronegativity differences between impurity and sputtered metal also play a role in modulating the surface mobility of the metal adatoms during deposition. The electronegativity decreases

in the following order: oxygen (3.32), nitrogen (2.85), carbon (2.37), and hydrogen (2.10). Most metals, including aluminum, have a lower electronegativity than any of these four impurity elements. It is therefore expected that of the four, oxygen will have the largest electronegativity difference from the metal and will react most strongly, followed by nitrogen, carbon, and hydrogen. Consideration of the Gibb's free energy of compound formation between aluminum and each impurity element also indicate which interactions are most stable. Hydrides are not thermodynamically stable, however, atomic hydrogen is stable in solution in aluminum.

The annealed grain size of the film is modulated by the recrystallization rate of the metal atoms. The grain growth is achieved by metal atoms diffusing across existing grain boundaries to high energy sites to reduce the overall lattice free energy. Since recrystallization is a diffusion process with an activation energy to overcome, conditions that increase the activation energy will slow the process down. Impurities in the bulk of the metal film locally strain the lattice. Grain boundaries interact with impurities resulting in a lower total lattice free energy. The grain boundary atmosphere formed by the interaction of impurities with the grain boundary must move with the migrating grain boundary during recrystallization by a series of atomic jumps. Impurities that do not inhibit these atomic jumps will not affect recrystallization rate or the post-annealed grain size. The impurity size factor arises again to explain the relative effects of the four impurity elements. Hydrogen, despite its large atomic Zunger pseudopotential radii sum, is reported to diffuse in the form of protons in an electron gas (i.e., the metal lattice).⁴⁶ This condition effectively makes hydrogen very small and gives it a high lattice diffusivity. This leaves carbon as the largest atomic impurity, followed by nitrogen, and oxygen.

Grain Boundary Diffusivity

The effects of impurities are not always expected to be detrimental to electromigration performance. At impurity concentrations below which there is an impact on film morphology, the presence of impurities at grain boundaries is expected to reduce the solvent diffusivity. The relative effects of different impurities on solvent diffusivity depends on their ability to migrate to the grain boundary and the strength of the interaction with the solvent metal once they arrive.

In substitutional alloys, the atomic size differences between the solutes and the solvent controls the solute solid solubility limits in the host matrix. In binary systems, there exists a correlation between solid solubility and segregation potency.³⁷ A linear relationship exists between the inverse of the solid solubility $(X_I^B)^{\max}$ and the enrichment ratio (r) defined as the ratio of grain boundary to bulk concentration $r = X_I^\Phi / X_I^B$. The segregation potential of interstitial impurities is expected to follow this same relationship for the following reason. Impurities such as O, C, H, and N are larger than the interstitial sites they occupy and therefore strain the lattice. If the size factor is the only consideration determining solid solubility, those interstitial impurities that strain the lattice the most will have the lowest solid solubility and hence the greatest segregation potential.

The activation energy barrier for interstitial diffusion opposes the driving force to lower the lattice free energy as solute size increases. The activation energy for interstitial diffusion is much lower than for substitutional atom-vacancy exchange diffusion due to the smaller interstitial atomic sizes in question. It still remains, however, that larger interstitial atoms will distort the lattice more than smaller interstitials during migration.⁴⁵ The larger interstitials will have a greater activation energy barrier to overcome and will diffuse at a lower rate.

Strictly from size considerations, carbon and nitrogen, being the two largest interstitial impurities, will have a larger potential to segregate to the grain boundaries. As mentioned above, the segregation potential of an interstitial impurity depends on its solubility limit in the host. Solubility has also been shown to decrease with increasing electronegativity difference between the host and solute.²¹ Oxygen and nitrogen have the two largest electronegativities of the four impurity atoms and are expected to have a greater segregation than carbon or hydrogen.

Solute atoms that have weak interaction with the grain boundary will not reduce the diffusivity of the solvent until the solute concentration exceeds a level where the grain boundary becomes saturated. In these cases, the grain boundary diffusivity of the solvent is first expected to increase, then decrease with increasing solute concentration. Oxygen is a very surface active solute, followed by nitrogen, as seen by the electronegativities. Both would therefore have a strong interaction with the grain boundary. This should result in a continuously decreasing aluminum grain boundary diffusivity with increasing oxygen or nitrogen concentration for a given grain boundary structure. The interaction of carbon with the aluminum at the grain boundary is much less stable and will not have a great effect on aluminum diffusivity. Hydrogen is not expected to interact chemically with the grain boundary.

6. DISCUSSION

6.1 RGA Measurements

The actual measured partial pressures in the sputtering system reported in Table 6 are slightly higher than the best controlled conditions studied by Frear, et al.²³ (Table 3), and are at least two orders of magnitude lower than contaminant partial pressures studied by Queirolo, et al.⁴(Table 4). The differences in deposition conditions between these systems is discussed in detail later to arrive at an expected impact of the measured partial pressures from Table 6 on the film properties related to electromigration performance.

The deposition temperatures used by Frear and Queirolo were 300 °C and 150 °C, respectively. The production sputtering system being modeled in this study was operated near room deposition temperature.

6.2 Equilibrium Partial Pressures

From the equilibrium partial pressure calculations, it is seen that a drastic shift in the partial pressures of other species occurs when the initial partial pressure of H₂ and O₂ are each varied independently of the other and independently of N₂ and CO₂. The actual point of transition is relative to the initial molar amounts of O, N, C, and H input into the calculation, but Figures 9 and 10 do show the general relationship between the different species based on free energy minimization in a steady state system. This is estimated to be the case in a PVD chamber at constant pressure without the presence of a sputtering plasma. As seen from Figures 9 and 10, as the partial pressure of H₂ or O₂ increases independently, the equilibrium partial pressures of the other decreases in favor of maintaining constant water vapor and CO₂ partial pressures. It appears that the reactions forming these two species are the more dominant reactions in the chamber.

The added effect of dissociation of various species is expected in the presence of a plasma during the film deposition process. The variations in partial pressures of H_2 , O_2 , and H_2O in an electron gun aluminum evaporator were discussed by Verkerk and Brankaert.² They identify two mechanisms occurring in the chamber during deposition. These are the dissociation of water vapor into H_2 and O_2 related to the emission current and reaction of H_2O and O_2 with freshly deposited aluminum. Applying these two mechanisms to an rf plasma sputtering system, electron stimulated decomposition of water vapor adsorbed on the target and regions in the immediate environment of the plasma causes the partial pressures of H_2 and O_2 to increase initially. As soon as aluminum begins to deposit on the substrate, a reaction between aluminum and H_2O forms an oxide or hydroxide with the release of H_2 into the chamber. This is exhibited in Figure 8 while the plasma is on. Reaction of aluminum with O_2 causes an oxide to form and the partial pressure of O_2 will decrease. This effect would modify the equilibrium conditions calculated for other species in the chamber. Regardless of the resulting decreases or increases in H_2 or O_2 partial pressures, it appears that the water vapor partial pressure remains unchanged according to the equilibrium pressure calculations.

The sputtering partial pressure conditions from Table 6 are used as initial values for equilibrium partial pressure calculations at the deposition temperature. Oxygen and carbon monoxide equilibrium partial pressures are far below the actual measured partial pressure values for these species as shown in Table 9. With this partial pressure difference, these two species have a significant driving force to be adsorbed on the film.

TABLE 9

EQUILIBRIUM PARTIAL PRESSURE CALCULATIONS AT 323 ° K

Species	Sputtering Partial Pressure (Torr)	Equilibrium Partial Pressure at 323° K (Torr)
H ₂	2.0 E-07	1.7 E-07
CH ₄	2.3 E-09	3.0 E-08
H ₂ O	4.0 E-08	6.0 E-08
N ₂	2.9 E-08	2.9 E-08
CO ₂	5.0 E-09	2.7 E-09
O ₂	5.0 E-09	3.9 E-74
CO	5.0 E-09	2.2 E-12
Ar	4.0 E-03	4.0 E-03

6.3 Impact of Gaseous Impurities on Electromigration

Several studies in the literature explore the impact of sputtering ambients on the resulting film microstructure and electromigration lifetime or energy. The results of these studies are discussed in terms of the models proposed in this work. The discussion is presented in three parts. First, the relative impact of the impurities on the film growth is discussed. The mechanisms related to impurity migration to grain boundaries where electrotransport is predominant is discussed next, followed by the impurity effects on the mechanisms of grain boundary diffusion.

Impurity Effects on As-Deposited Grain Size/Orientation

It is clear from data reported by Frear, et al. (Table 3) and Queirolo, et al., (Table 4) that increasing amounts of impurity gases (H₂O, N₂, O₂, and CO₂) all reduce the Al-1%Si grain size and preferred grain orientation of the as-deposited film. A similar study

of the effects of the different impurity gases was also performed by Nowicki.³⁶ The relative impact of the specific gases in each of these studies is discussed below.

Nowicki found that Al-1.5%Si films deposited at $\sim 240^{\circ}\text{C}$ with argon sputtering gases containing 1% N_2 ($\sim 3.8 \times 10^{-5}$ torr) had smaller grain size than those deposited with 1% O_2 . The 1% H_2 ambient did not have a measurable effect on grain size. In terms of grain orientation, Queirolo, et al.,⁴ found that increasing partial pressures of O_2 , CO_2 , and N_2 significantly reduced the crystallographic ratio (R_{Cr}) of preferred $\{111\}$ planes to $\{200\}$ planes compared to Al films deposited at 150°C under base pressure conditions of 9.8×10^{-8} Torr. The relative impact of the different impurity gases on the crystallographic ratio of as-deposited films showed N_2 to cause more significant reduction in R_{Cr} than O_2 at similar partial pressures. The largest reduction in as-deposited R_{Cr} was due to CO_2 .

The results of both Nowicki and Queirolo, et al., lend credence to the model that adsorbed impurity size modulates the as-deposited grain size. The results of both studies are consistent. The largest impact on grain size and crystal orientation appears to come from carbon (CO_2), followed by nitrogen (N_2), then oxygen (O_2) when these impurity gases are present at similar partial pressures. Hydrogen does not seem to have an adverse effect on as-deposited grain size according to Nowicki. As the model proposes, carbon is the largest of the four impurity elements, followed by nitrogen, oxygen, and hydrogen. Atomic impurity electronegativity differences from aluminum do not appear to impact the as-deposited grain size or orientation.

Frear also studied the impact of varying impurity gas partial pressures on the microstructure of deposited Al-1%Si films. Due to the fact that all contaminant gases were introduced into the sputtering chamber at one time by venting the chamber, it is difficult to segregate the individual contaminant effects. Figure 15 is an attempt to

highlight the individual effects. The graph shows the resulting as-deposited grain size as a function of the individual partial pressures at a deposition temperature of 300° C. The apparent affect of the O₂ partial pressure on the resulting grain size is more significant than that of either the H₂O or N₂ partial pressures. Oxygen is the only species present at consistently lower concentrations correlating to an increase in as-deposited grain size. In terms of the as-deposited grain size model presented earlier, the Frear study supports the theory that the electronegativity difference between impurity element and metal plays a more significant role in the as-deposited grain size.

Fig. 15. Residual Gas Contaminant Effects on As-Deposited Grain Size.²³

These differing results may not be inconsistent with each other for the following reasons. There are two differences between the study by Frear and the other studies. These differences are the relative partial pressures of contaminant gases and the

deposition temperatures. In the Nowicki and Queirolo studies, the partial pressures of impurity gases varied between 10^{-5} to 10^{-6} torr, while the impurity partial pressures in the Frear study were typically between 10^{-7} to 10^{-10} torr. It is possible that at lower impurity concentrations, the relative impact of electronegativity differences becomes dominant due to the higher surface reactivity of the particular contaminant species with the aluminum surface. At the higher deposition temperatures of the Frear study compared with the Nowicki and Queirolo studies, a larger distribution of O_2 rather than N_2 molecules are expected to dissociate. The dissociation energy of O_2 is ~70% that of N_2 . More elemental oxygen is available to react with the surface at higher substrate temperatures.

In the production sputtering system in this study, oxygen, nitrogen, and water vapor partial pressures were on the order of the best conditions measured in the Frear study. Despite the extremely low equilibrium partial pressure, oxygen is not expected to be of much concern to as deposited grain size at room temperature deposition compared with the 300° C deposition in the Frear study.

Impurity Effects on Annealed Grain Size/Orientation

An interesting effect is seen after annealing of the samples in the Queirolo study. As seen in Table 4, films deposited in an oxygen containing ambient recrystallize more rapidly than those deposited in similar concentrations of nitrogen and carbon containing ambients, respectively. This effect is apparently due to the drag the impurity solute places on the grain boundary during recrystallization and correlates well with the values of $(r_s + r_p)^2$ of the impurity elements. This result supports the model defining impurity size as the most dominant factor controlling post anneal grain size/orientation.

Impurity/solvent electronegativity differences do not appear to modulate the annealed film morphology as much as atomic impurity size.

Grain Boundary Diffusivity

The proposed model relating impurity atom size and electronegativity differences from the host metal to the resulting grain boundary diffusivity is discussed in terms of substitutional impurities investigated by Poate, et al.,³⁰ and the data reported by Queirolo. The electromigration mean time to failure of the different aluminum alloy metallizations presented by Poate were studied under equivalent deposition and testing conditions. These data, presented earlier in Table 2, are presented again in Table 10 with their respective values of the atomic size and electronegativity differences for comparison to the resulting alloy system behavior.

Table 10.-- Electromigration mean time to failure of various aluminum alloys compared with the atomic properties of the solutes.

Alloy	MTTF* (hours)	$(r_s + r_p)^z$ of solute	$ \Delta(r_s + r_p)_{AB}^z $	$ \Delta X_{AB}^{MB} $	Compound Formation
Pure Al	30	1.68			
Al-2 wt%Ag	45	2.38	0.700	0.57	Ag ₂ Al
Al-2 wt%Au	55	2.66	0.985	0.45	Al ₂ Au
Al-1.8 wt%Si	150	1.42	0.255	0.34	None
Al-2 wt %Mg	1000	2.03	0.355	0.33	Al ₂ Mg
Al-4 wt%Cu	2500	2.04	0.365	0.56	Al ₂ Cu
Al-1 wt%Ni	3000	2.18	0.505	0.12	Al ₃ Ni
Al-2 wt%Cr	8300	2.44	0.765	0.36	CrAl ₇

* Measured at $j=2 \times 10^6$ A/cm² and T=175° C.

The data supports the model that there is an interaction between atomic size and electronegativity in modulating the aluminum diffusivity at the grain boundary. Increasing impurity size typically correlates with improved electromigration MTTF performance. The increasing atomic radii differences for Al-Si through Al-Cr show this relationship with mean time to failure. Exceptions to this trend are seen with Ag and Au solutes and are discussed below.

The impurity electronegativity differences from aluminum are considered in conjunction with the impurity size when explaining the low MTTF values. As mentioned earlier, solubility decreases with increasing electronegativity difference between solute and solvent.²¹ For the largest solutes, Au, Cr, and Ag, the electronegativity differences from aluminum are also involved in determining the solubility limit of the solute in the aluminum matrix. While Cr falls between Ag and Au in atomic size, it has a much lower electronegativity difference from Al than the other two solutes. It is proposed that Ag and Au precipitate from the matrix quickly in the bulk of the grains and do not as extensively as the grain boundary. Precipitate growth rates are increased with greater availability of solute.¹⁴

The data of Queirolo⁴ (Table 4) demonstrates, in general terms, the effects of specific impurity gases on the Mean Energy to Failure (MEF) of a test structure. Figure 16 shows the MEF data as a function of impurity gas partial pressure. The highest MEF of Al-Si conductors was achieved with samples deposited in an O₂ containing ambient, followed by N₂, and then CO₂ when similar partial pressures are considered. As Queirolo noted, there is a positive correlation between MEF and the degree of preferred

Fig. 16. Mean Energy to Failure as a function of gaseous ambient.⁴

(111) orientation. As discussed earlier, the randomness of crystal orientations appear to be modulated primarily by impurity size. From this data, it is difficult to separate whether the impact of each of these impurities on the grain boundary diffusivity is due to their chemical interaction with the aluminum at the grain boundary or simply their physical impact on recrystallization. The MEF results appear to be more significantly related to the post-annealed crystallographic ratio than to impurity reactivity at the grain boundary.

6.4 Distribution of Electromigration Failures

Several electromigration lifetime test data points are available for comment regarding the distribution of failure times. Samples of electromigration test structures on individual wafers show significant variation in the failure time. Variation in the mean

failure times by wafer in a standard life test on stacked metal films is $MTTF = 144 \pm 20$ hours. The variation seen on one wafer from a separate evaluation showed a $MTTF = 248$ hours, and a log normal $\sigma = 0.16$. This log normal standard deviation equates to a full range of approximately 200 - 300 hours to failure within a single wafer at the test conditions used. It is assumed that all regions of a wafer see the same contamination environment during sputtering. This range of failure times across a single wafer strongly indicates that the electromigration failure of a particular conductor is due to a combination of sputtering chamber gas ambient effects on the grain size, orientation, impurity incorporation and impurity interaction with the grain boundary structure that is formed.

7. CONCLUSION

Models describing the relative effects of residual impurity gases on the resulting sputtered aluminum thin film morphology and electromigration behavior have been proposed and tested.

The modeling of equilibrium partial pressure conditions within a metal thin film vacuum deposition chamber under deposition pressures has led to the understanding that variations in O_2 and H_2 have a significant impact on partial pressures of other gas species potentially in the system. Changes in the initial partial pressures of N_2 have effects only of equivalent magnitude on other nitrogen containing species in the system. At partial pressures actually measured in a deposition system, O_2 and H_2 partial pressure increases of several orders of magnitude still leave the resulting pressures of many other species below detection limits of the RGA. Based on equilibrium partial pressure calculations, oxygen is the one specie with the greatest potential for affecting film morphology in the production sputtering system tested.

It is shown using data from the literature that the impurity atomic size modulates the as-deposited grain size and crystal orientation more significantly than electronegativity differences between impurity and aluminum at partial pressures $> 10^{-5}$ Torr and at lower deposition temperatures. Other results from the literature show that at partial pressures lower than 10^{-5} Torr, the electronegativity difference between the aluminum and the impurity solute appears to become the dominant factor controlling grain size.

Impurity atomic size is again shown to modulate the degree of recrystallization during post film deposition annealing processes. Larger impurities in the aluminum lattice hinder recrystallization and contribute to a greater degree of disorder in the lattice. Electronegativity difference between impurity element and aluminum does play a role in

affecting solubility limits and hence segregation potential of impurity atoms to the grain boundary.

The relative impact of gaseous impurity atoms on the grain boundary diffusivity of aluminum has been discussed in terms of the reactivity of the different impurity elements with aluminum. Impurities in excess of solubility limits will segregate more strongly to grain boundaries of higher energy (higher tilt angle). Oxygen and nitrogen concentrations that do not affect the growing film morphology are expected to decrease the grain boundary diffusivity of aluminum. Literature data does not clearly support this model as the effects of impurities on electromigration failure energies could not be distinguished from effects on the degree of recrystallization.

References

1. R.W. Springer and D.S. Catlett, "Rate and pressure dependence of contaminants in vacuum-deposited aluminum films," Journal of Vacuum Science and Technology **15**, no.2 (March/April 1978): 210-214.
2. M.J. Verkerk and W.A.M.C. Brankaert, "Effects of water on the growth of aluminum films deposited by vacuum evaporation," Thin Solid Films **139** (1986): 77-88.
3. R.A. Gasser Jr. and S.G. Johnson, "Auger electron spectroscopy evaluation of voids in aluminum-1% silicon integrated circuit metallization," Journal of Vacuum Science & Technology B **4**, no.3 (1986): 758-761.
4. G. Queirolo, M. Dellagiovanna, and G. De Santi, "Effect of the sputtering ambient contamination on the microstructure of Al-Si films," Journal of Vacuum Science and Technology A **7**, no. 3 (1989): 651-655.
5. G.F. Weston, Ultrahigh Vacuum Practice, Butterworth & Co. Ltd., (1985): 199.
6. UTI Instruments, QualiTorr IIITM brochure.
7. D.E Meyer, "Residual gas analysis studies during sputtering of reactive metals," Journal of Vacuum Science and Technology **11**, no.1: 168-173.
8. Hai Pham Longworth, Microstructural modification of thin films and its relation to the electromigration-limited reliability of vlsi interconnects, (MIT Doctoral Thesis, Semiconductor Research Corp. Technical Report T92116, 1992).
9. J.J. Cummings and D.T. Enloe, "A RGA study of the cross-contamination of dopant species and low level impurities and the use of RGA as a process monitor in a Varian 180XP", Nuclear Instruments & Methods in Physics Research B **55**, no. 1-4 (1991): 55-60.
10. S.P. Murarka, VLSI Technology, 2nd Edition, ed.S.M. Sze, (New York: McGraw-Hill Book Co., 1988): 411.
11. UTI-100C Operation Manual, Reference Spectra.

12. Jaeshin Cho, Effect of Microstructure of Aluminum Alloys on the Electromigration-Limited Reliability of VLSI Interconnects, (MIT Doctoral Thesis, Semiconductor Research Corp. Technical Report T90084, 1990).
13. Milton Ohring, The Materials Science of Thin Films (San Diego: Academic Press Inc, 1992).
14. Robert E. Reed-Hill, Physical Metallurgy Principles, 2nd Edition (New York: D. Van Nostrand Company, 1973).
15. F.M. d'Heurle, N.G. Ainslie, A. Gangulee, and M.C. Shine, "Activation energy for electromigration failure in aluminum films containing copper," Journal of Vacuum Science and Technology **9** (1972): 289.
16. J.R. Black, "Mass transport of Al by momentum exchange with conducting electrons," 6th IRPS/IEEE (1967): 148.
17. F.M. d'Heurle, L. Berenbaum and R. Rosenberg, "On the structure of Al films," Transactions TMS AIME **242** (1968): 502.
18. R. J. Borg and G.J. Dienes, An Introduction to Solid State Diffusion (San Diego: Academic Press Inc., 1988), 88.
19. G.E. Murch and A.S. Nowick, eds., Diffusion in Crystalline Solids (Orlando: Academic Press Inc., 1984).
20. I. Kaur and W. Gust, Fundamentals of Grain and Interphase Boundary (Stuttgart: Ziegler Press, 1989).
21. W.C. Johnson and J.M. Blakely, eds., Interfacial Segregation (Metals Park: American Society for Metals Publications, 1979).
22. M.R. Wehr, J.A. Richards Jr. and T.W. Adair III, Physics of the Atom (Addison-Wesley Publishing Company, 1978).
23. D.R. Frear, A.N. Campbell, B.L. Draper and R.E. Mikawa, "Structure and Properties of Al-1% Si Thin Films on Si as a Function of Gas Impurities During DC Magnetron-Sputtered Deposition," Journal of Electronic Materials **18**, no. 4 (1989): 514.
24. J.D. Reimer, "The effects of contaminants on aluminum film properties," Journal of Vacuum Science and Technology A **2**, no.2 (1984): 242-243.

25. D. Gupta and P.S. Ho, eds., Diffusion Phenomena in Thin Films and Microelectronic Materials (Park Ridge: Noyes Publications, 1988).
26. M.J. Attardo and R. Rosenberg, "Electromigration Damage in Aluminum Film Conductors," Journal of Applied Physics **41**, no. 6 (1970): 2381-2386.
27. H. Flynn, A. E. Morris and D. Carter, "An Iterative Gas-Phase Removal Version of SOLGASMIX", Proceedings of the 25th CIM Conference of Metallurgists, TMS-CIM, Toronto, Ontario (1986).
28. G. Eriksson, Chem. Scr. **8**, (1975): 100-103.
29. 41st School on Thin Film Technology - Advances in Magnetron Sputtering and Etching (Orangeburg: Materials Research Corporation, 1987).
30. J.M. Poate, K.N. Tu, and J.W. Mayer, eds., Thin Films - Interdiffusion and Reactions (Princeton: The Electrochemical Society Inc, 1978).
31. P. Villars, "A Three-Dimensional Structural Stability Diagram for 998 Binary AB Intermetallic Compounds," Journal of the Less Common Metals **92**(1983): 215-238.
32. P. Villars, "A Three-Dimensional Structural Stability Diagram for 1011 Binary AB₂ Intermetallic Compounds: II," Journal of the Less Common Metals **99** (1984): 33-43.
33. P. Villars, "Three-Dimensional Structural Stability Diagram for 648 Binary AB₃ and 389 A₃B₅ Intermetallic Compounds: III," Journal of the Less Common Metals **102** (1984): 199-211.
34. P. Villars, "A Semiempirical Approach to the Prediction of Compound Formation for 3486 Binary Alloy Systems," Journal of the Less Common Metals **109** (1985): 93-115.
35. Vossen & Kern, Thin Film Processes II, Academic Press, Boston, MA (1991).
36. R. S. Nowicki, "Influence of residual gases on the properties of dc magnetron sputtered aluminum-silicon," Journal of Vacuum Science and Technology **17**, no.1 (1980): 384-387.

37. Guttman and McLean, eds., Grain Boundary Segregation in Multicomponent Systems,
38. Andrew Zangwill, Physics at Surfaces, Cambridge University Press, New York (1988): 185.
39. K.L. Chopra, Thin Film Phenomena, McGraw-Hill Inc., New York, (1969).
40. T. Kwok, P.S. Ho, and H.-C. W. Huang, "Electromigration studies of Al-intermetallic structures," J. Vac. Sci. Technol. A2(2), Apr.-June 1984, p241.
41. A.J Learn, "Evolution and Current Status of Aluminum Metallization." Journal of Electrochemical Society, **123** (1976): 894.
42. H.A Shafft, T.C. Staton, J. Mandel, and J.D. Shott, "Reproducibility of Electromigration Measurements," IEEE Transactions on Electron Devices, V. ED-34, no. 3, (March, 1987): 673 - 680,.
43. B.N Agarwala, M.J. Attardo and A.P. Ingraham, "Dependence of Electromigration Induced Failure Time on Length and Width of Aluminum Thin-Film Conductors," Journal of Applied. Physics, **41** No 10, (1970): 3954-3960.
44. G.A. Scoggan, B.N. Agarwala, P.P. Peressini, and A. Brouillard, "Width Dependence of Electromigration Life in Al-Cu, Al-Cu-Si and Ag Conductors," in Proceedings of the 13th Reliability Physics Symposium, IEEE, New York (1975): 151.
45. D.A. Porter and K.E. Easterling, Phase Transformations in Metals and Alloys, Van Nostrand Reinhold (UK) Co. Ltd. Berkshire, England, (1981).
46. G. Alefeld and J. Volkl, eds., Hydrogen in Metals I, Springer-Verlag, Berlin, Germany, (1978): 199.
47. Sputtering Target Supplier Analytical Report, (1991).
48. J. Mulready, "Purity of Ultrapure Ar and N₂ bulk gases," Intel Internal Correspondence, (1991).