1993

Reticulation-etch resistance of positive photoresist

Chang-Lin Hsieh
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Hsieh, Chang-Lin, "Reticulation-etch resistance of positive photoresist" (1993). *Master's Theses*. 683.
DOI: <https://doi.org/10.31979/etd.7pwr-57sj>
https://scholarworks.sjsu.edu/etd_theses/683

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 1356466

Reticulation-etch resistance of positive photoresist

Hsieh, Chang-Lin, M.S.

San Jose State University, 1993

U·M·I

300 N. Zeeb Rd.
Ann Arbor, MI 48106

RETICULATION - ETCH RESISTANCE OF POSITIVE PHOTORESIST

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

Chang-Lin Hsieh

December, 1993

© 1993

Chang-Lin Hsieh

ALL RIGHTS RESERVED

APPROVED FOR THE DEPARTMENT OF MATERIALS ENGINEERING

10/25/93
Thesis Advisor: Dr. Peter S. Gwozdz

10-25-93
Committee Chairman: Dr. P. Pizzo

25 OCT 93
Committee Member: Dr. Melanie A. McNeil

APPROVED FOR THE UNIVERSITY

ABSTRACT

RETICULATION - ETCH RESISTANCE OF POSITIVE PHOTORESIST

by Chang-Lin Hsieh

This thesis addresses the effects of hard-bake processes and environmental moisture on photoresist reticulation. Reticulation refers to a wrinkled appearance on a photoresist surface after the plasma etching process. The hard-baking conditions of S1400-27 positive photoresist and selected etching parameters of the Applied Materials AME 8110 reactive ion etcher are investigated in this study.

The best hard-bake process to prevent reticulation was found to be a hard-bake at 150°C for 45 minutes. But resolution is compromised at 150°C by photoresist plastic flow. After a 130°C for 30 minutes hard-bake, no significant deterioration in etch resistance was observed even though the photoresist had been stored in a high moisture environment for one week.

The highest etch rate of silicon dioxide that was achieved without a reticulation problem was 632 angstrom/minute. The average selectivity was approximately 4.2.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
TABLE OF CONTENTS	iv
LIST OF FIGURES	v
LIST OF TABLES	vii
1.0 INTRODUCTION	01
2.0 REVIEW	
2.1 Photolithography	03
2.1.1 Photolithography Process	04
2.1.2 Photoresists	07
2.1.3 Baking Effects on Photoresist	13
2.2 Reactive Ion Etching (RIE)	14
2.2.1 Plasma Potential Distribution	16
2.2.2 Etching Mechanisms	19
2.3 Reticulation	21
2.4 Compressive Stress Due to Ion Incorporation	25
3.0 RESEARCH HYPOTHESIS and OBJECTIVES	26
4.0 EXPERIMENT	28
4.1 Experimental Design	28
4.2 Materials and Equipment	34
4.3 Experimental Procedure	37
5.0 RESULTS	40
5.1 Hard-bake Effect on Reticulation	40
5.2 Environmental Moisture Effect on Reticulation	51
5.3 Characteristics of AME8110 Etcher	55
5.4 Mechanism Verification	59
6.0 DISCUSSION	60
7.0 CONCLUSIONS	65
8.0 FUTURE WORK	66
9.0 REFERENCES	67

LIST OF FIGURES

		Page
Figure 1	SEM micrograph of reticulated photoresist	2
Figure 2	The relationships between photolithography and major IC process steps	6
Figure 3	Comparison of positive and negative photoresist in the optical lithographic transfer process	8
Figure 4	Photochemical decomposition of AZ 1400 positive-resist naphthoquinone diazide sensitizer	10
Figure 5	Schematics of (a) isotropic etching (b) directional etching	15
Figure 6	The configuration of time-averaged potential versus distance in plasma	17
Figure 7	The cross-link reaction in novolac resin species during plasma etch	23
Figure 8	Schematic of high humidity chamber	32
Figure 9	Schematic of AME8110 etcher	35
Figure 10	Schematics of a) non-reticulated b) reticulated photoresist	41
Figure 11	The relationship between etching conditions and reticulation at 110°C for 15 minute hard-bake	42
Figure 12	Baking time effect on reticulation at 110°C	47
Figure 13	Baking time effect on reticulation at 130°C	48
Figure 14	Baking time effect on reticulation at 150°C	49

		Page
Figure 15	Baking temperature effect on reticulation for 15 minute baking	50
Figure 16	Baking temperature effect on reticulation for 45 minute baking	52
Figure 17	Comparison of baking conditions on reticulation problem	53
Figure 18	The relationship between silicon dioxide etch rate and DC bias	57
Figure 19	Calculation of activation energy of reticulation $\ln(1/\text{baking time})$ versus $(1/\text{baking temperature})$	63

LIST OF TABLES

	Page
Table 1. Comparison of negative and positive photoresists	12
Table 2. The experimental design for hard-bake conditions, temperature and time	29
Table 3. The test matrix of etching parameters, pressure and DC bias	30
Table 4. The relationship between hard-bake conditions and maximum DC bias for non-reticulation	44
Table 5. The relationship between hard-bake conditions and minimum DC bias leading to reticulation	46
Table 6. Moisture effect on reticulation	54
Table 7. The etch rate of silicon dioxide at different DC biases and pressures	56
Table 8. Etch selectivity at different hard-bake conditions	58
Table 9. Comparison of AME8110 etching character reported by different authors	64

1.0 INTRODUCTION

As dimensions of integrated circuit devices achieve submicron scale, patterning by photolithography becomes increasingly difficult. Reactive ion etching (RIE) is a technology commonly used to satisfy the requirements of submicron photolithography [1-3]. Photolithography and RIE are reviewed in section 2.

One photoresist problem involved in reactive ion etching, shown in Figure 1 [4], is called reticulation. This phenomenon refers to a wrinkled appearance on a photoresist surface after the plasma etching process. The photoresist has an orange peel texture when examined under a microscope. To a naked eye inspection, the photoresist looks charred, or burned.

The factors causing reticulation have been investigated by several researchers [4-11]. These factors are pre-etch baking conditions, etching conditions, contact condition between wafer and wafer holder, and the nature of the photoresist. These papers will be described in more detail in the review section.

Pre-etch bake also is called hard-bake which is a process completed before etching to reduce the solvents, water and trapped gases in the photoresist. Hard-bake is a way to prevent reticulation. The primary objective of this thesis is to characterize how baking temperature and time affect reticulation. The secondary objectives are to investigate the environmental moisture effect on reticulation, to investigate the mechanism of reticulation and to analyze the characteristics of the AME 8110 etcher.

Figure 1. SEM micrograph of reticulated photoresist.

2.0 REVIEW

More and more integrated circuit (IC) device manufacturers are using positive photoresist and anisotropic etching. This review will cover photolithography, reactive ion etching, and reticulation. The following sections will elaborate on these basic concepts and principles.

2.1 Photolithography

Lithography is a process of transferring a circuit pattern from a mask to the underlying substrate. The lithographic process consists of two important steps^[12]:

- (1) transferring the desired circuit patterns to a resist layer by exposure and development;
- (2) transferring the patterns on the resist to an underlying substrate by the etching and stripping processes.

Examples of exposure tools are ultraviolet light (UV), electrons, x-ray, and ion beam. Photolithography uses UV light, while X-ray lithography uses x-ray as the exposure tool. The choice of exposure tool depends on the applications and requirements. The general photolithography process and photoresists are described in the following section.

2.1.1 Photolithography Process

Photolithography is the most used lithography process in integrated circuit (IC) manufacturing. The wavelength range of UV light is about 0.2 to 0.4 μm ^[13].

The general photolithography process can be accomplished by the following procedures [12,14]:

- (1) Wafer oxidization: In wafer oxidization, bare wafers are inserted into a furnace to grow a layer of silicon dioxide whose range in thickness is about 0.1-1 μm .
- (2) Resist coating: The oxidized wafers are coated with a layer of resist using a spinner. The speed of the spinner controls the thickness of the resist. Higher spin speed results in a thinner photoresist layer.
- (3) Soft bake: The resist-coated wafers are placed into an oven for 30 minutes at 90°C. The purpose of the soft bake is to lower the content of solvent and water in the photoresist.
- (4) Exposure: The resist-coated soft-baked wafers are inserted into an aligner for exposure. The light source is ultraviolet (UV) light.
- (5) Development: The exposed wafers are dipped into a developer solution until a clear image appears on the wafers.
- (6) Rinse and dry: Ultra pure water is used to clean the wafers, and compressed air is used to dry them.
- (7) Hard-bake: Wafers are baked again at 130°C for 30 minutes to increase the etch resistance of the remaining photoresist during plasma etching.
- (8) Etching: The exposed oxide is etched by reactive ion etching or chemical etching. The circuit image is thus transferred to the substrate.

(9) Stripping: The remaining photoresist can be removed by oxygen plasma etching or a chemical method.

After stripping the photoresist, the desired circuit designs have been transferred onto the wafers. The following processes, such as film deposition, ion implantation, and oxidation, can also be accomplished with the aid of photolithography technology. Figure 2 ^[15] shows the interaction between basic processes and photolithography.

Figure 2. The relationship between photolithography and major IC process steps.

2.1.2 Photoresists

In the photolithography process, photoresist transfers the desired circuit patterns to the substrates and acts as a mask to protect the underlying substrate during etching and ion implantation. The imaged photoresist must withstand the heat which is generated from harsh plasma etch conditions or from ion implantation, without any edge rounding and/or line distortion. Therefore, the pattern transfer requirements of photoresists should be good resolution, high selectivity, and excellent etch resistance [18,19].

In photolithography, the circuit transfer happens because of the different solubility in the developer solution between the exposed resists and unexposed resists. There are two kinds of photoresists used in the photolithography process, as shown in Figure 3 [13].

One kind is called negative photoresist. Negative photoresist consists of a variety of polymers combined with a photoactive compound (PAC). Prior to exposure, the negative photoresist is soluble in the developer. After exposure, the photoactive compound absorbs light energy to initiate a chemical reaction. This reaction causes the crosslinking of the polymers in the negative photoresist. Therefore, the chain of polymers becomes longer and the weight of the polymer molecules increases rapidly. This reaction results in the decrease of solubility in the developer for the exposed negative photoresist. In the image transfer process, the resists on the exposed area remain on the wafers whereas the unexposed resists are dissolved into the developer. As a result, the transferred image on the wafer is reversed with respect to the image on the mask.

Figure 3. Comparison of positive and negative photoresist in the optical lithographic transfer process.

The second type of resist is called positive photoresist. The main components in positive photoresists are: a photoactive compound (PAC) a base resin, organic solvents, and a few percent water [18]. PAC, formed by Diazonaphthoquinone (or DQN), is a phenolic polymer combined with a naphthoquinone diazine. The exposed positive photoresist is soluble in the alkali developer. Prior to exposure, the positive photoresist is insoluble in the alkali developer.

Figure 4 shows the chemical reactions of photoactive compounds from the soft-bake process to development [19-21]. When the PAC absorbs light energy, the PAC decomposes into N_2 and ketene which can react immediately with available water in the photoresist to form an indenecarboxylic acid. This reaction makes the exposed resists more soluble in the alkaline developer solution. As a result, the resists on the exposed area dissolve into the developer and the resists on the unexposed area remain on the wafer. The transferred image on wafer is exactly the same as the image on the mask.

Negative and positive photoresists each have advantages and disadvantages. The main advantage of negative photoresists is that they are more sensitive to radiation than positive ones. Therefore, they need less exposure time with a given exposure power. Consequently, the throughput is higher than that of positive photoresists. The main drawback of negative resists is their poor dimensional control after development. The swelling which results from the chemical crosslinking deteriorates the resolution of the circuit pattern transfer. If the space between the lines in the circuit design pattern is large, this swelling is not a problem. However, as the dimension and space of circuit

Two Isomers of Diazopaphthoquinone

R = functional group

Figure 4. Photochemical decomposition of AZ1400 positive-resist naphthoquinone diazide sensitizer.

design become smaller, this swelling could destroy the integrity of pattern designs.

On the other hand, a better resolution can be accomplished by using a positive photoresist because swelling does not occur at all. But positive photoresists need more energy and a longer exposure time which result in a lower throughput. Positive photoresists are dominant in VLSI technology because of the resolution requirement. Table 1 [16] shows a comparison between negative and positive photoresists.

Table 1. Comparison of negative and positive photoresists [16]

	negative	positive
radiation sensitivity	more sensitive	less sensitive
throughput	high	low
resolution	good	better
pattern transfer	exposed resist remains	exposed resist dissolves

2.1.3 Baking Effect on Photoresist

There are usually two bake processes in photolithography: soft-bake and hard-bake. Soft-bake, about 90°C, is performed after photoresist spin-coating. Hard-bake, about 130°C, is performed after development. The purpose of soft-bake is to lower the content of solvent and water in the photoresist film and to improve resolution. The purpose of hard-bake is to improve etch resistance and adhesion.

The photoresist investigated in this paper contains a solvent system which consists of cellosolve acetate (2-ethoxy-ethyl acetate, boiling point 156°C), n-butyl acetate (boiling point 126°C), and xylenes (boiling point 138 to 144°C) [37]. The general soft-bake condition, 90°C for 30 minutes, cannot remove sufficient solvent to achieve optimum etch resistance. However, as the soft-bake temperature goes up, the photoactive compound (PAC) undergoes severe degradation resulting in loss of photoresist photosensitivity, increasing scumming and excessive development time. In order to overcome the PAC degradation problem and keep good etch resistance, the higher temperature hard-bake is carried out before etching. The hard-bake condition for this photoresist is 130°C for 30 minutes. This temperature still is not high enough to remove all of the solvent. However, a higher hard-bake temperature will cause plastic flow of photoresist. Edges of photoresist defined by development become rounded and blurred above 130°C. Above 150°C, openings in photoresist may actually close up [38]. The hard-bake temperature of 130°C is around the range of solvent boiling point. These facts are important in the understanding of reticulation.

2.2 Reactive Ion Etching (RIE)

The fabrication of integrated circuit devices requires several etching steps. The characteristic of the etching process can be classified into two categories. One is isotropic etching where the etch rate is the same in all directions. The other is anisotropic or directional etching where the etch rate in the Z direction is much greater than the lateral (X or Y) directions, as shown in Figure 5 [22].

The line width and pitch of advanced VLSI circuits have recently decreased to submicron dimensions. Anisotropic etching is required for fine pattern transfer to silicon substrates because etched features widths are about the same as the feature depths. Anisotropic etching is almost always implemented in VLSI manufacture by means of RIE, which originally meant "Reactive Ion Etching". The acronym RIE is used to refer to systems in which wafers are placed on the powered electrode, a cathode. RIE is really "Ion Enhanced Etching". RIE combines controlled energetic ion bombardment with chemical reactions to achieve high selectivity and anisotropic etching at low pressure, 5-100 mTorr [23]. A typical radio frequency of 13.56 MHz is used in RIE to generate reactive species in a plasma from feed gases, such as CF_4 , CHF_3 , and CCl_4 .

In principle, any material which can react with plasma species to form volatile products can be etched by this method. In addition to satisfying the etching characteristic, chemical hazard and waste treatment problems are reduced. But the disadvantages of RIE still exist in high capital cost, inability to etch some materials, and radiation damage to devices [24-26].

Figure 5. Schematic of (a) isotropic etching (b) directional etching

2.2.1 Plasma Potential Distribution

Plasma, also called glow discharge, is a collection of electrons, ions, and neutral particles in which the density of the negatively charged particles is equal to that of the positively charged particles. In low pressure plasma, the degree of gas ionization is typically about 0.1-1%. The energy range of the electron is about 1-20 eV and the ion density is normally between 10^9 - 10^{12} cm⁻³ [27,28]. There are two distinct regions in a plasma reactor. One is light space where a lot of photoemission occurs by the excited electronic states. The other is dark space which is called the sheath. This cathode sheath is the acceleration area for the positive ions. The approximate configuration of time-averaged potential versus distance is shown in Figure 6 [13]. The plasma potential is positive compared to the potential of the cathode or anode. The potential relationship between the cathode and anode had been predicted from the classic theory of plasma characteristics developed in the 1970's:

$$V_c / V_a = (A_a / A_c)^4 \quad \text{Eq (1)}$$

where V_c and V_a are the potentials of the cathode and anode, respectively;

A_a and A_c are the areas of anode and cathode, respectively;

The larger the area ratio of the anode to cathode, the greater the potential ratio of the cathode to anode [29]. However, some investigators have reported that the potential ratio changes as the first power of the area ratio, instead of the fourth power [13].

In hexagonal cathode RIE reactors like the AME 8110 used in this project, the hexode where the wafers are placed is the cathode and the bell jar is the anode which is a larger area and grounded. The frequency of the RF generator

Figure 6. The configuration of time-averaged potential versus distance in plasma.

is 13.56 MHz. - As RF is applied in positive cycles, there are electrons bombarding the cathode and accumulating on the surface. The higher electron density resulting from the small area of the cathode will cause a higher negative potential on the cathode. On the other hand, the electrons are accelerated toward the anode in negative cycles. The anode also builds up a low negative potential due to its larger surface area. Therefore, a higher negative potential builds up on the cathode, where the wafers are located, and positive ions are attracted to it, bombarding and thus etching the wafers.

DC bias, the potential difference between plasma and cathode, chamber pressure and RF power are the most important etching parameters in RIE. For the AME 8110 system, these three parameters are dependent on each other and thus selection of two determines the third.

2.2.2 Etching Mechanisms

RIE is not really "Reactive Ion Etching", but "Ion Enhanced Etching"[30-34]. The detailed mechanism of ion enhancement depends upon the film being etched and upon the chemistry of the plasma.

This project uses $\text{CHF}_3 + \text{O}_2$ to etch SiO_2 in "RIE" mode. Although the atomic details are not scientifically proven, there is a consensus model in the literature. Manos and Flamm[31] explain the model in detail with several citations of literature by other authors. The model can be briefly outlined as follows:

- (1) Subfluorides of carbon, primarily CF_2 , are produced in the plasma.
- (2) Subfluoride polymers condense on all surfaces. This polymer is continuously partially oxidized by O, atomic oxygen from the plasma. The polymer grows thick on photoresist, enhancing selectivity, because the O from the SiO_2 also oxidizes the polymer.
- (3) The carbon subfluorides are not quite capable of reacting with SiO_2 .
- (4) Ion bombardment breaks chemical bonds in the SiO_2 , decreasing the energy requirements for attack by carbon subfluorides, probably primarily CF_2 . This does not occur on the sidewalls, because the walls are shadowed from ions by photoresist. Etching is highly anisotropic.
- (5) The carbon subfluorides react with the damaged SiO_2 , producing volatile silicon subfluorides, SiF_x .
- (6) The degree of anisotropic is determined by the ion energy.

It is known [31] that higher DC bias leads to better anisotropy. DC bias is increased by increasing power and by decreasing pressure. The AME 8110 is designed for maximum anisotropy. DC bias is limited by catastrophic failures,

such as sparking, heating, reticulation, etc.. For these reasons, this project focuses on DC bias and pressure.

In the etching process, the photoresist is used as a mask to protect the underlying materials. The underlying materials and photoresist are etched simultaneously by plasma etching or ion bombardment. "Selectivity" is derived from this simultaneous etching process. Selectivity is defined as the ratio of the etch rate of the target material to the etch rate of the photoresist. The etch rate of photoresist depends on not only the photolithography process, but also on the composition and structure of the photoresist itself [35]. Selectivity is commonly measured and reported in the literature as the primary index of etch resistance by photoresist. The focus of this thesis is another aspect of etch resistance: reticulation.

2.3 Reticulation

Reticulation is a catastrophic etch resistance failure of photoresist. Etch resistance of photoresist is represented herein by the maximum DC bias which does not lead to reticulation at a given condition.

Reticulation knowledge is passed by word of mouth in industry. A title and abstract key word search yielded nothing in the literature on reticulation. To find references, it was necessary to scan a larger number of articles. Reticulation had been mentioned in eight articles [4-11] and these articles were without quantitative data.

There is no documented proof that reticulation is always a fatal problem. But for good manufacturing practice, all wafers should be the same and no burned wafers should be used. Some disadvantages of reticulation have been observed. For example, the function of planarization is degraded by reticulation [3] and reticulated photoresist becomes more difficult to strip off due to its uneven thickness [4].

Two solutions to the reticulation problem are presented in the literature: good heat transfer and good hard-bake.

Ole Krogh et al. [8] concentrated on heat transfer. They speculated that reticulation was due to the different thermal expansion coefficients between the hardened surface and the photoresist bulk. Ole Krogh et al. defined reticulation as the state when the surface of photoresist became dull and non-reflective during the etching process. Under this condition, fine cracks appeared in the texture of an orange peel on the photoresist surface. They speculated that the heat generated by plasma etching cannot be dissipated promptly and reticulation

thus occurs under a certain thermal stress. Therefore, a good cooling system and a good contact between wafer and wafer holder are the solutions proposed for reticulation [4,7,8]. This mechanism will be examined in the following Discussion section.

Sawoska et al. [6] concentrated on hard-bake. They speculated that reticulation was due to the excessive movement/ shrinking of photoresist [4,6,7,11]. Sawoska et al. indicated that the reticulation of novolac-based photoresist depends on the glass transition temperature (T_g), which is determined by the molecule weight and diluents, the residual solvent and water. Either the low molecule weight resin or the trapped diluents will lower the T_g . Under a high temperature or energy exposure, the excessive movement/ shrinking of photoresist can be observed in the low T_g photoresist which has low molecular weight resin or residual solvent. The imaged photoresist will appear as a wrinkled or reticulated surface. Sawoska also reported that oxygen and the chlorine/ fluorine containing etch gas components could boost the cross-link mechanism further hardening the surface. Figure 7 demonstrates these chemical reactions [6]. In order to enhance the reticulation resistance, T_g must be increased. There are at least two ways to increase T_g . One is to use higher molecular weight resins [6,9]. The other is to remove solvents and water by baking photoresist at a higher temperature or for a longer time [36-38]. The effects of baking condition on reticulation will be shown in the Result and Discussion sections in this thesis.

Both solutions are really using the same model. The authors do not explicitly state their model, but this is their presumed model: somehow the surface of the photoresist becomes hard and compressive. The bulk of the

(1) Formation of excited oxygen atoms

(2) Proton abstraction/formation of transient free novolak species

Figure 7. The cross-link reaction in novolak resin species during plasma etch.

photoresist remains soft and experiences a tensile stress from the surface. This situation is unstable. Natural local inhomogeneities lead to local contractions and expansions. The surface compression is relieved by expanding the planar surface into a wrinkled surface. Reticulation can be prevented by minimizing photoresist surface compression or by hardening the photoresist bulk or both.

Ole Krough et al.'s^[8] assumption that the surface has a significantly greater thermal expansion than the bulk is dubious and redundant. Higher temperature should soften the bulk and lead to plastic flow even without increased thermal stress. In order to verify this assumption, a thermal shock test will be carried out in this project.

It is claimed by the Applied Materials representatives that reticulation is enhanced by exposure to atmospheric moisture after hard-bake. The Applied Materials representatives said that wafer heating was added to the reactor design to remove such adsorbed moisture. This oral claim was not found in the literature.

2.4 Compressive Stress Due to Ion Incorporation

It is well known that PECVD (Plasma Enhanced Chemical Vapor Deposition) films often have compressive stresses. These stresses are built up by the non-stoichiometric structure and large quantities of hydrogen incorporated from the process gases [43]. These stresses depend on the plasma characteristics, process gas mixture and wafer temperature. The stress causing reticulation is speculated by ion implantation during plasma.

My advisor assured me that sometimes sputtering and implantation also create stresses on films and pointed out that in 1981 Haiping Dun [44] speculated that the compressive stress may be caused by the simple expansion due to the added materials - positive ions. This speculation has never been proven in any research. The compressive surface stress causing reticulation can be explained by the positive ions implanted into the surface of the photoresist film during plasma etching.

3.0 RESEARCH HYPOTHESIS and OBJECTIVE

3.1 Model

Reticulation is caused by expansion of a hard, compressed photoresist surface film over a softer photoresist bulk. It is beyond the scope of this thesis to prove or disprove the model. We seek to confirm (not prove) or disprove the following:

3.2 Hypotheses

- (1) Higher temperature or longer time at hard-bake enhances reticulation resistance of photoresist by increasing the T_g and therefore preventing flow of the bulk.
- (2) Higher DC bias decreases reticulation resistance by increasing compressive surface stress due to implanted ions.
- (3) Atmospheric moisture decreases reticulation resistance after hard-bake by penetrating the bulk and softening it.
- (4) Poor thermal wafer contact causes reticulation by heating the wafer during plasma etching. Perhaps the surface of photoresist has a higher coefficient of thermal expansion.

3.3 Objectives

The primary objective of this study is:
to characterize and quantify the relationship between baking conditions and two etching parameters, DC bias and pressure, leading to reticulation.

The secondary objectives of this thesis are:

- (1) to investigate the effect of environmental moisture after baking on reticulation;
- (2) to document the etching characteristics of AME8110 etcher with emphasis on selectivity;
- (3) to investigate the effect of poor thermal wafer contact on reticulation; and
- (4) to investigate the effect of thermal shock on RIE etched photoresist.

4.0 EXPERIMENTS

4.1 Experimental Design

For hard-bake experiments, time and temperature were the variables. The hard-bake temperatures studied were 110°C, 130°C, and 150°C. The baking times were 15, 30, and 45 minutes. A control which was not hard-baked was included in the samples. The total number of hard-bake conditions was 7. The recommended hard-bake process for the photoresist used in my experiment was 130°C for 30 minutes. Therefore, two temperatures were picked up, 110°C and 150°C, which are around the solvent boiling temperatures. Each hard-bake condition was denoted by Ax, where x changes from 1 to 7, shown in Table 2. For example, hard-bake condition A4 was baked at 130°C for 15 minutes. Each wafer was soft-baked at 90°C for 30 minutes in a convection oven prior to exposure.

The occurrence of reticulation as a function of pressure and DC bias was also investigated at a given hard-bake time and temperature. RIE power pressure and DC bias are interdependent. Maximum achievable DC bias varied with pressure due to machine power limitations. The basic matrix of etching parameters, pressure and DC bias, is shown in Table 3. The other etching parameters, gas flow rates, hexode temperature, and etching time, are fixed. The gas flow rate of CHF₃ was 75 sccm and the flow rate of oxygen was 8 sccm. The etching time was 10 minutes. The temperature on the hexode was 35°C. There were 10 combinations of pressure and DC bias. Bx denotes the etching conditions where x varied from 1 to 10, see Table 3.

Table 2. The experimental design for hard-bake conditions, temperature and time

T i m e	Temperature			
	0°C	110°C	130°C	150°C
	0 minutes (A1)			
	15 minutes	(A2)	(A4)	(A6)
	30 minutes		(A5)	
	45 minutes	(A3)		(A7)

Table 3. The test matrix of etching parameters, pressure and DC bias

D C b i a s	Pressure		
	15 mTorr	45 mTorr	75 mTorr
	525 V	(B4)	(B8)
	550 V	(B5)	
	575 V	(B1)	(B9)
	600 V	(B6)	(B10)
	625 V	(B2)	(B7)
	675 V	(B3)	

The primary objective, to understand the effect of hard-bake on reticulation, was supported by the experiments of Table 2 and Table 3. The etching parameters in Table 3 were applied to each hard-bake condition in Table 2. Within a given hard-bake condition, reticulation occurred at some etching conditions and did not appear at other etching conditions. The etch resistance of photoresist is defined herein by the value of maximum DC bias without reticulation.

Another purpose of the experimental design was to study the effect of environmental moisture on reticulation. One group of wafers was hard-baked at 130°C for 30 minutes and then placed in a high humidity chamber for 1, 2, 4, and 8 days before etching. These wafers were then etched at marginally sub-reticulation etching conditions as determined after Table 3 conditions were fully explored. This high humidity was reached by bubbling compressed air through water at room temperature then flowing the moist air into the humidity chamber, as shown in Figure 8. The water vapor pressure was 17.5 mm Hg at 20°C and 1 atm. The relative humidity in the chamber was between 60% and 75% at 25°C. Therefore the water vapor pressure was between 10.5 and 13.1 mm Hg.

Another purpose of the experimental design was to modify heat flow. Two wafers were etched at the same time. All baking conditions and treatment were the same except one wafer was entirely attached by the dark tape on the back side. We assumed that the dark tape could block the heat dissipation during plasma etching.

The final purpose of the experimental design was to examine thermal shock. Two etched wafers, with marginally non-reticulated photoresist as determined from prior analysis, were inserted into liquid nitrogen for 15 minutes

Figure 8. Schematic of high humidity chamber.

and two other etched wafers were inserted into a 250°C oven for 30 minutes. All wafers were examined under a microscope to detect reticulation, when they were taken out from the testing environment to room temperature.

4.2 Materials and Equipment

The following is a list of materials and equipment used in this study.

- (1) The number of bare Si wafers used was 92.
- (2) All wafers were placed in an open furnace for 4 days. The temperature of oxidization is set at 1100°C and the feed gas is ambient air. Under these conditions, the oxide thickness is about 10,000 angstroms.
- (3) Positive S1400-27 photoresist produced by Shipley Corp. It was employed 2-Ethoxyethyl acetate, n-Butyl acetate, xylene are the components.
- (4) An Omnichunk three-step spinner was used. The speed of spinner determined the thickness of coated-resist.
- (5) Soft-baking and hard-baking are accomplished in a convection oven in 1 atmosphere air.
- (6) A simple image pattern mask was used.
- (7) An Applied Materials CA800 was used for exposure.
- (8) Type AZ400K developer produced by Hoechst Celanese Corp. was used.
- (9) An Applied Materials Inc. AME8110 model plasma etcher, shown in Figure 9, was used. This machine is designed for SiO₂ etching. This machine contains RF generator, matching unit, vacuum system, and main chamber. The reactant gases are CHF₃ and O₂. The variables in this machine are RF power, DC bias, pressure, gas flow rates, cooling loop temperature, and etching time.
- (10) A Nanometric Inc. Meas 4 model Nanospec/AFT was used to measure oxide and photoresist thicknesses.
- (11) An Olympus Inc. microscope was used to examine the surface of photoresist before and after etching.

Figure 9. Schematic of AME8110 etcher.

(12) A Hitachi H520 SEM was used to examine the reticulated photoresist after etching.

(13) A high humidity chamber with a humidity meter was used. This chamber is connected to 30 psi compressed air. Compressed air goes through water and carries moisture into the chamber.

(14) An Alpha-step was used to measure the roughness of the reticulated surface

(15) Liquid nitrogen was used for the thermal stress test.

4.3 Experimental Procedure

4.3.1 Baking effects on reticulation

The experimental procedure for the relationship between hard-bake and etching parameters leading to reticulation is illustrated in the following.

(1) Oxidation: Bare wafers were inserted into the furnace at 1200°C for four days in order to grow about 1µm of oxide film. The thickness of oxide was measured by a Nanospec/AFT machine. Each wafer was measured at five different spots, the center and four edges, with the oxide thickness taken as the average value.

(2) Photoresist coating: Approximate 1.1µm thick of S1400-27 photoresist was spin-coated on the oxidized wafers.

(3) Soft-bake: All wafers were baked at 90°C for 30 minutes in a convection oven.

(4) Exposure: The exposure time was 90 seconds under the Applied Materials CA800 aligner.

(5) Development: The development time was 30 seconds in AZ400K developer.

(6) Hard-bake: The hard-bake time and temperature were varied per Table 2. This process was carried out in a convection oven similar to that used in the soft-bake process.

(7) Photoresist thickness measurement: The photoresist thickness was measured in the same manner described in step 1 after hard-bake.

(8) Etching: The fixed etching parameters were 35°C hexode temperature, 10 minutes etching, 75 sccm Freon 23, and 8 sccm oxygen. The etching variables were DC bias and pressures per Table 3. The processing pressures were 15,

45, and 75 mTorr. The DC bias was increased until reticulation occurred. The minimum DC bias was 525V.

(9) Oxide and photoresist thickness measurements: The oxide and photoresist thickness is measured by the same method in step (1). If reticulation occurs, the photoresist thickness cannot be measured by Nanospec/AFT machine and it is marked "x". Reticulation could be determined by microscope inspection.

(10) Calculation of etch rates of oxide and photoresist: The etch rate of oxide is the difference of oxide thickness in step (2) and (9) divided by 10 minutes. The etch rate of photoresist is the difference of photoresist thickness in step (7) and (9) divided by 10 minutes.

(11) Selectivity index: The ratio of oxide etch rate to the etch rate of photoresist is the selectivity index.

4.3.2 Environmental moisture effect on reticulation

The procedure to determine the influence of environmental moisture that was picked up between the hard-bake and etching steps on reticulation is stated below:

Step (1) to (5) is the same as the former procedure.

(6) Hard-bake: Wafers were hard-baked at 130°C for 30 minutes and then stored in the high humidity chamber for 1, 2, 4, or 8 days.

(7) Photoresist thickness measurement: The thickness of photoresist was measured by the Nanospec/AFT machine.

(8) Etching conditions: The fixed etching parameters were 45 mTorr, 35°C hexode temperature, 10 minutes etching, 75 sccm Freon 23, and 8 sccm oxygen, the DC bias was varied between 625 and 650V. One of two wafers,

after 1, 2, 4, or 8 days delay, was etched with -625V DC bias. The other wafer was etched with a -650V DC bias.

Steps (9) to (11) were the same as in the previous experiment.

4.3.3 Mechanism verification

4.3.3.1 Dark tape test

- (1) Repeated steps 1 to 5 in the paragraph 4.3.1 .
- (2) Hard-baked wafers at 130°C for 30 minutes.
- (3) Covered one wafer entirely by dark tape on the back side of wafer before it was placed on wafer holder. The other wafer was not covered.
- (4) Etched wafers at 625V DC bias, 45 mTorr pressure and 10 minutes.
- (5) Examined wafers under microscope.

4.3.3.2 Thermal stress test

- (1) Used four etched wafers without reticulation from A5 in Table 2.
- (2) Dipped two wafers into liquid nitrogen for 15 minutes, and inserted two wafers into oven at 250°C for 30 minutes.
- (3) Removed them from testing environment and inspected at room temperature.

5.0 EXPERIMENTAL RESULTS

5.1 Hard-baking effects on reticulation

The raw etching data are shown in Appendix A. The comparison of the reticulated and non-reticulated photoresists is shown in Figure 10. The non-reticulated one, Figure 10a, shows a wafer free of any reticulation on the photoresist. The reticulated one, Figure 10b, shows wrinkled photoresist. In Figure 10a and 10b, wafers were etched at the same etching parameters which are 45 mTorr pressure, 600V DC bias, 35°C hexode temperature, 10 minutes etching, 75 sccm Freon 23, and 8 sccm oxygen. But they were hard-baked at 130°C for 30 minutes and 15 minutes, respectively. The roughness of these two wafers were measured by alpha-step. The wafer of Figure 10a shows a very smooth photoresist surface. The deviation of photoresist thickness was less than 200 angstroms. As a contrast, the reticulated one shows a rough photoresist surface. The thickness difference between the thickest and thinnest photoresist is surely much more than 1000 angstroms, because the probe needle cannot penetrate the crevices on the surface.

Figure 11 shows the relationship between etching conditions and reticulation at 110°C for 15 minutes hard-bake. The hollow points represent those etching conditions which do not lead to reticulation, and the solid points represent those etching conditions which result in reticulation. The area between the two curves is an uncertain region between reticulation and non-reticulation. Reticulation did not occur at those etching conditions which are under the lower curve shown in Figure 11. Therefore, the large the area under

Figure 10. Profilometer traces
 a) Non-reticulated photoresist. It shows a smooth photoresist surface after plasma etching.
 b) Reticulated photoresist. It shows a rough photoresist surface after plasma etching. Wrinkling is surely much worse, because the probe needle cannot penetrate the crevices.

Figure 11. The relationship between etching conditions and reticulation at 110°C for 15 minutes hard-bake. In this and subsequent figures, filled data points represent reticulation, open data points represent no reticulation after etch.

the curve, the better the etch resistance will be. A broad range of etching conditions can be used without reticulation.

The size of the uncertain region is a measure of the precision of our reticulation resistance measurement. The repeatability or accuracy of our reticulation measurement was not investigated beyond the self consistency as indicated by the data. In fact, the size of the uncertain region should be larger because of month to month and machine to machine variations due to unspecified manufacturing control parameters. In addition, uncertain arises with wafers which have marginal reticulation only over a small surface area. For ease of communication, these objections are set aside for the discussions which follow.

Table 4 shows the relationship between hard-bake conditions and the critical DC biases which are related to reticulation at different pressures. Table 4 indicates the maximum DC biases used without reticulation at 15, 45, and 75 mTorr. In other words, as long as DC bias is smaller than the value in Table 4, there is no reticulation on the photoresist. For example, the maximum DC bias without reticulation is 625V at 45 mTorr after a hard-bake at 130°C for 30 minutes. As a result, photoresist baked at 130°C for 30 minutes can endure any DC bias, which is smaller than 625V, without reticulation at 45 mTorr for 10 minutes etching. In this experiment, the best etch resistance of the photoresist occurs when the wafer is baked at 150°C for 45 minutes. After a hard-bake at 150°C for 45 minutes, the maximum DC biases used without reticulation are 775V, 675V, and 625V at 15, 45, and 75 mTorr, respectively.

At 75 mTorr, there is no reticulation found even when the RF power reaches the limitation of this machine, 2000W. This result is much better than

Table 4 The relationship between hard-bake conditions and maximum DC bias for non-reticulation

	Without Hard-bake	110°C		130°C		150°C	
		15 minutes	45 minutes	15 minutes	30 minutes	15 minutes	45 minutes
DC bias (V) 15 mTorr	625	625	675	675	700	725	775
DC bias (V) 45 mTorr	550	550	575	575	625	625	675
DC bias (V) 75 mTorr	525	525	575	550	550	625	625

that of the general hard-bake process at 130°C for 30 minutes. The maximum DC biases for this general process are 700, 625 and 550V at 15, 45, and 75 mTorr, respectively. The maximum DC biases without reticulation at 110°C for 15 minute hard-bake are the same as those without any hard-bake. This result means that the etch resistance is not significantly enhanced by a hard-bake process at 110°C for 15 minutes. As long as the processing DC biases are smaller than the critical DC bias in Table 4, reticulation will not occur under the same etching conditions.

In Table 5, the minimum DC biases shown are the critical values for reticulation. If the processing DC bias is larger than these values, reticulation will occur. For example, the critical value of DC biases after a hard-bake at 130°C for 30 minutes are 725, 650, 575V at 15, 45, 75 mTorr, respectively. If DC bias larger than 650V is used to etch those wafers hard-baked at 130°C for 30 minutes, reticulation will appear on the photoresist after 10 minutes etching at 45 mTorr.

From Figure 12, the non-reticulation etching range (that is the area under the curve) for hard-bake at 110°C for 45 minutes is broader than that at 110°C for 15 minutes. In order to compare the etch resistance for different hard-bakes, a bounding curve is drawn between the solid and hollow points. The area under the curve represents the quality of etch resistance. Figure 12 indicates that the etch resistance of photoresist is enhanced by a longer baking time. The similar results for 130°C and 150°C are observed in Figures 13 and 14. As a result, the longer the baking time, the better the etch resistance of photoresist.

Figure 15 illustrates that the etch resistance increases with increasing temperature at the same hard-baking time of 15 minutes. The non-reticulation

Table 5 The relationship between hard-bake conditions and minimum DC bias leading to reticulation

	Without Hard-bake	110°C 15 minutes	110°C 45 minutes	130°C 15 minutes	130°C 30 minutes	150°C 15 minutes	150°C 45 minutes
DC bias (V) 15 mTorr	675	675	700	700	725	775	825
DC bias (V) 45 mTorr	575	575	600	600	650	675	700
DC bias (V) 75 mTorr	550	550	600	575	575	635	No

"No" represents that no reticulation appears in this experiment design.

Figure 12. Baking time effect on reticulation at 110°C . In this and subsequent figures, some open data points which are overlapped by the filled data points cannot be seen in these figures.

Figure 13. Baking time effect on reticulation at 130°C .

Figure 14. Baking time effect on reticulation at 150°C .

Figure 15. Baking temperature effect on reticulation for 15 minute baking.

etching range at a 150°C hard-bake is larger than those at a 110°C and 130°C hard-bake. The non-reticulation etching range decreases as baking temperature decreases from 150°C to 110°C. Figure 16 shows the same result as Figure 15 does. The higher the baking temperature, the better the etch resistance of photoresist.

The entire range of baking effect on reticulation is shown in Figure 17. Each point on the curves represents one etching condition, DC bias and pressure, without reticulation at a given hard-bake. The etching parameter DC bias values on these points are the critical values for reticulation at a given pressure. If the DC bias value is smaller than the critical value, reticulation will not occur after etching. All etching conditions under the transition curve will not produce reticulation after 10 minutes etching. Therefore, the best hard-bake condition for etch resistance of photoresist is 150°C for 45 minutes. The poorest ones are at 110°C for 15 minutes and without any hard-bake.

5.2 Environmental moisture effects on reticulation

The etching results are shown in Table 6. As long as the DC bias is at 625V, there is no reticulation found on the photoresist. No matter how many days wafers were kept in the humidity chamber before etching, the environmental moisture did not degrade the etch resistance of photoresists which have been hard-baked at 130°C for 30 minutes in this experiment.

Figure 16. Baking temperature effect on reticulation for 45 minute baking.

Figure 17. Comparison of baking conditions on reticulation problem.

Table 6 The effect of environmental moisture on reticulation .

Delay time (days)	DC bias (V)	Power (W)	SiO ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
0-day	625	1320	501	136	3.68	good
0-day	650	1400	527	x	x	bad
1-day	625	1300	501	120	4.18	good
1-day	650	1410	526	x	x	bad
2-day	625	1290	488	121	4.03	good
2-day	650	1400	499	x	x	bad
4-day	600	1220	446	109	4.09	good
4-day	625	1320	496	129	3.84	good
4-day	650	1400	532	x	x	bad
8-day	625	1310	477	135	3.53	good
8-day	650	1400	503	x	x	bad

Wafers are hard-baked at 1300C for 30 minutes. Etching temperature and time are 350C and 10 minutes. Pressure is fixed at 45 mTorr. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively. The unit of etch rates is Angstrom/min. "x" represents that reticulation occurs. The values on above table is the average of two wafers which are processed at same time.

5.3 Characteristics of AME8110 etcher

Table 7 and Figure 18 show the relationship between the etching rate of SiO_2 and etch parameters, DC bias and pressure. The oxide etch rates at 45 mTorr for 600, 625, and 650V DC biases are 469, 490 and 527 angstrom/minute, respectively. The higher DC bias will cause more energetic ion bombardment which can enhance the etch rate. On the other hand, the etch rate of oxide varies from 298 to 626 angstrom/minute when the pressure changes from 15 to 75 mTorr under 625V DC bias. In short, the oxide etch rate increases with the increasing DC bias and pressure.

For selectivity of SiO_2 to photoresist, there is no special relationship found between baking conditions and selectivity in Table 8. However, after the same hard-bake process, the selectivity increases with increasing pressure. This may be due to the higher DC biases used at the lower pressure. These higher DC biases increase the physical etch and result in the loss of selectivity. The average selectivities at 15, 45, and 75 mTorr are 3.39, 4.23 and 4.87, respectively. The average selectivity in this experiment is approximately 4.16. This value is similar to Sawoska's [6].

The optimal throughput in this experiment is a hard-bake at 150°C for 15 minutes. The etch rate of oxide can reach 632 angstrom/minute without any reticulation problem. The selectivity can reach 3.90. The hard-bake at 150°C for 45 minutes has better etch resistance but the baking time is tripled. Also, the highest etch rate of oxide which can be accomplished in this baking process is similar to the 150°C for 15 minutes hard-bake.

It seems that higher temperature hard-bake would improve reticulation resistance beyond 150°C. But the resolution requirements usually restrict bake

Table 7 The relationships between DC bias and SiO₂ etch rate, as well as DC bias and RF power at 15, 45 and 75 mTorr

15 mTorr									
DC bias (V)	525	575	625	675	700	725	775	825	
SiO ₂ Etch rate (Å/min)	227	257	298	339	365	386	407	452	
RF power (W)	630	740	840	960	1040	1090	1200	1400	
45 mTorr									
DC bias (V)	525	550	575	600	625	650	675	700	
SiO ₂ Etch rate (Å/min)	369	392	435	469	490	527	551	594	
RF power (W)	1010	1050	1140	1230	1300	1400	1520	1610	
75 mTorr									
DC bias (V)	525	550	575	600	625	635			
SiO ₂ Etch rate (Å/min)	467	509	553	582	626	650			
RF power (W)	1330	1420	1540	1620	1720	1850

Figure 18. The relationship between silicon dioxide etch rate and DC bias.

Table 8 These data are the relationship between selectivity and hard-bake processes at different pressures.

	Without Hard-bake	110°C 15 minutes	110°C 45 minutes	130°C 15 minutes	130°C 30 minutes	150°C 15 minutes	150°C 45 minutes	Average Selectivity
Selectivity 15 mTorr	3.29	3.89	3.21	3.80	3.93	2.50	3.12	3.39
Selectivity 45 mTorr	3.41	5.46	4.42	4.13	4.70	3.57	3.93	4.23
Selectivity 75 mTorr	4.69	6.57	5.54	4.14	5.43	3.66	4.08	4.87
Average Selectivity	3.80	5.30	4.39	4.02	4.69	3.24	3.71	4.16

The values in the above table are the average calculated from the wafers without reticulation problem.

to 130- 140°C because of plastic flow (see review page 13). We have quantified the trade-off between resolution and reticulation resistance.

5.4 Mechanism verification

In the dark tape test, there was not any difference in etch resistance between those two wafers, even though one of them was covered by dark tape. In the thermal shock test, there was also no reticulation found on those wafers which were dipped either into liquid nitrogen or inserted into an oven. Thermal stress did not cause reticulation. The mechanism of reticulation involving thermal expansion coefficient was not proven or disproven in this study.

6.0 DISCUSSION

In Figure 11, there is an uncertain DC bias region between the maximum DC bias without reticulation and the minimum DC bias leading to reticulation. The DC bias above the uncertain region causes reticulation and the DC bias below the uncertain region does not cause any reticulation. The exact critical transition DC bias could be more precisely determined if more experiments were conducted in this range of DC bias.

It is predicted that either a higher baking temperature or a longer baking time can enhance the etch resistance of photoresist because baking removes residual solvent and water. Consequently, the hard-bake at 150°C for 45 minutes is the best one for etch resistance enhancement. The temperature effect on reticulation is more significant than that of the time effect on reticulation. This result can be observed in comparing Figures 14 and 16. Besides the hard-bake, the properties of photoresist also affect the reticulation resistance. There was only one photoresist used in this study. The relationship between reticulation resistance and the nature of photoresist was not discussed in this study.

From the results of dark tape and thermal stress testing, the reticulation mechanism due to the thermal expansion coefficient was not proven in this study. It might be that the Krogh's speculation was incorrect. It may conversely be that the induced stress was not great enough to cause reticulation in these two tests.

The data in these experiments is consistent with the model of a compressive layer on the photoresist surface. But the mechanism cannot be

distinguished from the data. Compression can be due to ion implantation, chemical cross-linking of photoresist, thermal expansion, or any combination thereof. Dependence on ion energy points to implantation.

The data are consistent with a bulk photoresist which hardens during hard-bake to resist tensile plastic flow imposed by a compressive surface.

The activation energy of reticulation resistance can be estimated by using the Arrhenius equation. The hardening of the bulk photoresist is hypothesized to prevent reticulation, perhaps by crosslinking polymers. There is no doubt a range of activation energies involved, but a typical activation energy is obtained from a log rate vs $1/T$ graph. Rate is the reciprocal of the bake time for reticulation. Those hard bake conditions in which reticulation occurred at some minimum DC bias and pressure were selected to calculate the activation energy from Table 5. For example, reticulation occurred at DC bias 700 V and pressure 15 mTorr after both 110°C for 45 minutes and 130°C for 15 minutes baking. The activation energy can be calculated by applying these two sets of baking temperatures and times to the Arrhenius equation.

$$R = R_0 \exp (-E_a / kT) \quad \text{Eq (2)}$$

where E_a is the activation energy (eV) of reticulation, k is the Boltzmann constant equal to 8.6×10^{-5} eV/K, and T is the temperature (K). R is the reaction rate equal to $1/\text{time}$. The activation energy of reticulation can be expressed :

$$t_1 / t_2 = R_2 / R_1 = \exp [E_a / k (1/T_1 - 1/T_2)] \quad \text{Eq (3)}$$

$$E_a = k \ln (t_1/t_2) T_1 T_2 / (T_2 - T_1) \quad \text{Eq (4)}$$

where $t_1 = 45$ minutes, $T_1 = 110^\circ\text{C}$, $t_2 = 15$ minutes, and $T_2 = 130^\circ\text{C}$

The activation energy of reticulation, E_a , is about 0.73eV. This activation energy is an estimated value because there are only two data points, as shown in Figure 19. The magnitude of activation energy is reasonable for a chemical process.

The various characteristics of AME8110 had been studied before, but each author focused on different topics and etching conditions. Khan^[41] and Khathuria^[42] were especially interested in low DC bias or power etching. The value of DC bias at the same RF power and pressure shown in Khan's report is about 20-30% higher than that of other authors. The DC bias used in this paper is higher, from 525 to 825V. Table 9 shows the brief comparison of our common data. Since there is not too much overlapping, it is difficult to make a complete comparison to our project. The data are a measure of machine consistency, in a control environment not very different from typical manufacturing control.

Figure 19 Calculation of activation energy of reticulation $\ln(1/\text{baking time})$ versus $(1/\text{baking temperature})$

Table 9. Comparison of AME8110 etching character generated by different authors

Author	Pressure (mTorr)	DC bias (V)	Power (W)	SiO ₂ Etch rate (Å/min)
Hsieh	45	-550	1050	392
Kwan [40]	45	-550	1300	440
Khan [41]	45	-550	1060	440
Khathuria [42]	45	-550	1152	
<hr/>				
Hsieh	45	-600	1140	467
Kwan [40]	45	-600	1500	470

7.0 CONCLUSION

Reticulation is a function of hard-bake, and etching parameters. A longer baking time and higher baking temperature enhance reticulation resistance of photoresist. Higher DC bias and lower pressure promote reticulation. Environmental moisture does not significantly affect the etch resistance of photoresist after a hard-bake at 130°C for 30 minutes. Thermal flow blockage and thermal shock fail to cause reticulation. The mechanism of reticulation caused by thermal expansion coefficient is not proven in this project.

The highest oxide etch rate without reticulation in this experiment is about 632 angstrom/minute. The average selectivity is about 4.16, but there is no special relationship found between hard-bake and selectivity.

All the experimental data are consistent with our model that reticulation is due to a thin, hard, compressive stressed layer of photoresist over a plastic bulk.

8.0 FUTURE WORK

This thesis investigated the relationship between baking conditions and etching parameters leading to reticulation and to improve the understanding of the environmental moisture effect on reticulation for one photoresist. Upon completion of this study, I had several suggestions for those who are interested in this topic. The following are my suggestions:

- (1) Choose other types of photoresist to study the relationship between the nature of photoresist and reticulation.
- (2) Study more etching parameters, such as etching time, gas flow rate and hexode temperature.
- (3) Quantify reticulation by using a better method than alpha-step to measure the difference of the thickest and the thinnest reticulated photoresist thickness. We may define a quantitative unit as reticulation percentage equal to $(\text{the difference thickness} / \text{initial thickness}) * 100\%$.

9.0 REFERENCES

1. Herbert H. Sawin, "A Review of Plasma Processing Fundamentals," *Solid State Technology*, **28**, 211 (1985).
2. C. Grant Wilson and Murrae J. Bowden, "Recent Advances in Organic Resist Materials," *Chemtech.*, 182 (Mar. 1989).
3. George E. Gimpelson and Cheryl L. Russo, "Plasma Planarization with a Non-Planar Sacrificial Layer," *IEEE CHMT*, 37 (1986).
4. J. Hackenberg, B. Holbrook, and T. Ingwersen, "Photoresist reticulation problems associated with plasma etching," *Plasma Proceedings*, 317 (1988).
5. Pete Gwozdz oral communication, Materials Engineering Department, San Jose State University.
6. David A. Sawoska, "High Contrast Positive Resist(s) for Use in Megabit Processing with Broad Process Latitude," *Proceeding of SPIE*, **1262**, 173 (1990).
7. J. Poission, L. Gagnon, and D. Gagnon "Via Contact Dry Etching Using a Plasma Low Resistance Photoresist," *IEEE V-MIC*, 308 (1986).
8. Ole Krogh, Harry Slomowitz, and Yosias Melaku, "Spectroscopic Diagnostics of Photoresist Erosion in an Aluminum Etch Plasma," *J. Electrochemical Society*, **134**, 2045 (1987).
9. John J. Grunwald and Allen C. Spencer, "A Novel, Aqueous Surface Treatment to Thermally Stabilize High Resolution Positive Photoresist Images," *SPIE*, **631**, 62 (1986).

10. A. Gutmann, A. Kleinhaus, and W. Bade, "Thermal Stability and Etching Resistance of Formaldehyde and Deep UV- Hardened Photoresist," *Microelectric Engineering*, **3**, 329 (1985).
11. K. Heiman, "Lam introduces the Rainbow 4500i simultaneous isotropic and anisotropic etching," *Lam research Corp. Interface*, **2**, (1991).
12. Masanobu Onodera and Tooru Nonaka, "Outgas Free Photoresist Processing," *Solid State Technology*, **34**, S7 (1991).
13. S.M. Sze, VLSI Technology, 2nd Edition, McGraw-Hill Book Company, 141 (1988).
14. Tom Batchelder and John Piatt, "Bake Effects in Positive Photoresist," *Solid State Technology*, **26**, 211 (1983).
15. Ronald R. Bowman and David S. Cochran, Practical Integrated Circuit Fabrication, Shieh-Hom Science Book Company, (1984).
16. S.M. Sze, Semiconductor Devices physics and Technology, 428 (1988).
17. Elliott David, Integrated Circuit Fabrication Technology, McGraw-Hill Book Company, 182 (1982).
18. C.Grant Wilson and Murrae J. Bowden, "Resist Materials for Microelectronics," *Chemtech.*, 102 (Feb. 1989).
19. W.S. DeForest, Photoresist, 48 (1975).
20. H. Gokan, S. Esho, and Y. Ohnishi, "Dry Etch Resistance of Organic Materials," *J. Electrochem. Soc.*, **130**, 143 (1983).
21. Lester A. Pederson, "Structural Composition of Polymer Relative to Their Plasma Etch Characteristics," *J. Electrochem. Society*, **129**, 205 (1982).
22. J.W. Coburn, Plasma etching and Reactive Ion Etching, The Education Committee American Vacuum Society, (1982).

23. L. Daneil, "Basic Chemistry and Mechanisms of Plasma Etching," *J. Vacuum Science Technology*, **B1**, 23 (1983).
24. S.J. Pearton and U.K. Chakrabarti, "Electron Cyclotron Resonance Plasma Etching of InP in CH₄/H₂/Ar," *J. Applied Physics Letter*, **56**, 1424 (1990).
25. Takashi Matsuura, "Directional Etching of Si with Perfect Selectivity to SiO₂ Using Ultraclear Electron Cyclotron Resonance Plasma," *J. Applied Physics Letter*, **56**, 1339 (1990).
26. Toshiro Ono, "Reactive Ion Stream Etching Utilizing Electron Cyclotron Resonance Plasma," *J. Vacuum Science Technology*, **B4**, 696 (1986).
27. Russ A. Morgan, Plasma Etching in Semiconductor Fabrication, Elsevier Science Publishing Company Inc.,(1985).
28. D. Bollinger, S. Lida, and O. Matsumoto, "Reactive Ion Etching: Its Basis and Future," *Solid State Technology*, **27**, 111 (1984).
29. H.R. Koenging and L.I. Maissel, "Application of RF. Discharges to Sputtering," *IBM J. Research Development*, **14**, 168 (1970).
30. H. R. Bruce, "Anisotropy Control in Dry Etching," *Solid State Technology*, **24**, 64 (1984).
31. P. Dennis, M. Manos, and Daniel L. Flamm, Plasma Etching : An Introduction, Boston :Academic Press Inc., (1989).
32. Stanley Wolf and Richard N. Tauber, Silicon Processing for the VLSI Era, Lattice Press, (1987).
33. Herbert H. Sawin, "A Review of Plasma processing Fundamentals," *Solid State Technology*, **28**, 211 (1985).

34. D. Bolinger and S. Lida, "Reactive Ion Etching: Its Basic and Future," *Solid State Technology*, **27**, 167 (1984).
35. I. Schnitzer and A. Katzer, "Monitoring processes in photoresist using infrared optical fibers and tunable diode laser," *SPIE*, **1228**, 246 (1990).
36. S.F. Yoon, P.L. Villa, M. Calzavara, and G. Degiorgis, "The Effects of Elevated Softbake Temperature on High Resolution Positive Photoresist," *Solid State Technology*, **32**, 89 (1989).
37. J.M. Shaw, M.A. Frisch, and F.H. Dill. "Thermal Analysis of Positive Photoresist Films by Mass Spectrometry," *IBM J. Res. Develop.*, **21**, 219 (1977).
38. F.H. Dill and J.M. Shaw, "Thermal Effects on the Photoresist AZ1350J," *IBM J.Res. Develop.*, **21**, 210 (1977).
39. CRC handbook of chemistry and physics, 66th edition, D190
40. Ming S. Kwan, "Characterization of An AME8110," Center for Electronic Materials and Devices College of Engineering, San Jose State University, (1990).
41. Mahin M. Khan, "Characterization of an AME8110 Hexode Plasma Etcher, Specific to Etch Rates of Silicon-Dioxide, Silicon-Nitride and Positive Photoresist," San Jose State University, General Engineering Master Thesis, (1993).
42. Ashok M. Khathuria, "Selective and Anisotropic Etching of Silicon-Dioxide, Silicon-Nitride, and Positive Resist in AME8110 Hexode Reactor," San Jose State University, General Engineering Masters Thesis, (1993).

43. Dragan B. Ilic, "Thin Films Formed by Plasma Enhanced Chemical Vapor Deposition," *Hewlett Packard Journal*, 24 (Aug. 1982).
44. Haiping Dun, "Mechanisms of Plasma Enhanced Silicon Nitride Deposition Using SiH₄/N₂ Mixture," *Electrical Transport Properties*, **128** p1555 (1981).

10.0 APPENDIX A

This appendix provides the original experimental data at different hard-bake conditions. DC bias and chamber pressure are the etching variables. RF power is determined by the setting of DC bias and pressure. Selectivity is the ratio of the oxide etch rate to the photoresist etch rate. Some photoresist etch rates are marked "x", instead of value. It means that photoresist thickness cannot be measured by Nanospec/AFT machine when reticulation occurs because the reticulated photoresist surface is a very rough surface. The Nanospec/AFT machine cannot be used to measure this rough photoresist surface. The "good" etch resistance means no reticulation problem at these etching conditions. The "bad" etch resistance means that reticulation occurs at these etching conditions.

Appendix A.1 The etching data are without hard-bake. Etching temperature and time are 35°C and 10 minutes. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively.

Pressure mTorr	DC bias (V)	Power (W)	Si O ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
15	525	640	215	61	3.52	good
15	575	740	249	75	3.32	good
15	625	850	294	97	3.03	good
15	675	960	337	x	x	bad
45	525	1000	385	109	3.53	good
45	550	1050	394	120	3.28	good
45	575	1150	435	x	x	bad
45	625	1280	473	x	x	bad
75	525	1290	460	98	4.69	good
75	550	1430	512	x	x	bad
75	575	1600	570	x	x	bad

The unit of etch rates is Angstrom/min. "x" represents reticulation.

Appendix A.2 The etching data for hard-bake conditions are 110°C for 15 minutes. Etching temperature and time are 35°C and 10 minutes. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively.

Pressure mTorr	DC bias (V)	Power (W)	SiO ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
15	525	630	229	47	4.86	good
15	575	720	258	75	3.44	good
15	625	830	294	87	3.38	good
15	675	950	327	x	x	bad
45	525	990	344	66	5.21	good
45	550	1050	400	70	5.71	good
45	575	1120	416	x	x	bad
75	525	1330	453	69	6.57	good
75	550	1390	501	x	x	bad
75	575	1530	546	x	x	bad

The unit of etch rates is Angstrom/min. "x" represents reticulation.

Appendix A.3 The etching data for hard-bake conditions are 110°C for 45 minutes. Etching temperature and time are 35°C and 10 minutes. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively.

Pressure mTorr	DC bias (V)	Power (W)	SiO ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
15	575	740	247	70	3.53	good
15	625	850	298	91	3.27	good
15	675	960	342	121	2.83	good
15	700	1040	360	x	x	bad
45	525	1010	365	88	4.15	good
45	575	1130	426	91	4.68	good
45	600	1240	463	x	x	bad
45	625	1300	499	x	x	bad
75	525	1370	463	77	6.01	good
75	575	1500	568	112	5.07	good
75	600	1580	584	x	x	bad

The unit of etch rates is Angstrom/min. "x" represents reticulation.

Appendix A.4 The etching data for hard-bake conditions are 130°C for 15 minutes. Etching temperature and time are 350°C and 10 minutes. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively.

Pressure mTorr	DC bias (V)	Power (W)	SiO ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
15	675	990	342	90	3.80	good
15	700	1050	355	x	x	bad
15	725	1100	373	x	x	bad
45	525	1020	388	114	3.40	good
45	575	1130	470	97	4.85	good
45	600	1240	473	x	x	bad
75	525	1330	498	115	4.33	good
75	550	1450	506	128	3.95	good
75	575	1530	546	x	x	bad

The unit of etch rates is Angstrom/min. "x" represents reticulation.

Appendix A.5 The etching data for hard-bake conditions are 130°C for 30 minutes. Etching temperature and time are 350°C and 10 minutes. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively.

Pressure mTorr	DC bias (V)	Power (W)	SiO ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
15	525	640	236	69	3.42	good
15	625	850	315	78	4.04	good
15	675	970	349	86	4.06	good
15	700	1050	380	90	4.22	good
15	725	1100	390	x	x	bad
45	525	1010	377	63	5.98	good
45	575	1140	440	93	4.73	good
45	600	1200	470	107	4.39	good
45	625	1320	501	136	3.68	good
45	650	1400	527	x	x	bad
75	525	1330	476	75	6.35	good
75	550	1430	518	114	4.51	good
75	575	1530	564	x	x	bad

The unit of etch rates is Angstrom/min. "x" represents reticulation.

Appendix A.6 The etching data for hard-bake conditions are 150°C for 15 minutes. Etching temperature and time are 350°C and 10 minutes. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively.

Pressure mTorr	DC bias (V)	Power (W)	SiO ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
15	625	840	290	93	3.12	good
15	675	950	331	158	2.09	good
15	725	1080	396	173	2.29	good
15	775	1200	405	x	x	bad
45	525	990	352	100	3.52	good
45	575	1150	422	119	3.76	good
45	625	1290	488	132	3.42	good
45	675	1500	535	x	x	bad
75	525	1310	463	127	3.65	good
75	575	1520	541	141	3.42	good
75	625	1700	632	162	3.90	good
75	635	1850	650	x	x	bad

The unit of etch rates is Angstrom/min. "x" represents reticulation.

Appendix A.7 The etching data for hard-bake conditions are 150°C for 45 minutes. Etching temperature and time are 35°C and 10 minutes. The flow rates of oxygen and Freon 23 are 8 and 75 sccm, respectively.

Pressure mTorr	DC bias (V)	Power (W)	SiO ₂ Etch rate	Resist etch rate	Selectivity	Etch resistance
15	575	750	272	81	3.36	good
15	675	970	345	94	3.67	good
15	700	1030	359	133	2.70	good
15	775	1200	409	149	2.74	good
15	825	1400	452	x	x	bad
45	575	1150	436	119	3.66	good
45	675	1530	567	135	4.20	good
45	700	1610	594	x	x	bad
75	525	1350	456	107	4.26	good
75	600	1650	579	141	4.11	good
75	625	1740	620	160	3.88	good

The unit of etch rates is Angstrom/min. "x" represents reticulation.