THE EFFECT OF PLASMA ON SILICON NITRIDE, OXYNITRIDE AND OTHER METALS FOR ENHANCED EPOXY ADHESION FOR PACKAGING APPLICATIONS

Sneha Sen Gaddam, M.S.

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APPROVED:

Jeffry A. Kelber, Major Professor
Thomas R. Cundari, Committee Member
Jincheng Du, Committee Member
Mohammad A. Omary, Committee Member
William E. Acree, Jr., Chair of the Department of Chemistry
Mark Wardell, Dean of the Toulouse Graduate School
The effects of direct plasma chemistries on carbon removal from silicon nitride (SiNₓ) and oxynitride (SiOₓNx) surfaces and Cu have been studied by x-photoelectron spectroscopy (XPS) and ex-situ contact angle measurements. The data indicate that O₂, NH₃ and He capacitively coupled plasmas are effective at removing adventitious carbon from silicon nitride (SiNₓ) and Silicon oxynitride (SiOₓNx) surfaces. O₂ plasma and He plasma treatment results in the formation of silica overlayer. In contrast, the exposure to NH₃ plasma results in negligible additional oxidation of the SiNₓ and SiOₓNx surface. Ex-situ contact angle measurements show that SiNₓ and SiOₓNx surfaces when exposed to oxygen plasma are initially more hydrophilic than surfaces exposed to NH₃ plasma and He plasma, indicating that the O₂ plasma-induced SiO₂ overlayer is highly reactive towards ambient corresponding to increased roughness measured by AFM. At longer ambient exposures (>~10 hours), however surfaces treated by either O₂, He or NH₃ plasma exhibit similar steady state contact angles, correlated with rapid uptake of adventitious carbon, as determined by XPS. Surface passivation by exposure to molecular hydrogen prior to ambient exposure significantly retards the increase in the contact angle upon the exposure to ambient. The results suggest a practical route to enhancing the time available for effective bonding to surfaces in microelectronics packaging applications.
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By

Sneha Sen Gaddam
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CHAPTER 1
INTRODUCTION

1.1 Motivation

The work presented in this dissertation focuses on the fundamental understanding of plasma reactions on several substrates including silicon nitride (SiNx), silicon oxynitride (SiOxNy) and copper (Cu). The goal was to develop a plasma cleaning method that is better than the wet cleaning technique and a passivation technique for longer shelf life for substrates used in the industry. The gases used for the plasma cleaning include oxygen, ammonia, helium and hydrogen. The plasma cleaning is also compared to the cleaning done by radicals (produced by a thermal cracker). Although effective removal of carbon and other surface contamination is an important issue in plasma cleaning, the composition of the plasma-treated surface, and hydrophilicity of the surface upon and during ambient exposure are also of practical importance. Another objective for this project was to develop a plasma cleaning method for surface activation and maintaining the hydrophilicity of the surfaces after exposure to ambient, as hydrophilicity is generally correlated with bondability to epoxy and other polar adhesives. Passivation of the plasma-exposed surface was explored by using several gases for post plasma exposure. Hydrogen was the most successful in maintaining the hydrophilicity of the substrate.

1.2 Background

In past decades, the semiconductor industry has observed a trend of doubling the number of transistors per integrated circuit (IC) roughly every two year. This trend was first described by Gordon Moore in 1965 and is known as” Moore’s law”, and is due primarily to the
unceasing shrinkage in transistor and IC feature sizes. This trend in shrinking IC feature size over the last four decades is illustrated in Figure 1.1 [1]. To accommodate the increase in the number of transistors, the diameter of wafers is increased to 200 mm and is progressing to 300 mm and beyond [2].

![Figure 1.1. Representation of the Moore’s law [1].](image)

As the integrated circuits continue to shrink in size, the associated decrease in size of the wire bond pad on both the die and substrate presents substantial challenges in the manufacturing process. To ensure high device reliability and minimize manufacturing costs, it is important to optimize the wire bonding process to ensure good bond strengths and yields. Plasma technology can be used to clean pads prior to wire bonding to improve bond strengths and yields. The objective of the plasma process is to maximize wire-pull strength, thereby
minimizing failures and increasing yields. These are some of the reasons industry is moving away from wet plasma processing techniques. [3].

Figure 1.2 depicts the examples of plasma aided manufacturing techniques for surface modification. Due to these recent advances in the industry, and the reduction in the circuit and component size, plasma gas treatment is becoming the choice method of treatment. The need for hydrophilic surfaces for adequate adhesion has fueled the development of new methods and use of new gases in the plasma surface modification industry [4].

1.3 What is Plasma?

Gas phase plasma is an electrically neutral mixture of electrons, ions, radicals, photons, recombination products and neutrals created by the application of energy, such as radio
frequency (RF), to a source gas contained within a vacuum chamber. When one provides energy to a solid, the relative motion among its constituent atoms or molecules increases.

This results in a transition to the liquid state, then to a gas. If the energy supply increases even further, collision processes among the constituent particles become violent enough for these to break apart; this results in the formation of equal number densities of electrons and ions. This latter state, plasma, is therefore often called the “fourth state of matter”. The Figure 1.3 summarizes the active species that are present in oxygen plasma. The reactive radical species (and photons and electrons) are generally responsible for surface chemical reactions, while ionized species are also capable of physical reaction through sputtering. Photon emission within plasma is a result of the excited neutrals, ions and free radicals formed in the plasma losing their excess energy. The wavelengths of the emission depend on the gases involved, but often are more than sufficient to break chemical bonds, and can be useful when treating polymeric materials as well as surface modification [5,29].

Plasma processing techniques are one of the cornerstones of modern semiconductor fabrication which can achieve high radical density, high selectivity, and anisotropic etch profiles at low temperatures and mild voltages. Due to this moderate environment, this process prevents unwanted diffusion and degradation of materials due to ion bombardment. It has also been proved that plasma processing has a minimal effect on the wafer structure, which is essential for large scale (CMOS) integration [6].

Typical materials employed in the microelectronics and optoelectronics industries include ceramics, glass, polymers and metals—such as gold, copper, aluminum, nickel,
palladium, tungsten, and silver. The effectiveness of the plasma on these complex interfaces is determined by the plasma source gases, the configuration of the plasma system and the plasma operating parameters. Surface modification processes can be classified into four categories: contamination removal, surface activation, etch and cross linking. [7]

Figure 1.3. Schematic of the species present in oxygen plasma [5].

The focus of this dissertation is primarily on (a) removal of surface contamination; and (b) plasma activation of surface sites for subsequent reactions with background gases and ambient.

1.4 Plasma Applications

Plasma has been utilized in the semiconductor industry for the promotion of adhesion through the removal of contaminants and surface activation of materials. This is particularly important during “packaging”—the application of adhesives and moldings to the completed IC to for protection in ambient and attachment to external electrical leads. Plasma processing is commonly used to improve wire bond adhesion and reliability [30], adhesion of molding compounds to lead frames [31, 32, 33] and substrates as well as improving the adhesion of under fill materials in flip chip packages to minimize voiding and delamination [34]. Besides the
obvious benefits of increased yield and product reliability, plasma treatment has increasingly become an enabling technology that provides the means to utilize more cost efficient materials and processes. Also, plasma cleaning is important due to continually shrinking package sizes and corresponding decrease in pad geometries and pitch which dictate that the bonding surfaces be properly prepared and free of contamination in order for a reliable bond to be formed [8].

As mentioned, the motivation for the dissertation is to find a plasma treatment is to remove the surface contamination and to modify the surface and passivation of the substrate for better hydrophilicity and to also maintain the hydrophilic properties upon exposure to ambient.

Surface contamination removal generally involves either physical and/or chemical processing to remove the surface contaminants. The physical reaction involves the bombardment of the positive ions on the surface which dislodge the contaminants from the surface while causing surface roughening on the microscopic level. A chemical reaction involves reaction with the epoxy or other contaminants and this might include some kind of surface modification by covalent bonding. The new functional groups have strong chemical bonds with the bulk material and have the capability to further bond with epoxy to promote better adhesion. The Table 1.1 has an overview of the applications for plasma surface enhancements that are used in the industry.
Table 1.1. Process applications for plasma surface enhancements [4].

1.5 Substrates Used in the Experiments

Silicon nitride and oxynitride are widely used as passivation layers in micro electro mechanical systems (MEMS) and IC devices [9, 10]. These substrates are generally the passivation layers and will react with physically or chemically with an epoxy during packaging. There is very less literature on the effect of plasma on the silicon nitride and oxynitride and the chemistry between the silicon nitride and the epoxy used. This project focuses on understanding the chemical properties and changes after the plasma exposure, which results in the change in the hydrophobic properties and also the change in the chemical properties after post plasma exposure to ambient. Cu is also a surface of concern as it is now the most widely used metal for leadframes and plays an important role in packaging. The deterioration of the epoxy-resin molded IC s is a big problem in the semiconductor industry [11-13]. To avoid this problem better adhesion between the die-pad and epoxy was advised. From [14] it has been proven that plasma processing greatly improves adhesion of mold compounds by increasing the
substrate surface energy and results in increased package reliability. Figure 1.4 a and b, displays the effect of plasma on adhesion of mold compound on a copper lead frame. Figure 1.4 a displays an adhesive failure while 1.4 b which is after the plasma treatment displays a cohesive failure. Plasma cleaning has been widely applied in the packaging industry prior to wire bonding [15-16] and molding [17-18] processes to improve wire bondability and adhesion between mold compound and chip carrier. These applications generally involve plasma cleaning of “exposed” surfaces such as bonding pads or laminate substrates. Positive effects from an optimized plasma cleaning process include the following surface modifications: removal of surface contaminants and weak boundary layer, increase in surface energy or wetting enhancement through incorporation of polar groups, crosslinking or formation of functional groups that aids bonding to the adhesive, and surface roughening to increase the effective surface area and mechanical interlocking [19-21]. These effects can help to improve interfacial adhesion. Although plasma cleaning is generally thought to be an easy-to-implement solution, the pitfall is that results may be more detrimental if the plasma process is not optimized. [17-18]

Figure 1.4. Pull test on a molded lead frame without plasma treatment [14].
Figure 1.5. Pull test on a molded lead frame with plasma treatment [14].

Figure 1.6. Cross section of leadframe chip scale package [35].

Figure 1.7. Schematic of the Si$_3$N$_4$ structure [22].
Various Si$_3$N$_4$ cleaning processes involving wet chemical treatment and/or Ar$^+$-ion bombardment have been evaluated [23] using XPS or ion scattering spectroscopy (ISS). The wet-chemical methods considered to date [24-25] do not appear to be completely effective in removing surface contamination.

With the introduction of copper wire to replace gold as a cost saving initiative, the effectiveness of the plasma process becomes even more critical than before. The intrinsic material properties of copper play a part in this shift. Copper has a higher hardness than traditional gold wire and this makes obtaining an intimate contact between the copper and bonding surface a bigger challenge. Thus the copper wire bond process is more sensitive to micro contamination on the bonding surfaces, and requires a highly effective and repeatable plasma process to ensure reliable wire bonds are obtained [26]. The die attach and adhesive cure steps during packaging can cause contamination to form on substrate or package copper bond pads. Untreated, this can lead to no-sticks or low ball shear at the wire bonding operation. Oftentimes the problem is mistakenly assigned to the wire bonder, resulting in attempts to alter the recipe to improve bondability [27]. The need for contamination-free copper surfaces prior to Cu-Cu wafer bonding is critical and becomes increasingly important in the semiconductor industry especially when lower temperature bonding processes (<400°C) are desired. Two key requirements for a clean copper surface include 1) complete removal of undesirable copper oxide layers, and 2) complete removal of organic contaminants and Cu corrosion inhibitors from previous steps [28].

1.6 Present Work

In order to address concerns discussed above concerning surface processing for
microelectronics packaging, a series of surface science studies were carried to out to explore the effects of free radical and plasma chemistries on Si₃Nₓ, SiOₓNy, and on Cu surfaces. The studies address both plasma-induced changes to surface chemical composition and topography, but also the evolution of surface hydrophilicity upon subsequent exposure to ambient. Chapter 2 describes the experimental set up and characterization tools used to analyze the results. The details about the samples description and the ultra-high vacuum chamber used for generating capacitively coupled plasma (CCP) are discussed in this chapter. Different gases like O₂, NH₃ and He are used to generate the plasma. A description of characterization tools like FTIR (Fourier transformed infrared spectroscopy), XPS (X-ray photoelectron spectroscopy), AFM, (atomic force microscopy), Goniometer and Thermal cracker is given here.

Chapter 3 deals with the effect of O₂ and NH₃ plasma on SixNy and SiOxNy substrates. XPS was used to characterize the formation of the silica overlayer on the SixNY and a Goniometer was used to understand the hydrophilicity of the substrates upon exposure to the ambient. The surface passivation upon exposure to Hydrogen and other gases were also characterized with contact angle measurement.

The effect of oxygen radicals and He plasma on the silicon substrates is described in Chapter 4. AFM was used to determine the etching and roughness of the substrates upon exposure to the radicals and plasma. In-situ XPS and ex-situ FTIR was used to characterize the samples.

It is important to understand the effect of plasma on the other substrates like Copper that are used in the industry. Plasma cleaning of Cu and other metals and the surface
modification is important to avoid delamination. Chapter 5 discusses the in-situ XPS and ex-situ AFM results of Cu after exposure to several plasmas and oxygen radicals.

1.7 Chapter References


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CHAPTER 2

EXPERIMENTAL METHODS

2.1 Plasma Exposure and Characterization: Ultra-High Vacuum Chamber

This study is concerned with the evaluation of surface cleaning efficiency of a capacitively coupled plasma. Several papers in the literature discuss the effects of plasma on metals and silicon.[1-5] Similarly, the salient features that occur during a plasma etching process are also discussed in literature[6]. But, the effects of plasma on the surface hydrophilicity on epoxy adhesion have been rarely been studied. Studies were undertaken in a combined ultra-high vacuum (UHV) and deposition system both turbo-molecularly pumped and connected to each other via a gate valve, which facilitates transfer between the two without exposure to ambient conditions using a vacuum feed-through. Figure 2.1 is a schematic of the experimental chamber setup with the UHV system on the right and the deposition chamber on the left. The UHV system is equipped with a hemispherical electron energy analyzer with a 15 channel plate detector (PHI), dual anode x-ray source (PHI), and a bi-directional sample manipulator (X,Ѳ). The manipulator enables resistive heating and liquid N₂ cooling of the sample and the sample temperature was monitored using a K-type thermocouple spot welded to the center of the sample stage. The chamber also has an ion source gun (PHI) for ion sputter cleaning of substrates and a low energy electron gun (Kimball Physics) for cleaning of substrates if necessary. The main chamber was also fitted with the thermal cracker and control variable leak valves that are used to dose/leak oxygen and other gases for radical production.

The plasma exposure chamber (Figure 2.1 left side) consists of multiple ports for retrofitting several components and gas handling supplies. The chamber is fitted with a
modified 2.75"CF metal nipple, which is used to generate the conductively coupled plasma. It is fitted with a 3 turn Al coil (20" long uncoiled) connected to a home-built matching network and RF supply (see section 2.2.). The chamber also has two manual variable leak valves for other gases like Helium and ammonia. The chamber's pressure is monitored by both an ion gauge and a baratron gauge.

![Figure 2.1. Combined ultra-high vacuum analysis chamber and plasma exposure chamber.](image)

2.2 Plasma Matching Network

The plasma was generated using a commercially available RF power (ENI, model no: ACG-6B) supply operated at 13.56 MHz and 20 watts. In order to match the load of the coil and plasma chamber a home built matching network was employed. The matching network was developed by Swayambhu Behera and Qing Wang [22], and consisted of two variable capacitors (50-1200 pF) connected in series. Figure 2.3 is a picture of the matching network and
equivalent circuit diagram [7]. Radio frequency (13.56 MHz) generators are designed to operate at $50\Omega$ load per the international standard. In order to get maximum forward power, the matching network is required. A schematic of the power supply for generating RF plasma in capacitively coupled plasma unit is shown in the Figure 2.3.

![Figure 2.2. A schematic for RF plasma generation.](image)

Oxygen and helium plasmas were generated by capacitively coupled plasma for all the experiments. The RF generator (13.56 MHz) is connected the stainless steel (4 way cross with 2.75” CF) chamber through a custom-made matching network by BNC cables. The matching network (L type) is a combination of variable capacitors (50-1200 pF) and inductor (400 nH). The picture of the CCP matching network is shown in Figure 2.2 (top) and equivalent circuit diagram is shown in bottom of Figure 2.2. One electrode in CCP unit was Al coil of several turns and inner diameter 3/4” while the chamber ground was used as another electrode.
Figure 2.3. (Top): Picture of matching network for CCP unit. (Bottom): Equivalent circuit diagram.

Details of the experimental set up and parameters of plasma generations are discussed in the individual chapter. Various characterization methods like x-ray photoelectron spectroscopy (XPS) for surface chemistry and for chemical analysis, atomic force microscopy (AFM) were used measuring the surface topography of the samples and a goniometer was used to measure the contact angle measurements.
During the plasma exposure, the sample was connected to ground but could also be set to a specific bias potential if desired by using a DC power supply. The plasma exposure of gases is done in the introduction chamber and the radical exposure was done by transferring the sample into the main chamber (Figure 2.1) via the feed-through and rotating the sample so that the surface is centered and facing the thermal cracker (Figure 2.1, 2.4). The turbo-molecular pump was "shuttered" with a gate valve and the chamber was back filled with the gas vapor from to a pressure of 50 m torr. Once the chamber pressure was stable at 50 m torr of gas, the plasma was generated. Once the plasma was generated the plasma pressure was maintained at this pressure during exposure by adjusting the leak valve. The ion gauge pressure maximum is 5.0 X 10^{-3} Torr so during plasma operation the pressure was monitored using a baratron gauge that was calibrated with the ion gauge.

Figure 2.4. Schematic of the introduction chamber which includes the aluminium coil and the sample on a feedthrough.
We also acknowledge the support of Verbeck group in UNT for the design of the matching network.

2.3 Characterization Methods

2.3.1 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a very useful surface/mid surface (<10 nm) characterization method that can yield information relating to film composition, chemical bonding environments, and oxidation states. XPS spectra displayed in the following chapters were collected using a Physical Electronics 140 mm mean radius hemispherical electron analyzer operated at constant pass energy. Core-level photoemission spectra are collected by bombarding the surface with characteristic x-ray radiation at energies of either 1253.6 or 1486.6 eV corresponding to Mg Kα and Al Kα, respectively. Exposing a surface to x-ray radiation causes the ejection of core-electrons (photoelectrons) as diagramed in Figure 2.4.

The binding energy of core elections can be found using [19, 20]:

\[
BE = hv - KE - \Phi \tag{Eq. 2.1}
\]

where \(BE\) is the binding energy of the core electron (eV), \(hv\) is the excitation x-ray energy, \(KE\) is the kinetic energy of the core electron (eV) and \(\Phi\) is the work function of the electron energy analyzer (eV). The work function term is from the analyzer and not the sample and corrects for the difference in vacuum levels between the sample and the analyzer. In a typical instrument setup, Fermi level of the sample and the analyzer align due to being held at ground [8,9]. The work function values are typically around 3-5 eV.
Figure 2.5. Schematic of the X-ray source and analyzer are calibrated to an internal standard. This takes into account any surface charging that is usually present in semi-conducting and insulating samples. All the XPS spectra reported in sequential chapters were either referenced to C (1s) at 285.0 eV [8,9].

Figure 2.6. Core-level photoemission process.

The fact that XPS is surface/near surface sensitive allows for overlayer film thickness to be calculated from XPS core-level spectra based on how the photoelectrons from the substrate interact with the overlayer. There are two methods to calculate the film thickness: (1) absolute
intensity attenuation of the substrate with overlayer growth and (2) comparing the overlayer intensity to the intensity of the substrate. The later is usually the chosen method as the first method does not account for different flux of x-rays to the surface. However, in both cases the experimental error in thickness measurements are <10 %. The XPS intensity from the substrate is [19]:

\[ I_B = I_B^\infty e^{-\frac{d}{\lambda \cos(\Theta)}} \]  
(Eq. 2.2)

where \( I_B \) and \( I_B^\infty \) are the intensity and atomic sensitivity factor (ASF) for substrate, \( d \) is the overlayer thickness (Å), \( \lambda \) is the inelastic mean free path (IMFP) of a photoelectron from the substrate through the overlayer, and \( \cos(\Theta) \) is the angle between the surface normal and the axis of the analyzer. When using the absolute attenuation model (1) equation 2.2 can be solved for \( d \):

\[ d = -\ln\left(\frac{I_B}{I_0}\right) \cdot \lambda \]  
(Eq. 2.3)

where \( I_B \) and \( \lambda \) are the same as above and \( I_0 \) is the initial intensity of the substrate before deposition/overlayer film growth. In using method (2), a relationship for the overlayer where the overlayer intensity is [19]:

\[ I_A = I_A^\infty (1 - e^{-\frac{d}{\lambda \cos(\Theta)}}) \]  
(Eq. 2.4)

where \( I_A \) and \( I_A^\infty \) are the intensity and ASF from the overlayer, \( \lambda \) is now the IMFP for the photoelectron in the overlayer through the overlayer, and \( d \) and \( \cos(\Theta) \) are the overlayer thickness (Å) and angle between the sample and the analyzer axis, respectively. The thickness of the overlayer can be found by plotting equations 2.2 and 2.4 as a function of overlayer thickness (d) and where the two lines intersect is the overlayer thickness.
In order to determine the overlayer thickness via the above method and what makes
XPS surface/near surface sensitive in the IMFP ($\lambda$) of photoelectrons is relatively small (<50Å)
when the kinetic energies are <1000 eV [21]. The IMFP is defined as the average distance an
electron can travel without enduring an inelastic collision [21]. IMFP values are calculated
based on the TPP-2M model [8, 10, 11]:

$$\lambda = \frac{E}{E_p^2} [\beta \ln(y E) - (C/E) + (D/E^2)] \quad (Å) \quad (Eq. 2.5a)$$

$$\beta = -0.10 + 0.944 (E_p^2 + E_g^2)^{-1/2} + 0.069 \rho^{0.1} \quad (Eq. 2.5b)$$

$$y = 0.191 \rho^{-1/2} \quad (Eq. 2.5c)$$

$$C = 1.97 - 0.91 U \quad (Eq. 2.5d)$$

$$D = 53.4 - 20.8 U \quad (Eq. 2.5e)$$

$$U = N_v \rho / M = E_p / 829.4 \quad (Eq. 2.5f)$$

where $E_p = 28.8 (N_v \rho / M)^{1/2}$ (eV) and is defined as the free electron plasmon energy, $E_g$ (eV) is
the band gap of the material, $\rho$ is the density (g cm$^{-3}$), $N_v$ is the number of valence electrons
per atom, and $M$ is the atomic weight.

2.3.2 Atomic Force Microscopy (AFM)

AFM was used to monitor the surface topography of the OSG film before and after various
plasma treatments. All the measurements were done in contact mode by using a silicon nitride
probe over an area of 1 µm × 1µm. As shown in Figure 2.9, it operates by a scanning tip
attached to the end of the cantilever across the sample surface and monitors the changes in the
cantilever deflection by a photodiode detector [12]. The force between the tip and the sample
is kept constant by maintaining a constant cantilever deflection. The constant deflection is
maintained by a feedback loop. The distance the scanner moves vertically at each data point on the sample surface is used to make the topographic image of the sample surface.

Figure 2.7. Schematic of an AFM in contact mode.

Details about the surface morphologies of the silicon nitride film during various plasma exposures are discussed in Chapter 5.

2.3.3 Thermal Cracker

Oxygen radicals in the experiment were generated from a commercially available thermal cracker. A schematic of the thermal cracker is shown in Figure 3.2. High purity oxygen gas from the cylinder was fed through the leak valve, which thermally dissociates when pass through the Ir tube (at roughly at 1000°C by filament heating) [13]. Thermal shielding of the source resulted in negligible sample temperature increase (<20 K). The source was operated at
a total O$_2$ pressure of 5X10$^{-6}$ torr resulting in 45% dissociation efficiency[14, 15]. Exposure uncorrected for ion gauge sensitivity or flux to the sample are reported in terms of Langmuir (L); 1 L=10$^{-6}$ torr sec. To correct for sample charging during exposure to x rays, the peak C(1s) XPS binding energy was set to 285.0 eV in agreement with the experimental value for adventitious carbon [16]. This resulted in core level binding energies for the silicon and copper surface similar to those reported previously, after accounting for the shift in the C (1s) reference peak to 285 eV.

![Schematic of the commercially available thermal cracker.](Image)

Figure 2.8. Schematic of the commercially available thermal cracker.

2.3.4 Contact Angle Measurements

A goniometer was used to measure the contact angles on the silicon nitride and oxynitride samples before and after the plasma exposure. These measurements allow insight...
into the most fundamental properties of both liquids and solids, including their cohesive forces, adhesive behavior, wetting properties, and morphological properties[17]. Silicon surfaces in the industry are modified both by wet-chemical and dry plasma surface treatments [18]. We have chosen, in this investigation, to explore the wetting properties of surfaces obtained after some commonly used plasma etching procedures. In addition, we have also included a few surface treatments that could be expected to generate very stable hydrophilic and surfaces. The degree of hydrophilicity of different surfaces, and the stability after each plasma exposure are parameters of interest. The hydrophilicity is believed to be important for the interaction between the silicon surface and epoxy. We have investigated the passivation of the silicon nitride surface after the plasma exposure by different gases.

The theory behind the measurement of contact angle with the goniometer is Young’s equation [19]. Young's equation is used to describe the interactions between the forces of cohesion and adhesion and measure what is referred to as surface energy. The interaction between a liquid and a solid involves three interfaces; the solid-liquid interface, the liquid-vapor interface and the solid-vapor interface. Each of these interfaces has an associated surface tension, $\gamma$, which represents the energy required to create a unit area of that particular interface. At equilibrium, force equilibrium along the X axis provides a relation between the angle, $\theta$, and the surface tensions of the three interfaces. This is called Young's equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos(\theta) \quad (19)$$

where $\gamma_{SG}$, $\gamma_{SL}$ and $\gamma_{LG}$ are the surface tensions of interfaces solid/gas, solid/liquid and liquid/gas respectively. $\theta$ is the angle between a liquid drop and a solid surface, called the contact angle.[ 19]
The Figure 2.9 below illustrates the relationship between contact angle, surface tension of the solvent and the nature of the substrate. A hydrophilic substrate results in complete wetting, which corresponds to high surface tension and the hydrophobic substrate results in partial wetting.

Even though the theory mentioned above explains the relationship between contact angle and surface energy, relatively little work has been published on the contact angles on real engineering surfaces, and how roughness dictates the change in the contact angle and surface energy. Wenzel [19] proposed a theory in which the increase in the surface area of a roughened plane is shown to be responsible for the change of the contact angle. His theory was based on the assumption that a rough surface extends the solid-liquid interface area in comparison to the projected smooth surface. Wenzel’s relation thus shows that surface roughness will decrease the contact angle for a droplet on a hydrophilic surface and increase the contact angle for a droplet on a hydrophobic surface [19-21].

This thesis discusses the contact angle after exposure to the oxygen, helium and ammonia plasma and after the passivation of the substrates with hydrogen and ammonia and the relationship between the roughness of the surfaces and contact angle measurements.
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CHAPTER 3

SURFACE CLEANING FOR ENHANCED ADHESION TO PACKAGING SURFACES: EFFECT OF OXYGEN AND AMMONIA PLASMA

3.1 Introduction

Oxygen plasma cleaning is a well-known method for removing carbon and other contaminants from Si, silicon nitride (Si₃N₄) and silicon oxynitride (SiOₓNy) surfaces [1-3] in order to enhance wettability (hydrophilicity) [4] and bondability to adhesives [5]. Although effective removal of carbon and other surface contamination is an important issue in plasma cleaning, the composition of the plasma-treated surface, and hydrophilicity of the surface upon and during ambient exposure are also of practical importance. Hydrophilicity is generally correlated with bondability to epoxy or similar polar adhesives [5].

In-situ (non-plasma) cleaning of well-characterized Si₃N₄ surfaces has been studied by surface science methods [6], and the effects of O₂ plasma cleaning of nitrides prior to photoresist deposition have been analyzed with respect to effects on surface blistering [7]. However, an understanding of the specific chemical changes induced by direct plasma treatment –either O₂ or other gases is sparse. Key scientific and practical issues for plasma cleaning therefore include plasma-induced changes in surface composition, and the hydrophilicity of such surfaces as a function of time of exposure to ambient.

This report presents in-situ XPS results comparing the effects of O₂ plasma and NH₃ plasma treatments on the surface composition of SiOₓNy surfaces. Similar results have been obtained for corresponding plasma treatments of Si₃N₄ surfaces. Additionally, ex-situ contact angle data are presented regarding the evolution of contact angle (and therefore
hydrophobicity) with post-plasma exposure time to ambient. XPS results reported here indicate that both O₂ and NH₃ plasma treatments of SiOₓNy and SiNx surfaces effectively remove contaminant surface carbon, but yield surfaces with different chemical compositions. Oxygen plasma treatment yields formation of a highly reactive silica overlayer ~25Å thick. In contrast, NH₃ plasma yields some additional surface oxidation but no substantial silica overlayer formation. Both plasma treatments result in surfaces with similar evolution of contact angle vs. time of exposure to ambient; although O₂ treated surfaces have a lower initial contact angle. Post- O₂ plasma exposure to NH₃ vapor prior to ambient exposure has a negligible effect on the rate of increase in contact angle with ambient exposure. However, post-O₂ plasma exposure to H₂ significantly retards the increase in contact angle as a function of subsequent time of exposure to ambient. The results indicate that such a methodology may provide a practical approach to enhancing the hydrophilicity/bondability of surfaces exposed to ambient after plasma cleaning.

3.2 Experimental

XPS measurements were carried out in a surface science system described previously in detail [8]. Briefly, the system consisted of a sample introduction/reaction chamber, turbo molecularly pumped (base pressure; 1 x 10⁻⁷ Torr) and a turbomolecularly pumped UHV analysis chamber (base pressure 5 x 10⁻⁵ Torr), with sample transport between chambers accomplished by a re-entrant transfer rod/sliding Teflon seal arrangement without sample exposure to atmosphere.

In the reaction chamber, a RF source operating at 13.56 MHz was used to generate the plasma in capacitively coupled mode. The turbo pumping speed was controlled by a butterfly
valve to allow millitorr pressure and dynamic flow for plasma generation. Plasma conditions were 20W power, 45 millitorr pressure and at ambient temperature. 

Samples consisted of SiOxNy or SiN samples scored into 1 cm x 1 cm samples. These wafers were intentionally contaminated with mold release and used without further surface preparation. Since both SiN and SiOxNy samples were exposed to ambient for long time periods prior to these experiments, both the nominal nitride and oxynitride surfaces had surface oxygen and nitrogen, as well as contaminant carbon due to exposure to a common mold-release compound and exposure to ambient. Similar results to those reported here were also observed for both SiN and SiOxNy wafer samples contaminated with adventitious carbon without mold release. Therefore the data presented here do not appear to be specific to the source of adventitious carbon or to the detailed Si/O/N composition of the surface.

XPS data were acquired in the UHV analysis chamber with an unmonochromatized MgKα x-ray source operating at 15 kV and 300 W, and a 100 mm mean radius hemispherical sector analyzer with channeltron detector, operated in constant pass energy mode (23 eV). XPS data were analyzed by standard methods [9]. Sample temperature during plasma exposure was monitored using a thermocouple connected to the Ta sample holder. To correct the sample charging during XPS, the peak maximum for the C(1s) feature was set at binding energy 285.0 eV.

Contact angle data were acquired ex-situ using a commercial goniometer in ambient, with de-ionized water. Contact angles were acquired after varying periods of time on a given sample, in order to determine the evolution of contact angle with time of exposure.
3.3 Results and Discussion

3.3.1 XPS Results for NH$_3$ and O$_2$ Plasma Treatment

The evolution of XPS C(1s) and Si(2p) spectra are shown in Figure 3.1 for an SiO$_x$N$_y$ surface exposed to NH$_3$ plasma (Figure 3.1a-b, respectively), and to an O$_2$ plasma (Figures 3.1c-d, respectively). Corresponding data for O(1s) and N(1s) core levels are shown in Figure 3.2. (Very similar results were obtained for NH$_3$ or O$_2$ plasma treatment of SiN$_x$ surfaces). The data in Figure 3.1a-b demonstrate that NH$_3$ plasma effectively removes contaminant carbon from the surface region (Figure 3.1a) with a small increase in Si(2p) intensity and shift towards higher binding energy (Figure 3.1b). The observed increase in Si(2p) intensity is consistent with removal of the attenuating carbon overlayer, as no further change in Si(2p) signal is obtained after the initial 3 min plasma exposure that removes surface carbon (Figure 3.1a). The shift in Si(2p) binding energy—from 102.3 to ~ 103 eV—indicates enhanced oxidation of Si within the surface region of the substrate[10].

The data in Figure 3.1c-d indicate that O$_2$ plasma similarly removes carbon from the sample (Figure 1c), but with a substantial enhancement of Si (2p) intensity and shift towards a binding energy of 103.3 eV, characteristic of SiO$_2$ [10]. These changes are consistent with surface oxidation, but greater changes in Si (2p) intensity and binding energy observed for O$_2$ plasma treatment indicate a substantially greater degree of surface Si oxidation than that observed for NH$_3$ treatment.

These observations are consistent with the data in Figure 3.2. NH$_3$ plasma treatment yields a slight increase in N (1s) intensity and shift towards higher binding energy (Figure 2a). The observed increase in N (1s) peak binding energy, from 398.5 eV to ~ 399 eV is consistent
with the further oxidation of surface silicon nitride species to oxynitride species [11]. In contrast, O₂ plasma treatment yields a significant increase in N (1s) intensity for 3 min plasma treatment, and slight shift towards higher binding energy, but then a sharp decrease in N (1s) intensity at longer treatment times (Figure 2c). O₂ plasma treatment also yields an initial significant increase in O (1s) intensity, and shift to higher binding energy after 3 min plasma exposure (Figure 2d), with little significant further change in intensity, and perhaps a slight broadening in the width of the peak, at longer treatment times.

The data in Figures 3.1 and 2.2 are consistent with NH₃ plasma removal of surface carbon species, coupled with the increased oxidation of the sample surface. The negligible change of N (1s) intensity with longer treatment times, however, indicates that the treated surface does not exhibit formation of a significant silica or other non-nitride overlayer. In contrast, O₂ plasma treatment particularly at longer exposure times induces a significant decrease in N(1s) intensity (Figure 3.2c) and corresponding changes to the O(1s) spectra (Figure 3. d) that indicate formation of a silica overlayer. Attributing the decrease in N (1s) intensity at longer treatment time to attenuation by an SiO₂ overlayer indicates an SiO₂ overlayer thickness of ~25 Å after 20 min O₂ plasma treatment.

Similar results were observed for NH₃ and O₂ plasma treatment of SiₓNᵧ surfaces demonstrating that results shown in Figures 3.1 and 3.2 are not specific to silicon nitride/oxynitride surfaces of a specific composition. In general, both O₂ and NH₃ plasmas efficiently remove surface carbon, but prolonged exposure to O₂ plasma yields formation of a silica overlayer. In contrast, such overlayer formation is significantly inhibited during longer NH₃ plasma exposure times.
3.3.2 Contact Angle Measurements

The evolution of contact angle measurements for SiO$_x$N$_y$ surface after 30 min exposure to NH$_3$ plasma and subsequent exposure to ambient is shown in Figure. 3.3 (open circles). Corresponding data after 30 min O$_2$ plasma exposure are also shown in Figure. 3.3 (closed circles). The data indicate that O$_2$ plasma treatment initially yields a contact angle of ~ 0 degree, substantially more hydrophilic than that observed immediately after NH$_3$ plasma treatment, and indicating that the SiO$_2$-like surface developed upon significant O$_2$ plasma exposure is extremely polar. However, immediately upon exposure, the contact angles of both NH$_3$ plasma-treated and O$_2$ plasma-treated SiO$_x$N$_y$ treated surfaces increase rapidly with ambient exposure over the next ~ 5 hours, although the contact angle for the O$_2$ plasma treated surface is still lower than that of the NH$_3$ plasma-treated surface (Figure 3.3.) At longer times, the contact angles of both NH$_3$ plasma-treated and O$_2$ plasma-treated surfaces relax to a limiting value of ~ 400, similar to that observed before plasma treatment. XPS spectra acquired as a function of time of ambient exposure (not shown) indicate that this increase in contact angle is associated with the re-growth of an adventitious carbon layer.

The data in Figure 3.3 raise the issue as to whether plasma-treated surfaces can be passivated to slow the increase in contact angle (decrease in hydrophilicity) with time of ambient exposure. Therefore, surfaces exposed to O$_2$ plasma were subsequently exposed to either NH$_3$ gas (i.e., no plasma) or H$_2$ gas with the sample at room temperature, but prior to any ambient exposure. Gas exposure conditions were: pressure = 1×10$^{-4}$ Torr, exposure time = 1000 sec.
Contact angle data for evolution of an O$_2$-plasma cleaned SiO$_x$N$_y$ surface subsequently exposed to NH$_3$ gas are compared in Figure 3.4 to the contact angle evolution for a similarly treated surface but without NH$_3$ post- O$_2$ plasma exposure. The data indicate that the NH$_3$ post-O$_2$ plasma treatment had no significant effect on the evolution of contact angle with time of exposure to ambient.

In contrast, data in Figure 3.5 demonstrate that post-plasma exposure to H$_2$ gas yields a substantial passivation effect. The data show that an initial exposure to H$_2$ gas prior to ambient exposure still results in a rapid initial rise in contact angle over the first ~ 2-4 hours of ambient exposure to ~ 250. However, at longer time, the contact angle for the H$_2$ treated surface remains roughly constant or only slowly increases. In contrast, the contact angle of the O$_2$ plasma-treated surface increases monotonically at longer times to a value of ~ 440, similar to behavior observed in Figures 3.3 & 3.4, for O$_2$ plasma treated surfaces without any post plasma treatment or with exposure to NH$_3$ gas. The data in Figure 3.5 therefore demonstrate that exposure to H$_2$ gas immediately after O$_2$ plasma treatment but prior to any ambient exposure substantially slows the increase in contact angle due to adventitious carbon recontamination after exposure to atmosphere. The failure of NH$_3$ post plasma treatment to have any effect on the evolution of contact angle vs. time (Figure 3.4) strongly suggests reactive sites at the O$_2$ plasma-treated silica surface are acidic in nature, so that electron donation via the NH$_3$ lone pair does not occur to any large extent. In contrast, a surface defect resulting in a Si or O radical or negative ion could result in a facile reaction with H$_2$, e.g.:

\begin{align*}
(1a) \text{SiO}^\bullet + H_2 & \rightarrow \text{SiOH} + \text{Hadsorbed} \\
(1b) \text{Hadsorbed} + \text{Hadsorbed} & \rightarrow H_2
\end{align*}
Further experimental work is required to understand this chemistry in detail. Clearly, however, post-plasma treatments are possible to retard increase in contact angle upon ambient exposure, and H\textsubscript{2} plasma treatment can make a significant difference of plasma exposure times beyond \(~\)4 hours under these conditions (Figure 3.5). Additionally, gases other than H\textsubscript{2} may be preferred for safety or other concerns, and experiments in this area are on-going.

3.4 Summary and Conclusions

The data reported here e that O\textsubscript{2} or NH\textsubscript{3} plasma treatment of silicon nitride or silicon oxynitride surface yields removal of surface carbon, but with the growth of an SiO\textsubscript{2} overlayer \(~\)25 Å thick under the plasma conditions employed. In contrast, NH\textsubscript{3} plasma treatment results in the removal of surface carbon, but with significantly less surface oxidation, and a silica-like overlayer average thickness \(<\)25 Å. Both O\textsubscript{2} and NH\textsubscript{3} plasma treatments yield low surface contact angles (lower for O\textsubscript{2} treatments), but hydrophobicity and contact angle increase rapidly upon exposure to ambient, particularly during the first \(~\)5 hours of ambient exposure, but also at longer ambient exposure times. Post plasma exposure to H\textsubscript{2} (gas, no plasma at room temperature prior to ambient exposure, however, significantly retards the increase in contact angle at ambient exposure times longer than \(~\)48 hours. In contrast, similar post-plasma exposures to NH\textsubscript{3} had no significant effect. The data therefore indicate that post plasma exposure to H\textsubscript{2} or perhaps other agents is a promising route towards maintaining surface hydrophilicity upon ambient exposure.
Figure 3.1. Evolution of (a) C(1s) and (b) Si(2p) core level spectra, respectively, as received (solid trace), and upon NH$_3$ plasma treatment of SiOxNy after (-+-) 3 min plasma treatment and after (-o-) 20 min plasma treatment; (c,d) corresponding data after O$_2$ plasma treatment.

Figure 3.2. (a,b); Evolution of N(1s) and O(1s) core level spectra, respectively, as received (solid trace), upon NH$_3$ plasma treatment of SiOxNy after (+-) 3 min plasma treatment, and after (-o-) 20 min plasma treatment; (c,d) corresponding data after O$_2$ plasma treatment.
Figure 3.3. Evolution of contact angle for SiOxNy exposed to (●) 20 min O2 plasma treatment and subsequent exposure to ambient atmosphere; (○) 20 min NH3 plasma treatment and subsequent exposure to ambient atmosphere.

Figure 3.4. Evolution of contact angle with time of ambient exposure for SiOxNy surface exposed to (▼) O2 plasma, or (●) O2 plasma + NH3 gas exposure.
Figure 3.5. Evolution of contact angle with time of ambient exposure for SiOxNy surface exposed to ■ O₂ plasma, or ▲ O₂ plasma + H₂ gas exposure.

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CHAPTER 4

SURFACE CLEANING FOR ENHANCED ADHESION TO PACKAGING SURFACES: EFFECT OF O₂ RADICALS AND He PLASMA

4.1 Introduction

O₂ plasma cleaning is a well-known method for removing carbon and other contaminants from Si, silicon nitride (SiNₓ) and silicon oxynitride (SiOₓNᵧ) surfaces [1-3] in order to enhance wettability (hydrophilicity) [4] and bondability to adhesives [5]. Although effective removal of C and other surface contamination is an important issue in plasma cleaning, the composition of the plasma-treated surface, and maintenance of surface hydrophilicity upon ambient exposure are also of practical importance.

In-situ (non-plasma) cleaning of well-characterized Si₃N₄ surfaces has been studied by surface science methods [6], and the effects of O₂ plasma cleaning of nitrides prior to photoresist deposition have been analyzed with respect to effects on surface blistering [7]. However, an understanding of the specific chemical changes induced by direct plasma treatment –either O₂ or other gases—is sparse. Key scientific and practical issues for plasma cleaning are plasma-induced changes in surface composition, surface roughness, and the hydrophilicity of such surfaces as a function of time of exposure to ambient.

This report presents in-situ XPS and ex-situ AFM data comparing the effects of O₂ plasma and He plasma treatments on the surface composition, topography, and hydrophilicity of SiOₓNᵧ surfaces. Similar results have been obtained for corresponding plasma treatments of SiₓNᵧ surfaces. Additionally, ex-situ contact angle data are presented regarding the evolution of contact angle (and hydrophilicity) with post-plasma time of exposure to ambient. XPS results
reported here indicate that O₂, He plasma and O radical treatments of SiOₓNᵧ and SiNₓ surfaces effectively remove contaminant surface carbon, but yield surfaces with different chemical compositions. Oxygen plasma and He plasma treatment yield formation of a highly reactive silica over layer ~25Å thick. In contrast, O radicals yield some surface oxidation but no substantial silica over layer formation, indicating that silica overlayer growth is due to surface interactions with non-oxygen factors in the plasma environment. O₂ plasma-treated surfaces have a lower initial contact angle and higher surface roughness than the He plasma-treated surfaces, due to greater surface roughness of the O₂ plasma-treated surface. The results indicate that O₂ plasma is more effective than He plasma in enhancing the hydrophilicity/bondability of surfaces exposed to ambient after plasma cleaning.

4.2 Experimental

XPS measurements were carried out in a surface science system described previously in detail [8]. Briefly, the system consisted of a sample introduction/reaction chamber, turbo molecularly pumped (base pressure; 1 x 10⁻⁷ Torr) and a turbomolecularly pumped UHV analysis chamber (base pressure 5 x 10⁻⁵ Torr), with sample transport between chambers accomplished by a re-entrant transfer rod/sliding Teflon seal arrangement.

In the reaction chamber, a RF source operating at 13.56 MHz was used to generate the plasma in capacitively coupled mode. The turbo pumping speed was controlled by a butterfly valve to allow millitorr pressure and dynamic flow for plasma generation. Plasma conditions were 20W power, 45 millitorr pressure and at ambient temperature. The oxygen radicals were generated using a commercial thermal cracker that generates radicals by dissociation against a hot Ir surface, producing O(³P) radicals [9]. The cracker was operated at 50W power, and 1x10⁵
torr total O$_2$ pressure. The estimated O$_2$ dissociation efficiency under these conditions is < 50% but was not measured directly. Therefore, O radical exposures are described simply in terms of total (O$_2$ + O) partial pressure and time of exposure; 1 Langmuir (L) = 10$^{-6}$ Torr-sec.

Samples consisted of SiO$_x$N$_y$ or Si$_x$N$_y$ wafers scored into 1 cm x 1 cm samples. These wafers were intentionally contaminated with mold release and used without further surface preparation. Since both Si$_x$N$_y$ and SiO$_x$N$_y$ samples were exposed to ambient for long time periods prior to these experiments, both the nominal nitride and oxynitride surfaces had surface oxygen and nitrogen, as well as contaminant carbon due to exposure to a common mold-release compound and to ambient. Similar results to those reported here were also observed for both Si$_x$N$_y$ and SiO$_x$N$_y$ wafer samples contaminated with adventitious carbon without mold release. Therefore the data presented here do not appear to be specific to the source of adventitious carbon or to the detailed Si/O/N composition of the surface.

XPS data were acquired in the UHV analysis chamber with an unmonochromatized MgK$_\alpha$ x-ray source operating at 15 kV and 300 W, and a 100 mm mean radius hemispherical sector analyzer with channeltron detector, operated in constant pass energy mode (23 eV). XPS data were analyzed by standard methods [10]. Sample temperature during plasma exposure was monitored using a thermocouple connected to the Ta sample holder. To correct the sample charging during XPS, the peak maximum for the C(1s) feature was set at binding energy 285.0 eV.

Contact angle data were acquired ex-situ using a commercial goniometer and de-ionized water in ambient. Surface roughness data were acquired ex-situ using a Veeco AFM in direct contact mode. Contact angles were acquired after varying periods of time of exposure to
ambient on a given sample, in order to determine the evolution of contact angle with time of exposure.

4.3 Results

4.3.1 XPS Results for O2 Plasma and O Radicals Treatment

The evolution of C(1s) and Si(2p) XPS spectra are shown in Figure 4.1 for an SiOxNy surface exposed to O radicals (Figure 4.1a,b respectively), and to an O2 plasma. (Figures 1c,d respectively). Corresponding data for O(1s) and N(1s) core levels are shown in Figure 4.2. (Very similar results were obtained for corresponding treatments of SixNy surfaces. The data in Figure 4.1a,b demonstrate that O radicals effectively remove contaminant carbon from the surface region (Figure 4.1a) with a small increase in Si(2p) intensity and shift towards higher binding energy (Figure 4.1b). The observed increase in Si(2p) intensity is consistent with removal of the attenuating carbon overlayer, as no further change in Si(2p) signal is obtained after the initial 3 min plasma exposure that removes most of the surface carbon (Figure 4.1a). The shift in Si(2p) binding energy—from 102.3 to ~ 103 eV—indicates enhanced oxidation of Si within the surface region of the substrate [11].

The data in Figure 4.1c,d indicate that O2 plasma similarly removes carbon from the sample (Figure 4.1c), but with a substantial enhancement of Si(2p) intensity and shift towards a binding energy of 103.3 eV, characteristic of SiO2 [11]. These changes are consistent with surface oxidation, but greater changes in Si(2p) intensity and binding energy observed for O2 plasma treatment indicate a substantially greater degree of surface Si oxidation than that observed for exposure to O radicals.
These observations are consistent with the data in Figure 4.2. Oxygen radical treatment yields a slight increase in N(1s) intensity and shift towards higher binding energy (Figure 4.2a). The observed increase in N(1s) peak binding energy, from 398.5 eV to ~ 399 eV is consistent with the further oxidation of surface silicon nitride species to oxynitride species [12]. In contrast, O₂ plasma treatment yields a significant increase in N(1s) intensity for 3 min plasma treatment, and slight shift towards higher binding energy, but then a sharp decrease in N(1s) intensity at longer treatment times (Figure 4.2c). O₂ plasma treatment also yields an initial significant increase in O(1s) intensity, and shift to higher binding energy after 3 min plasma exposure (Figure 4.2d), with little significant further change in intensity, and perhaps a slight broadening in the width of the peak, at longer treatment times.

The data in Figures 4.1 and 4.2 are consistent with O radical removal of surface carbon species, coupled with the increased oxidation of the sample surface. The negligible change of N(1s) intensity with longer treatment times, however, indicates that the treated surface does not exhibit formation of a significant silica or other non-nitride overlayer. In contrast, O₂ plasma treatment, particularly at longer exposure times, induces a significant decrease in N(1s) intensity (Figure 4.2c) with significant increase in the intensity of O(1s) spectrum (Figure 4.2d) that indicates formation of a silica overlayer. Attributing the decrease in N(1s) intensity at longer treatment time to attenuation by an SiO₂ overlayer yields an an estimate for average SiO₂ overlayer thickness of ~ 25 Å after 20 min O₂ plasma treatment.

The effects of He plasma treatment on core level XPS spectra from a SiOₓNᵧ surface are shown in Figure 4.3a. 3 min plasma treatment effectively removes the contaminant C overlayer (Figure 4.3a). There is also a substantial increase in the intensity of the Si(2p) feature (Figure
4.3b) and a shift towards higher binding energy, which corresponds to additional oxidation of the Si bonding environment, similar to what is observed for O\textsubscript{2} plasma treatment (Figure 4.1d). The increase in intensity of the O(1s) feature (Figure 4.3c) and decrease in the intensity of the N(1s) peak in Figure 4.3d also indicate the formation of a silica overlayer.

Similar results were observed for O\textsubscript{2} radicals and plasma treatment of Si\textsubscript{x}N\textsubscript{y} surfaces, demonstrating that results shown in Figures 4.1 and 4.2 are not specific to silicon nitride/oxynitride surfaces of a specific composition. In general, both O\textsubscript{2} plasma and radicals efficiently remove surface carbon, but prolonged exposure to O\textsubscript{2} plasma and He plasma yields formation of a silica overlayer. In contrast, such overlayer formation is significantly inhibited during longer oxygen radicals exposure times. The data shows us that this overlayer formation is not due to the O radical-surface interactions, and that it also occurs in a non-O\textsubscript{2} plasma environment.

4.3.2 Contact Angle Measurements and AFM

The evolution of contact angle measurements for SiO\textsubscript{x}N\textsubscript{y} surface after 30 min exposure to He plasma and subsequent exposure to ambient is shown in Figure 4.4 (open circles). Corresponding data after 30 min O\textsubscript{2} plasma exposure are also shown in Figure 4.4 (closed circles). The data indicate that O\textsubscript{2} plasma treatment initially yields a contact angle of ~0 degree, substantially more hydrophilic than that observed immediately after He plasma treatment, and indicating that the SiO\textsubscript{2}-like surface developed upon significant O\textsubscript{2} plasma exposure is extremely polar. However, immediately upon exposure, the contact angles of both He plasma-treated and O\textsubscript{2} plasma-treated SiO\textsubscript{x}N\textsubscript{y} treated surfaces increase rapidly with ambient exposure over the next ~5 hours, although the contact angle for the O\textsubscript{2} plasma treated surface is still lower than
that of the He plasma-treated surface (Fig. 4.4.) At longer times, the contact angles of He plasma-treated and O₂ plasma-treated surfaces relax to limiting values of ~ 55° and 40° respectively. XPS spectra acquired as a function of time of ambient exposure indicate that this increase in contact angle is associated with the re-growth of an adventitious carbon layer (Figure 4.6).

The AFM data that is shown in Figure 4.5 demonstrate that plasma exposure to He and O₂ plasma yield different root mean square (rms) values. The AFM results show that an exposure to O₂ plasma yields a higher rms value (surface roughness) than that of the sample exposed to He plasma. Figure 4.5 shows that the surfaces exposed to O₂ plasma are rougher (rms value=0.822nm) and have a lower contact angle at 0° (Figure 4) whereas the surfaces exposed to He plasma are smoother (rms value=540nm) and have higher contact angle at 40° [13]. From the results, it can be recognized that the hydrophilicity of the substrate increases with increase in its roughness (RMS) value. Similar results were found after the plasma exposure on the Si₃Ny surfaces as well. The as-received SiOₓNy sample is rougher (Figure 4.4), but has a higher contact angle due to the contamination on the surface which is hydrophobic in nature. These results are also consistent with the XPS results after the post-plasma exposure to ambient (Figure 4.6), where the carbon coverage is very similar to the as-received substrate. Further experimental work is required to understand the difference in the chemistry of oxygen vs helium plasma in detail. The experiments regarding the passivation of He plasma exposed surfaces are under way.

4.4 Discussion

Data show that the O radical and O₂ plasma both remove the surface carbon. In case of
O radicals, we observed surface oxidation and formation of a silica overlayer (similar to a white paper). The growth of the silica overlayer is indicated by the N (1s) intensity, shift in the Si (2p) peak and the increase in the O(1s) intensity. Similar results were observed after exposure to He plasma which proves that the oxidation is not a direct function of the O species, but due to the reaction of the reactive surface sites formed due to the ions and VUV in the plasma with background gases like O₂ and H₂O. From Antoneko et al[14], it has been observed that the physical factors are responsible for the high rate of oxidation of silicon in a helium plasma containing a small amount of oxygen. It is believed that the determining factor is that the spectrum contains the intrinsic optical emission of excited helium atoms of the intense short-wave component in the near-ultraviolet (UV) region with a photon energy greater than 2.3 eV, which is greater than the value of 2.3–3.2 eV is associated with the Si–Si bond energy; it is also noted that the energy strength of Si–O bonds is twice the strength of Si–Si bonds. Thus, the optical emission of helium promotes the breaking of Si–Si bonds in the front of the oxidation reaction and thereby increases the rate of formation of oxide even at a low concentration of any oxidizer, residual oxygen in the chamber in this case.

This AFM data acquired and the comparison with contact angle is consistent with the Wenzel theory [13] which explains the importance of surface roughness on wettability of a surface. This theory is based on the fact that, given attractive interactions at the solid-liquid interface, a rough surface will be able to extend the solid-liquid surface interface area and therefore reduce the contact angle.

4.5 Summary and Conclusions

The data reported here proves that O₂ and He plasma treatment of silicon nitride or
silicon oxynitride surface yields removal of surface carbon, but with the growth of an SiO$_2$ overlayer ~ 25 Å thick under the plasma conditions employed. In contrast, O radical treatment results in the removal of surface carbon, but with significantly less surface oxidation. These results indicate that the oxidation of silicon by He plasma is not due to a chemical reaction but due to the physical factors, which break the Si-Si bonds and result in the formation of silica due to a reaction with the residual H$_2$O and O$_2$ in the chamber. Both O$_2$ and He plasma treatments yield low surface contact angles (lower for O$_2$ treatments), but hydrophobicity and contact angle increase rapidly upon exposure to ambient, particularly during the first ~ 5 hours of ambient exposure, but also at longer ambient exposure times. The AFM data also proves that exposure to oxygen plasma results in a more hydrophilic due to the higher roughness when compared to the He plasma.

Figure 4.1. (a) C(1s) and (b) Si(2p) XPS spectra of SiO$_x$N$_y$ exposed to a flux of O radicals. (c,d) corresponding data for O$_2$ plasma treatment. (a,b) or to an O$_2$ plasma (c,d). Solid trace is the as-received spectra, (+-) trace is after 600L exposure and (-o-) trace is after the 12,000 L plasma exposure.
Figure 4.2. XPS spectra of the SiO\textsubscript{x}N\textsubscript{y}. Solid trace is the as-received spectra, (−−+) trace is after 3 min exposure and (−o−) trace is after the 20 min plasma exposure. (a) and (c) are the N(1s) spectra for O radicals and O\textsubscript{2} plasma respectively. (b) and (d) are the O(1s) spectra for O radicals and O\textsubscript{2} plasma.

Figure 4.3. XPS spectra of the SiO\textsubscript{x}N\textsubscript{y} after He plasma exposure. Solid trace is the as-received spectra, (−−+) trace is after 600 L exposure and (−o−) trace is after the 12,000 L plasma exposure. (a) are the C(1s) spectra (b) are Si (2p) spectra, (c) are O(1s) spectra and (d) are the N(1s) spectra.
Figure 4.4. Graph of time of exposure to ambient vs. contact angle after 12,000 L plasma exposure on SiO$_x$N$_y$. Closed circles - O$_2$ plasma; open circles – He plasma.

Figure 4.5. Atomic force microscopy (AFM) obtained for: (a) fresh SiN, (b) after 12,000 L He plasma, (c) after 20 min O plasma, along with the corresponding root mean square (RMS) roughness values.

RMS = 1.061 nm  
RMS = 0.540 nm  
RMS = 0.822 nm
Figure 4.6. XPS spectra of the SiO$_x$N$_y$ (-O-) trace is the as-received spectra, (- ▲ -) trace is after exposure to ambient after exposure to 20 minutes of oxygen plasma.. (a) is C(1s) spectra, (b) is the N(1s) spectra, (c) is the O(1s) and (d) is the Si(2p)spectra.

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CHAPTER 5

SURFACE CLEANING OF COPPER FOR ENHANCED ADHESION: EFFECT OF PLASMA AND RADICALS

5.1 Introduction

Oxygen plasma cleaning is a well-known method for removing carbon and other contaminants from Cu, silicon nitride (SiNₓ) and silicon oxynitride (SiOₓNᵧ) surfaces [1-3] in order to enhance wettability (hydrophilicity) [4] and bondability to adhesives [5]. Although effective removal of carbon and other surface contamination is an important issue in plasma cleaning, the composition of the plasma-treated surface, and hydrophilicity of the surface upon and during ambient exposure are also of practical importance. Hydrophilicity is generally correlated with bondability to epoxy or similar polar adhesives [5],

In-situ (non-plasma) cleaning of well-characterized copper surfaces has been studied by surface science methods [6], However, an understanding of the specific chemical changes induced by direct plasma treatment—either O₂ or other gases—is sparse. Key scientific and practical issues for plasma cleaning therefore include plasma-induced changes in surface composition, and the hydrophilicity of such surfaces as a function of time of exposure to ambient.

This report presents in-situ XPS results comparing the effects of O₂ plasma and NH₃ plasma treatment on the surface composition of copper surfaces. XPS results reported here indicate that O₂ plasma treatments of copper surfaces effectively remove contaminant surface carbon, but the NH₃ plasma is not effective in removing the carbon contamination. O₂ plasma treatment yields formation of a copper oxide overlayer. In contrast, NH₃ plasma yields the removal of the oxide overlayer on the as-received sample. Both plasma treatments result in
surfaces with similar evolution of contact angle vs. time of exposure to ambient, although O$_2$ treated surfaces have a lower initial contact angle. Post- O$_2$ plasma exposure to hydrogen radicals prior to ambient exposure has a negligible effect on the copper oxide. However, post-O$_2$ plasma exposure to NH$_3$ and H$_2$ plasma results in the removal of most of the copper oxide. From these experiments, it is observed that removal of carbon can be accomplished by exposure to oxygen plasma and the resulting copper oxide can then be exposed to a reducing plasma like hydrogen or ammonia plasma for a Cu surface.

5.2 Experimental

XPS measurements were carried out in a surface science system described previously in detail [8]. Briefly, the system consisted of a sample introduction/reaction chamber, turbo molecularly pumped (base pressure; 1 x 10$^{-7}$ Torr) and a turbo molecularly pumped UHV analysis chamber (base pressure 5 x 10$^{-5}$ Torr), with sample transport between chambers accomplished by a re-entrant transfer rod/sliding Teflon seal arrangement without sample exposure to atmosphere.

In the reaction chamber, a RF source operating at 13.56 MHz was used to generate the plasma in capacitively coupled mode. The turbo pumping speed was controlled by a butterfly valve to allow millitorr pressure and dynamic flow for plasma generation. Plasma conditions were 20W power, 45 millitorr pressure and at ambient temperature.

Samples consisted of copper foil scored into 1 cm x 1 cm samples. These samples, were inserted without further surface preparation. Since the copper samples were exposed to ambient for long time periods prior to these experiments, these surfaces had surface oxygen as well as contaminant carbon due to exposure to ambient.
XPS data were acquired in the UHV analysis chamber with an unmonochromatized MgKα x-ray source operating at 15 kV and 300 W, and a 100 mm mean radius hemispherical sector analyzer with channeltron detector, operated in constant pass energy mode (23 eV). XPS data were analyzed by standard methods [9]. Sample temperature during plasma exposure was monitored using a thermocouple connected to the Ta sample holder. To correct the sample charging during XPS, the peak maximum for the C(1s) feature was set at binding energy 285.0 eV.

5.3 Results and Discussion

5.3.1 XPS results for O₂ and NH₃ Plasma Treatment

The evolution of XPS C(1s), O(1s) and Cu(2p) spectra are shown in Figure 5.1 for a Cu surface exposed to O₂ plasma (Figure 5.1a-c, respectively), and to NH₃ plasma (Figures 1d-f, respectively). The data in Figure 5.1a-c demonstrate that O₂ plasma effectively removes contaminant carbon from the surface region (Figure 5.1a) with a large increase in O(1s) intensity and shift towards higher binding energy (Figure 5.1b). The carbon thickness is reduced from 27Å on the as-received sample to 2 Å after the plasma exposure. The observed increase in O(1s) intensity (Figure 5.1b) is consistent with removal of the attenuating carbon overlayer. The shift in the O(1s) spectra from a higher binding energy to a lower binding energy and increase in the intensity was also observed. These results along with the shift in the Cu(2p) peak (Figure 5.1c) from 933.4 eV to 934.7 eV indicates enhanced oxidation of Cu, which corresponds to a change from Cu(OH)₂ in the as-received sample to CuO on the O₂ plasma exposed within the surface region of the substrate.
The data in Figure 5.1d-f indicate that NH₃ plasma does not completely remove carbon from the sample (Figure 5.1d), but a substantial increase of CuO intensity and decrease in the peak of a binding energy of 933.4 eV characteristic of CuO is observed, along with an increase in the feature at 932.7 eV, characteristic of Cu metal [10]. These changes are consistent with contamination removal, but greater changes in Cu oxide intensity and binding energy observed for NH₃ plasma treatment indicate a substantially greater degree of reduction of the copper oxide surface than observed for the sample that was treated with O₂ plasma. The carbon thickness before the plasma exposure was 32Å but more than 5Å of carbon was still remaining after the NH₃ plasma exposure.

The data in Figure 5.1 demonstrates that the oxygen plasma exposure results in the complete removal of carbon from the Cu surface but also results in further Cu oxidation. The sample exposed to oxygen plasma was then exposed to reducing plasmas like hydrogen and ammonia to attempt to reduce the oxide overlayer and to obtain a clean Cu surface. The data in Figure 5.2 show the XPS spectra of post plasma exposure to H₂ (Figure 2a-c) and NH₃ plasma (2d-f) respectively after oxygen plasma treatment. NH₃ plasma exposure after the oxygen plasma results in a significant removal of oxide overlayer, the calculated oxide thickness was ~2Å, which corresponds to the reduction in the intensity of the oxygen (1s) spectra (Figure 5.2b). Similar results were observed after the post plasma exposure to H₂ plasma but with a slightly less removal of oxide. The oxide thickness calculated after the H₂ plasma was ~3Å (Figure 5.2e). The post-plasma exposure by both NH₃ and H₂ plasma of the oxygen plasma treated surface yields an increase in CuO (2p) intensity (Figure 5.2c and 5.2f). These results along with the changes in the O(1s) spectra show that there is reduction of surface copper
oxide to the copper metal surface [11]. The data in Figure 5.3 show the XPS spectra of post plasma exposure to H radicals (Figure 5.3a-c) and H2 plasma (3d-f). The post-plasma treatment on the oxidized copper surface had slightly different results after exposure to H radicals and H2 plasma. The hydrogen radical exposure (30 minutes) induces a significant decrease in O(1s) intensity (Figure 5.3b) and corresponding changes to the Cu(2p) spectra (Figure 5.3-c) indicate the removal of the oxide, until approximately 9 Å of oxide is remaining on the surface. While, the H2 plasma also has similar effects after O2 plasma, H2 plasma is more effective in the removal of the Cu oxide, there is only ~3 Å oxide overlayer remaining after 30 minute exposure.

In general, both O2 and NH3 plasmas efficiently remove surface carbon, but prolonged exposure to O2 plasma yields formation of a oxide over layer which can be removed by post plasma exposure to a reducing plasma. In contrast, such an oxide overlayer formation is significantly inhibited during longer NH3 plasma exposure times, but with a less efficient removal of carbon.

5.3.2 Helium Plasma on Silicon Nitride and Copper Surfaces

The evolution of the XPS spectra of the C(1s) spectra of the Cu and SiOxNy surfaces after the exposure to He plasma is shown in Figure 5.4. The data indicate that He plasma treatment completely removes the carbon contamination, upon exposure on Silicon nitride and oxynitride surfaces, while not being effective on copper surfaces after the same exposures. The helium plasma also oxidizes the silicon nitride surfaces to form a SiO2 overlayer, while there was no oxidation observed on the copper surfaces. A corresponding graph of the rate of removal of Carbon vs time of exposure is shown in Figure 5.5. The rate of removal of the carbon contamination on silicon surfaces was faster when compared to copper (Figure 5.5). It was also
observed that the there is no change in the carbon removal after about 20 minute He plasma exposure. It is also observed that most of the carbon is removed in the first 3 minute exposure to helium on Si$_x$N$_y$ and SiO$_x$N$_y$ while the rate of removal of carbon on Cu is highest at approximately 20 minutes and stabilizes after that.

5.4 Summary and Conclusions

The data reported here shows that O$_2$ plasma treatment of copper surface yields complete removal of surface carbon, but with the growth of an Cu oxide overlayer ~ 25 Å thick under the plasma conditions employed. In contrast, NH$_3$ plasma treatment results in the incomplete removal of surface carbon, but with significantly less surface oxidation. Post-plasma exposure of the surfaces to the H$_2$ plasma and H$_2$ radicals yield less change in the oxide overlayer thickness while post plasma treatments with the NH$_3$ yield complete removal of the Cu oxide resulting in a metal surface. The Cu surfaces when exposed to the He plasma showed little effect on the removal of carbon overlayer while the same exposure resulted in a total removal of the carbon along with the surface oxidation. The data therefore indicate that post plasma exposure to NH$_3$ plasma after O$_2$ plasma is a promising route towards getting a surface free of contaminants and oxide overlayers.
Figure 5.1. (a,b,c) Evolution of C(1s), O(1s) and Cu(2p) core level spectra, respectively, as received (solid line), upon plasma treatment of Cu (○) after 15 min O₂ plasma treatment; (d,e,f) corresponding data after NH₃ plasma treatment.

Figure 5.2. (a,b,c) Evolution of C(1s), O(1s) and Cu(2p) core level spectra, respectively, as received (solid line), upon plasma treatment of Cu (▲) after 15 min O₂ plasma treatment, and (○) after 15 O₂ plasma + 45 mins H₂ plasma treatment; (d,e,f) corresponding data after O₂ plasma + NH₃ plasma treatment.
Figure 5.3. (a,b,c) Evolution of C(1s), O(1s) and Cu(2p) core level spectra, respectively, as received (solid line), upon plasma treatment of Cu(- ▲ -) after 15 min O₂ plasma treatment, and (-○-) after 15 O₂ plasma + 30 min H₂ radicals treatment; (d,e,f) corresponding data after O₂ plasma + H₂ plasma treatment.

Figure 5.4. (a); Evolution of C(1s) core level spectra, as received (solid trace), upon He plasma treatment of Cu (○) after 3 min plasma treatment, and (▲) after 20 min plasma treatment; (b) corresponding data upon He plasma treatment for SiON surface.
Figure 5.5. Evolution of rate of removal with time of ambient exposure to He plasma for (■) Cu surface or for (▲) SiON.

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CHAPTER 6

CONCLUSIONS AND FUTURE PROSPECTS

The effect of plasma and radicals on silicon nitride and oxynitride are discussed in this dissertation. The data reported here shows that O$_2$, He plasma treatment of silicon nitride or silicon oxynitride surface yields removal of surface carbon, but with the growth of an SiO$_2$ overlayer $\sim$ 25 Å thick under the plasma conditions employed. In contrast, NH$_3$ plasma and O radical treatment results in the removal of surface carbon, but with significantly less surface oxidation, and a silica-like overlayer average thickness <25 Å. Both O$_2$, He and NH$_3$ plasma treatments yield low surface contact angles (lower for O$_2$ treatments), but hydrophobicity and contact angle increase rapidly upon exposure to ambient, particularly during the first $\sim$ 5 hours of ambient exposure, but also at longer ambient exposure times. Post plasma exposure (after O$_2$ plasma) to H$_2$ (gas, no plasma at room temperature prior to ambient exposure, however, significantly retards the increase in contact angle at ambient exposure times longer than $\sim$ 48 hours. In contrast, similar post-plasma exposures to NH$_3$ had no significant effect. The data therefore indicate that post plasma exposure to H$_2$ or perhaps other agents are a promising route towards maintaining surface hydrophilicity upon ambient exposure. The AFM results on the samples exposed to He and O plasma showed that the hydrophilicity and the surface roughness are related and that the substrates with higher RMS values are more hydrophilic. The results also proved that the oxidation due to He plasma is due to the chemical reaction of the plasma, but due to the physical factors which break the Si-Si bonds and form a silica overlayer with the residual oxygen and water vapor in the chamber.
The data reported here also shows that the O$_2$ plasma treatment of copper surface yields complete removal of surface carbon, but with the growth of a Cu oxide overlayer $\sim 25$ Å thick. In contrast, NH$_3$ plasma treatment results in the incomplete removal of surface carbon, but with significantly less surface oxidation while the He plasma showed little to no change in the carbon spectrum. Post-plasma exposure of the surfaces to the H$_2$ plasma and H$_2$ radicals yield little to change in the Oxide overlayer thickness while post plasma treatments with the NH$_3$ yield complete removal of the Cu oxide resulting in a metal surface. The data therefore indicate that post plasma exposure to NH$_3$ plasma after O$_2$ plasma is a promising route towards getting a surface free of contaminants and oxide overlayers.
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