

REMOVING CONTAMINANTS FROM SILICON WAFERS
TO FACILITATE EUV OPTICAL CHARACTERIZATION

By

Ross Robinson

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Advisor: David D. Allred

Thesis Coordinator: Justin Peatross

Signature: _____

Signature: _____

Department Chair: Scott D. Sommerfeldt

Signature: _____

ABSTRACT

The extreme ultraviolet (EUV) is becoming increasingly important. The principle applications are space based astronomy and future lithography for integrated circuit computer chips. The main impediment to further development of efficient mirrors is the lack of reliable optical constants for various materials in this region of the electromagnetic spectrum. One reason for the unreliability of the optical constants is that the sample surfaces are contaminated with organic material when they are exposed to laboratory air. Opticlean®, oxygen plasma etch, high intensity UV light and Opticlean® followed with an oxygen plasma etch are evaluated as possible methods for removing the organic contaminants from the surface of silicon wafers. Processes are compared by experientially determined effectiveness, cleaning time and ease of use. DADMAC (polydiallyldimethyl-ammonium chloride) on silicon wafers is used as a standard contaminate. Effectiveness is judged by how well the DADMAC is removed and how clean the surface is. Ellipsometry is used to thickness of surface layers. XPS is used to look for trace contaminants, particularly carbon from DADMAC. Opticlean® leaves a residue. Oxygen plasma rapidly removes contaminants but can quickly oxidizes the silicon surface. The UV light leaves the surface clean after 5 minutes with little additional oxidation. Oxygen plasma effectively removes the Opticlean® residue. The recommended procedure is 5 minutes of high intensity UV light.

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CHAPTER I. EUV BACKGROUND

1.1 Importance of EUV Research

Recently, the extreme ultraviolet (EUV) region of the electromagnetic spectrum has become increasingly important in technological applications. Both EUV astronomy and EUV computer lithography require optical devices: mirrors, lenses, and other imaging equipment.

EUV lithography is the principle area that will see large scale use of EUV technology in the near future. In two generations of computer chip designs (each generation lasts eighteen months) the semiconductor industry will switch to using EUV lithography. Lithography uses a light source to project a computer chip pattern onto a silicon wafer covered with photosensitive material, much like exposing photographic paper to produce an image. However, unlike photography which uses visible light with wavelengths about 500 nm, EUV lithography uses much shorter wavelengths so that the chip components can be extremely small (down to a few nm, about 10 times the size of small molecules or large atoms). Thus, chips can be produced with significantly smaller feature size. By switching from visible light to EUV lithography, the manufacturing computer processor with core clock speeds in the 12-30 GHz (gigahertz) range will be possible. Current speeds are in the 3 GHz range.

1.2 Difficulties

Work in the EUV region is new because it is difficult. The poorly understood nature of interactions of light in this region with matter, together with contamination are the two main barriers that make further progress in this area difficult..

1.2.1 Interaction with matter

The behavior of light at these wavelengths as it passes through various materials is not well known. This behavior is quantified as the optical constants n and k (index of refraction and adsorption coefficient). For visible light, n and k have been tabulated for a vast array of materials. However, comparatively few materials have been examined in the EUV range and most tables that do exist are at least partially wrong. Additionally, at these short wavelengths, light interacts strongly with everything. Even air will completely absorb a EUV light beam in a few inches.

1.2.2 Contamination

The second barrier to progress is that the samples become contaminated in air. We have found that even when preventative measures are taken a layer of organic material (hydrocarbons) accumulates over time. This layer originates from the environment, is one or more nanometers thick and usually increases with exposure time. The presence of this contaminant layer makes it difficult to determine accurate optical constants because the effects of contaminates cannot be separated from the material under study. Ideally, the layer should be removed immediately prior to taking measurements. A detailed discussion of contamination sources and their effect on reflection is given in Appendix B.

1.3 Cleaning Methods

Attempting to find a solution to the hydrocarbon contamination problem, students in the Brigham Young University Department of Physics & Astronomy's EUV Research Group have researched three contaminant cleaning methods. The first method involves applying Opticlean[®], an industrial optical surface cleaner, to the silicon wafer samples. After the Opticlean[®] cures, it is peeled off. The peeled layer takes with it the larger contaminant particles that were on the surface. In the second method, a plasma etching system uses an oxygen plasma to remove the hydrocarbon buildup. The third method exposes the silicon wafer samples to a strong UV light from a commercial UV lamp in a cleaning station. The high energy UV light breaks up many of the hydrocarbon bonds, forming smaller molecules which then evaporate. This thesis reports the experimentally determined effectiveness, cleaning time, and ease of cleaning of each method.

For all three methods, a spectroscopic ellipsometer was used to measure the change of apparent thickness of the contaminant layer before and after cleaning. Furthermore, x-ray photoelectric spectroscopy (XPS) and scanning electron microscopy (SEM) were used to determine whether the cleaning methods had changed or damaged the original sample surface. A discussion of these diagnostic methods is found in Appendix A.

CHAPTER II EXPERIMENTAL METHOD

2.1 DADMAC

To study contaminate removal a standard contaminate is needed. This allows for the effect of the cleaning method in question to be separated from effects arising from variations in contamination. For these studies, we selected DADMAC (polydiallyldimethyl-ammonium chloride) as our standard material.

2.1.1 Background

DADMAC is a well characterized polymer used in nanotechnology for its self assembling properties. When dissolved in water it acquires a positive charge. To coat a surface, DADMAC is mixed into a salt solution. It will precipitate, coating any objects placed in the solution. As DADMAC precipitates on the surface, it arranges itself into long hydrocarbon-type chains.

The thickness of the polymer layer is limited by the fact that each DADMAC molecule is positively charged. As the polymer layer thickens by successive additions of monomer units, the total positive charge on the surface increases. This increasing positive charge repels new monomer units from the surface. This limits the polymerization to a thin film on the surface.

Thus, the presence of salt ions is a critical factor in determining final thickness. The salt disassociates in the DADMAC solution, forming positive sodium and negative chloride ions. The positively charged polymer film attracts the negatively charged chloride ions toward the surface. This layer of chloride ions shields the solution from the positive film charge. With the negative ions shielding the positive film, the DADMAC

units in solution are more likely to diffuse across the potential barrier, thus making the layer thicker. The result is that increasing the salt concentration increases the DADMAC film thickness.

The time the sample is in the salt and DADMAC solution also has an effect on the thickness of the sample. Initially, with very little DADMAC on the wafer surface there is only a weak positive charge on the surface and the film grows rapidly. As the film thickens the surface becomes increasingly positively charged, which slows film growth. Film thickness will asymptotically approach a final thickness. The asymptote is determined by the shielding effects of the salt ions. Thus after the initial period of rapid film growth, thickness is only loosely dependent on time in solution. This allows for several test wafers to be coated with very similar DADMAC films without precision equipment.

2.1.2 Use In This Study

In the oxygen plasma and UV studies we used DADMAC as the standard contaminate. We used a 1 milli-mol solution of DADMAC and 100 milli-mol of salt in this study. This produces an apparent equilibrium thickness of about 1 nm after 15-30 minutes. This thickness is a reasonable approximation of accumulated contamination. This thickness was determined by spectroscopic ellipsometry. The surfaces of clean silicon wafers quickly acquire a coat of silicon dioxide in air.

We measured the thickness of this native oxide layer (usually 1.6 to 1.9 nm) for each sample before depositing DADMAC. The apparent thickness of DADMAC is determined by subtracting this oxide thickness from the apparent total thickness.

This thickness is referred to as being the apparent thickness because ellipsometry is unable to distinguish between the DADMAC and the silicon dioxide underneath. Two facts are seen as contributing this situation. First, the silicon dioxide on the wafer and DADMAC have very similar index of refraction over the light wavelength range used by the ellipsometer. Second, the 1 nm thickness of the polymer film is 1/500 to 1/1000 the size of a wavelength of the light being used to analyze it. The overall effect is that there is not much to measure. We found that if both the thickness of the polymer and silicon dioxide layers are fitted for by ellipsometer modeling program as free parameters, the program will consistently fit the data so that the layer thicknesses are assigned either entirely to silicon dioxide or entirely to the polymer. This is unphysical, but in either case the thickness of the DADMAC layer can be calculated by simply subtracting the native oxide thickness measured prior to DADMAC application from this observed total thickness. In this thesis apparent oxide thickness refers to the thickness reported by the ellipsometer modeling software when both the native oxide and DADMAC are modeled together as silicon dioxide. The DADMAC solutions we used were prepared by Professor Robert Davis's research group in Professor Matthew Linford's laboratory. The procedure for application is simple and outlined in appendix C.

2.2 Opticlean[®]

We tested Opticlean[®] as a possible thin film cleaning technique. Specifically, we were concerned with determining first whether Opticlean[®] would leave behind a residue, and second would the application and removal process damage our thin films, for example, by pulling off pieces of our film.

2.2.1 Theory of Operation

Opticlean[®] is applied using a small brush, very much like fingernail polish. While drying, the polymer sticks to the surface, and the contaminants thereon. After drying a few moments, the polymer film is peeled from the surface. The theory is that contaminants and dust on the surface will bind to the polymer and be taken off with it.

2.2.2 Test Method

We used the following procedures to test whether Opticlean[®] would effectively clean thin films. We first measured the thickness of the native oxide on a test wafer of silicon with the ellipsometer. Then, we applied Opticlean[®] and removed it after a few minutes. We then immediately ran the same ellipsometry tests as before, modeling with the same silicon dioxide on silicon model as before applying Opticlean.

Next, we determined whether peeling Opticlean[®] off to remove it would damage thin films. We applied it to 10 – 30 nm thick thin films of uranium, scandium, and vanadium that had been sputtered onto three different wafers. These are thin films commonly studied in the EUV group. Then we carefully removed the polymer and examined it further. Two measurement devices were used to detect if any portion of the thin films were removed with the Opticlean[®]: a scanning electron microscope (SEM) fitted with an energy-dispersive x-ray spectroscopy (EDS)¹ and x-ray photoelectron spectroscopy

(XPS). See appendix A for more information on these devices. With the SEM, the presence of large amounts of any of these metals would show that Opticlean[®] was not only removing hydrocarbon contaminant, but also removing our thin film oxides. We also used XPS to more conclusively determine if the Opticlean[®] had, when peeled off, taken any metallic film off the wafer with it.

2.3 Oxygen Plasma Etch

Plasma etches are commonly used in commercial computer chip manufacturing. Chip manufacturing includes many steps such as pre-treatment cleaning of the silicon substrate or base, lithography, etching, and post treatment cleaning.² A commercial plasma etcher manufactured by Matrix was used for this study. All plasma etching experiments were conducted in the BYU Electrical and Computer Engineering Department's (EcEn) Integrated Microelectronics Laboratory (IML) clean room.

2.3.1 Theory of Operation

The etching processes most often includes the production of hydrogen, oxygen or fluoride plasmas (atomic ions and free electron). The etching cleans samples by bombarding the surface with the high energy particles formed in the plasma. The plasma is formed between two capacitor plates by inducing a radio frequency (RF) electric current across the plates as shown in figure 1.

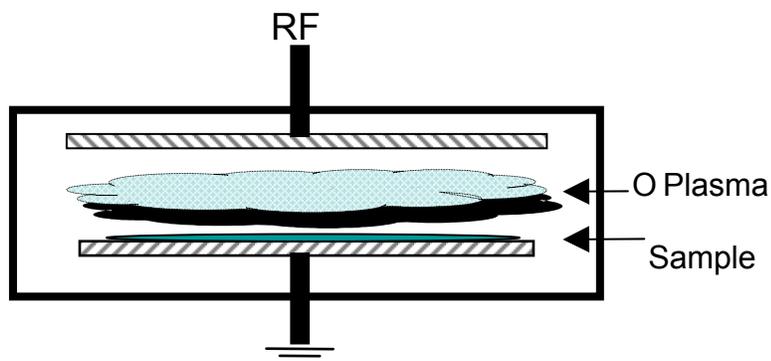


Figure 1: Sketch of O Plasma Etch. The applied radio frequency voltage (RF) causes the oxygen to ionize, bombarding the sample with high energy oxygen ions and free electrons.

Anything on the sample surface (i.e. organic contaminants) will be removed in two ways. First, the high energy ions mechanically break up molecular bonds of the surface molecules and effectively blast the molecular particles off the sample surface. Second, atomic oxygen in the plasma readily reacts with the surface contaminants, breaking them up into smaller and more volatile pieces which easily evaporate off the surface.

2.3.2 Test Method

We used ellipsometry to measure the thickness of the silicon dioxide layer on the surface at the center of the silicon wafer substrate. Next, we coated the wafers with DADMAC as described in appendix C. After applying DADMAC, we measured the apparent thickness of the silicon dioxide layer with ellipsometry again at the center of the sample. The change in the apparent thickness of the silicon dioxide layer is attributed to the DADMAC thickness as discussed in section 2.1.2. After applying DADMAC and re-measuring thickness, we broke each wafer up into nine roughly rectangular fragments. From each wafer two fragments were used as controls and not exposed to the plasma. Each individual piece was measured with ellipsometry before oxygen plasma etching.

The wafer pieces were kept and transferred in plastic Petri dishes to reduce additional contamination.

The plasma etch system was run for three times for 4 minutes to ensure initial cleanliness prior to cleaning wafer fragments. Three DADMAC coated wafer fragments were loaded on top of a silicon wafer and the wafer placed into the wafer boat. The etcher was programmed with gas flow, pressure, radio frequency (RF) power and plasma run time. When the program is started the etcher removes the wafer from the boat and places it in the plasma chamber. After, the proscribed pressure is reached RF power is applied for the programmed time. The thirty-eight fragments were exposed to plasma for various amounts of time. The system was programmed for RF power of 250 Watts, 0.120 Torr of pressure, and an oxygen flow of .75 SCCM (standard cubic centimeters per minute). The additional heating option of the lower chuck or plate was turned off. After plasma cleaning, the wafer pieces were again measured and analyzed by ellipsometry.

2.4 UV Lamp

The third cleaning method we implemented was an ultraviolet-ozone clean. We wanted to determine if the UV lamp would remove organic contaminants from samples and how long it took to remove them. A commercial UV lamp from Eximer, housed in a plexiglas demonstration unit, was used for this study as shown in figure 2. The lamp is force gas cooled and if oxygen is used unhealthy levels of ozone will be generated in the cooling gas.

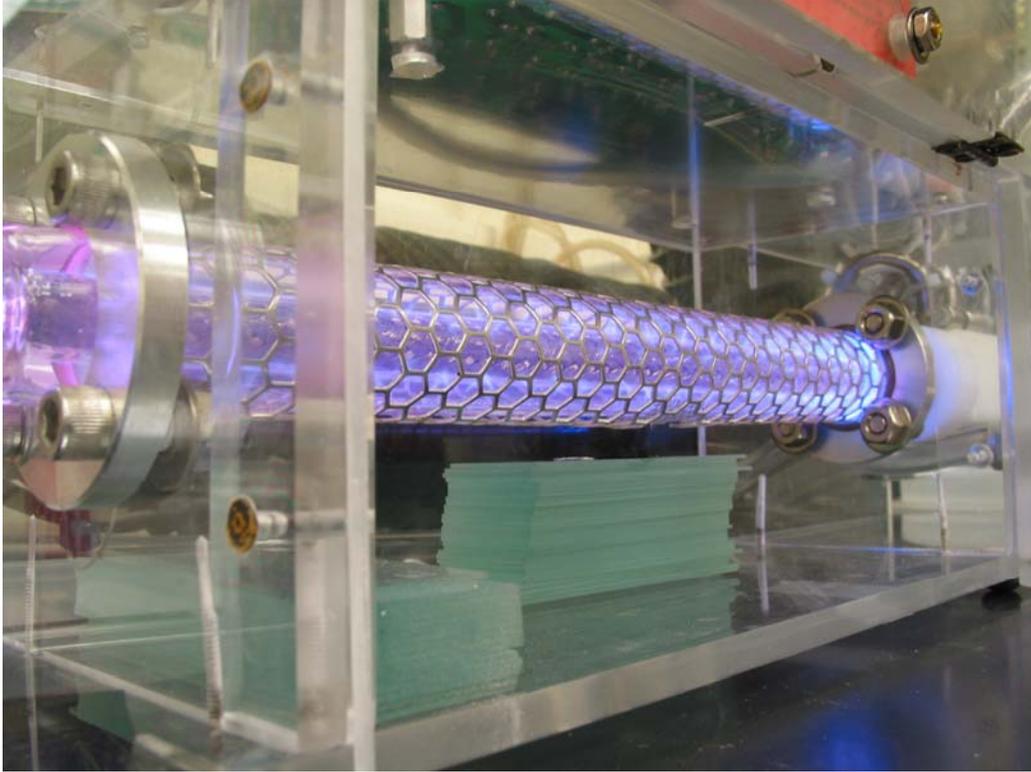


Figure 2: Eximer UV lamp. The lamp and Plexiglas housing used for this study. The wafer fragment to be cleaned is on top of the stack of glass microscope slides.

2.4.1 Theory of Operation

Ultraviolet light from the UV lamp cleans the surface through two pathways. First, the high energy photons interact directly with the hydrocarbon bonds. The UV photons have sufficient energy to break the hydrocarbon chains into smaller segments. The smaller segments are more volatile and a fraction will leave the surface. Secondly the UV light interacts with the oxygen in the air below the lamp, breaking up oxygen molecules, forming oxygen atoms which react with O_2 to create ozone. In the presence of UV, this ozone then reacts with the hydrocarbon contaminants at the surface of a wafer placed below the lamp, effectively oxidizing the organic compounds and allowing them to evaporate into the air. For example, carbon would be oxidized to carbon dioxide. One drawback to this method is that the ozone might react with the substrate underneath the

contaminant layer, in this case leaving behind a residue of silicon dioxide. Results are discussed in section 3.2.

2.4.2 Test Method

For this test, we used ellipsometry, following the same process that we used in the previous cleaning processes to determine the thickness of the oxide layer. A difference is that the wafers were plasma etched and then measured prior to DADMAC application. After applying the layer of DADMAC, we measured the apparent thickness and then broke each wafer into 9 pieces. We then measured the apparent thickness of the layer on each of the 9 fragments. We determined the thickness of the DADMAC layer by taking the difference between the apparent thickness before and after applying the DADMAC solution. We then placed coated wafer pieces under the UV lamp for different amounts of time and measured the change in the apparent thickness of each fragment. The wafer pieces were placed directly under the lamp on top of 30 glass microscope slides so that the wafer fragments would be within a few cm of the lamp.

2.5 Opticlean[®] and Oxygen Plasma

After conducting the Opticlean[®] process described in section 2.2, we determined that Opticlean[®] alone would not suffice as a thin film cleaning method due to the 2 nm of polymer residue left after removing the Opticlean[®]. We wanted to see if plasma etching would effectively remove the residue, so we ran the same process described in section 2.3 on a piece of silicon wafer. Our theory was that Opticlean[®] would remove the dust and larger hydrocarbons, and that plasma etching would remove the hydrocarbon residue. Results are discussed in section 3.4

CHAPTER III RESULTS AND DISCUSSION

3.1 Opticlean[®]

We had two concerns with the Opticlean[®] process. First, if it left a residue and second, whether it damaged our thin film surfaces. Through previous use in cleaning optical surfaces, we knew that Opticlean[®] was effective in removing larger nano-contaminants. Therefore, our first tests measured whether Opticlean[®] left a residue. On two separate tests, we saw an increase in apparent thickness of 1.7 and 2.0 nm with ellipsometry. Thus, we concluded that Opticlean[®] did in fact leave behind a layer of contaminants.

Our second concerns were tested with SEM and XPS. After reviewing the EDS results from the SEM, we saw no trace amounts of uranium, scandium, or vanadium on the removed polymer. These results with the SEM images of the sample surfaces showed no damage on the sputtered thin films. XPS also found no trace amounts of the metals used in the thin films on the removed polymer.

The XPS scan results of the removed polymer are included in Figure 3. From these results, we concluded that Opticlean[®] effectively removed nanoparticles and bulk contaminants safely from our metal oxide thin films. However, it leaves a residue on the surface. Therefore, Opticlean[®] by itself is not a suitable cleaning method for our thin films.

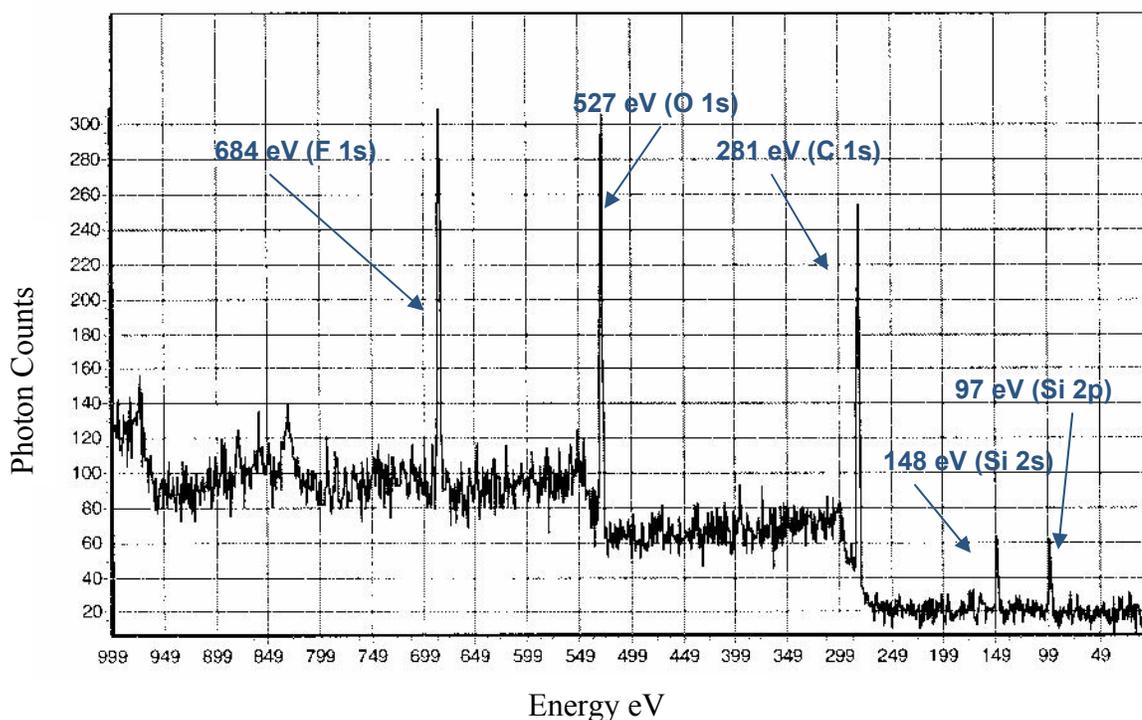


Figure 3: XPS results of removed Opticlean® polymer. Photoelectron count versus photon energy (eV). (The unit eV—electron volt—is inversely proportional to wavelength, so higher energy means shorter wavelength). Notice XPS revealed the components of Opticlean® (F,O,Si,C), but not heavier metals used in thin films. Prominent thin-film lines: U-380 eV, V-515 eV, Sc-400 eV.

3.2 Oxygen Plasma

We found that the DADMAC was removed extremely rapidly. The very reactive ionized oxygen and the physical collisions of the sputtering (oxygen atoms impacting the surface) combine to remove the contaminants very effectively.

Figure 4 also shows upper and lower trend lines. This is probably due to the time samples spent in a Petri dish before measuring the thickness. The fifteen-second, one-minute and twenty-second and three-minute samples were etched after the other samples were measured. We found that approximately 2 Å of contaminants were accumulated

during the 20-40 minutes that the majority of the sample spent in transfer between the Clyde and the Benson buildings.

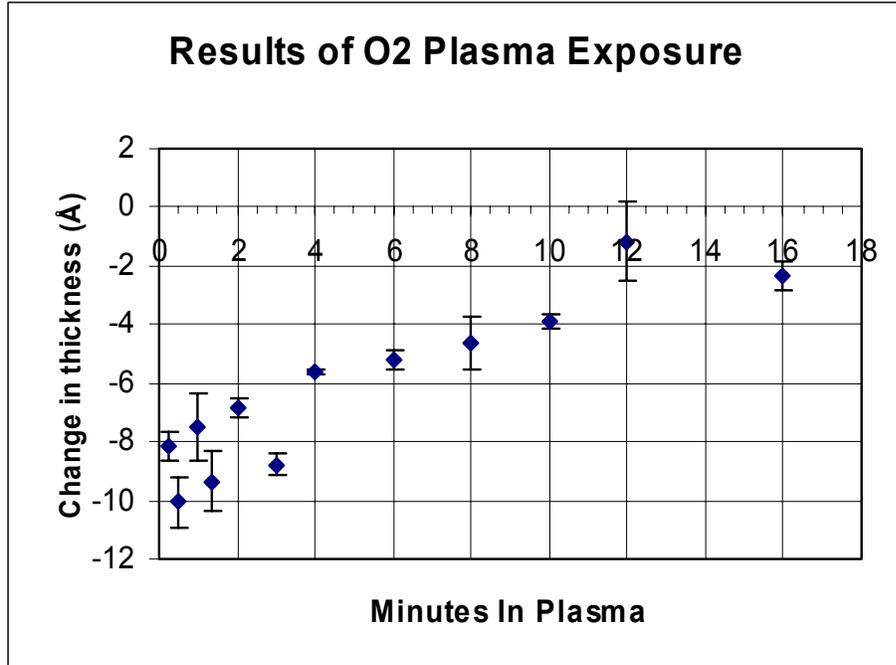


Figure 4: Results of O₂ Plasma Exposure. Change in apparent thickness with exposure to oxygen plasma.

With further exposure to the plasma the apparent oxide thickness increases. This trend is clearly evident in Figure 4. The logical conclusion is that the free oxygen reacts with the surface to produce additional silicon dioxide. However, this is not necessarily the case. It is possible that contaminants from the plasma chamber are accumulating on the surface. XPS results in Figure 4 clearly show only oxygen (532.7 eV) and silicon (150.5 eV). (The unit eV—electron volt—is inversely proportional to wavelength, so higher energy means shorter wavelength). The peaks around 750, 880 and 580 eV are

thought to be phantoms from the detector and have no physical significance.

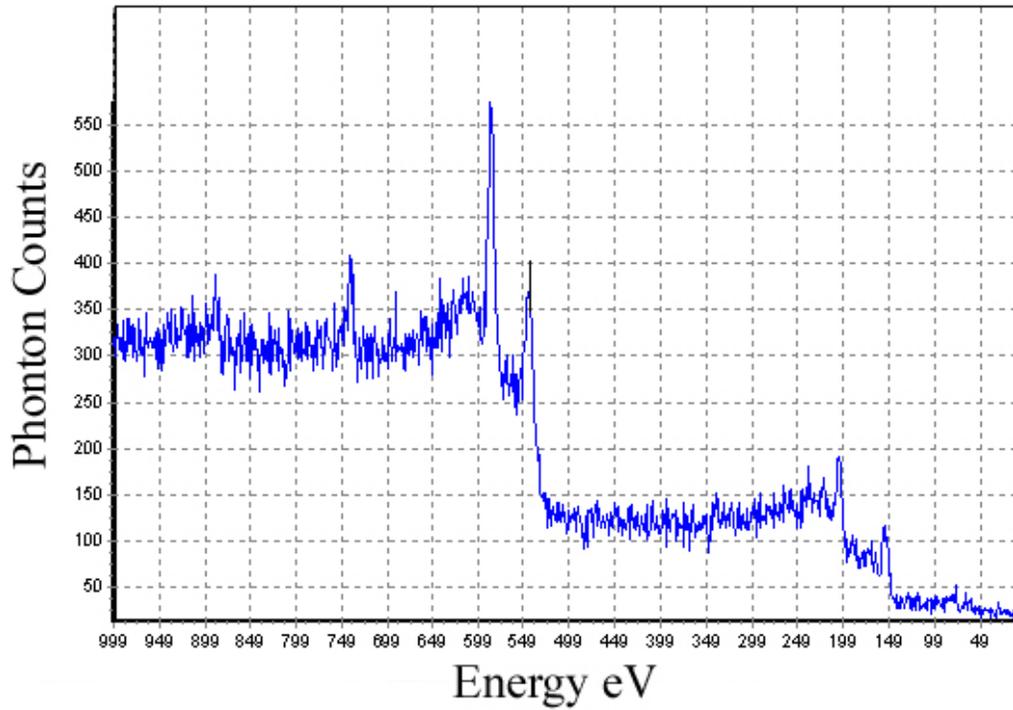


Figure 5: XPS of Si wafer cleaned in O₂ Plasma. No carbon found.

The most important result of Figure 5 is that no carbon (281 eV) was found on the surface of plasma treated wafers. This indicates that the DADMAC was completely removed. However, a small chlorine peak at 200 eV is present. This could be due to the sodium chloride present in the DADMAC solution dissolving into the silicon dioxide. No detectable sodium (500 eV and 50 eV) is present on the surface.

3.3 UV Lamp

The wafers were measured before and after the DADMAC process to calculate the thickness of the hydrocarbon layer. The DADMAC was found to be approximately 4.5 Å thick. Figure 6 shows that the DADMAC was removed rapidly. Within about 5 minutes of exposure the apparent thickness was back to its value before the DADMAC deposition. One of the 20 minute samples suggests that one of the samples was adulterated; perhaps it was touched accidentally.

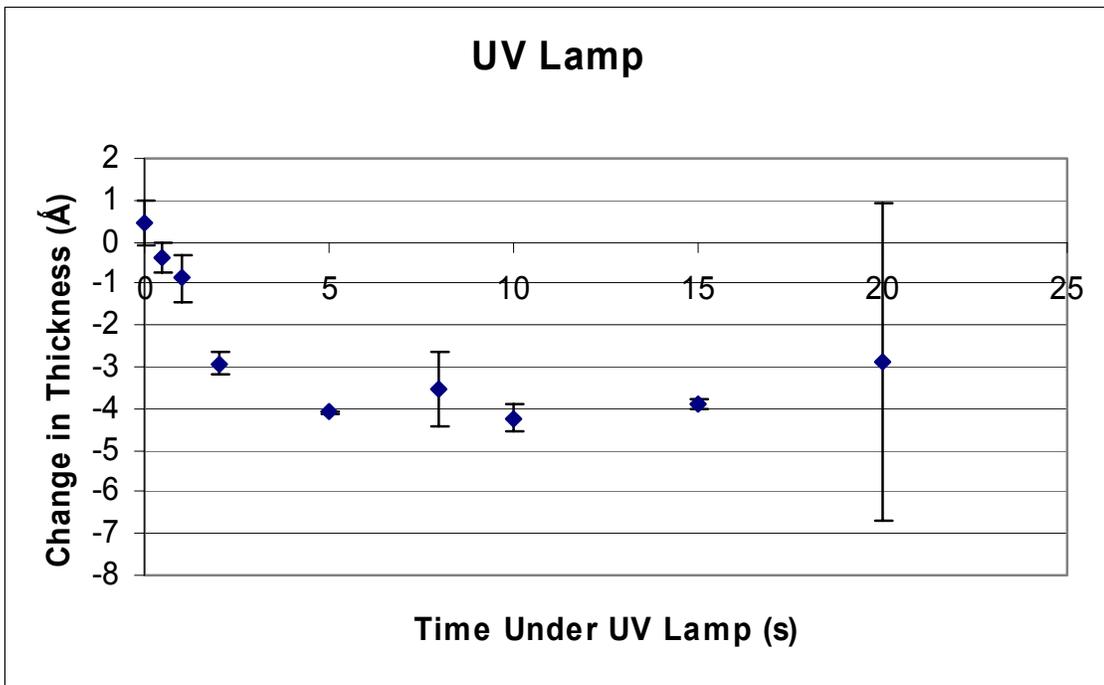


Figure 6: Results of UV lamp exposure. Change in apparent thickness versus exposure time of UV lamp.

XPS analysis on a DADMAC coated sample exposed to UV for 5 minutes shows no carbon presence. Figure 7 shows the data from the XPS done on the samples cleaned by the UV lamp. The 1000 eV and 550 eV lines are false readings by the detector. Only oxygen (532.8 eV) and silicon (150.8 eV, 97 eV) are present. Additionally, the spectrum is qualitatively clearer than the plasma results. This clearness can be taken to mean that contaminates levels are much below the detection limits.

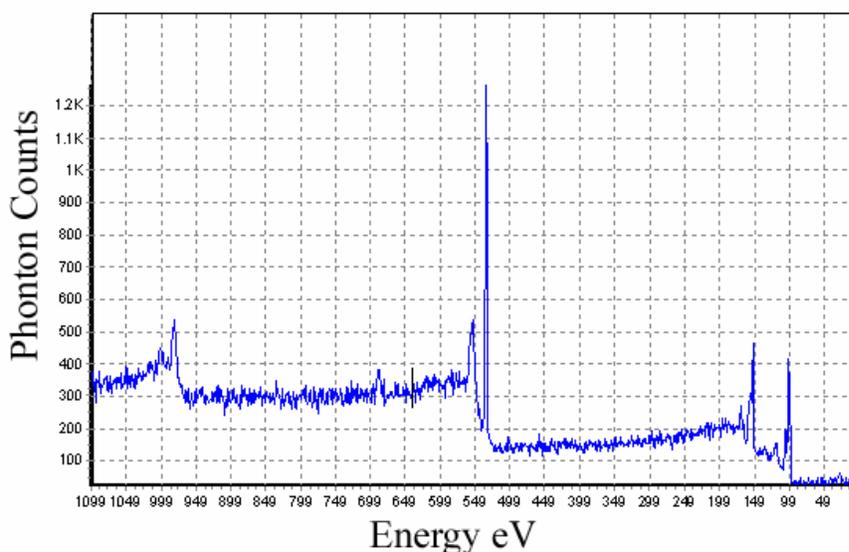


Figure 7: XPS Spectrum of UV cleaned sample. Only oxygen (532.8 eV) and silicon (150.8 eV, 97 eV) are present. The 1000 eV and 550 eV peaks are detector artifacts.

3.4 Opticlean® + Plasma

As stated in section 3.1, the Opticlean® process left a residue approximately 2 nm thick. We wanted to remove this hydrocarbon residue, so we tested whether Plasma etching could remove it. One of the samples used to test if Opticlean® left a residue was measured to have 2.2 nm of residue with ellipsometry. We placed that sample in the oxygen plasma described above for 1 minute and 20 seconds. Ellipsometry showed that after oxygen plasma cleaning, approximately 2.15 nm were removed from the surface.

We thus concluded that oxygen plasma etching effectively removes the residue left from the Opticlean[®] cleaning process. We suggest that when requiring rigorous cleaning, Opticlean[®] followed by oxygen plasma etching provides the best method for a combination of large (dust particles) and small contaminant cleaning.

3.5 Recommended cleaning procedure

This thesis examines three different methods of cleaning surfaces for EUV research. Additionally, one combined method was tried. During the trials DADMAC substituted for contaminants. The factors considered are effectiveness, ease of use and cleaning time. Table 1 summarizes the experimental results.

Method	Effectiveness	Cleaning Time	Ease of Use	Notes
Opticlean [®]	Left residue	Must wait for polymer to cure	Can be difficult to peel off.	Good for dust etc..
Oxygen Plasma	Effective. Cl not completely removed	Setup takes a few minutes. Clean under a minute	Equipment in clean room. Complex to setup.	Builds up silicon dioxide
Eximer UV Lamp	Effective	1 to 5 minutes	Very easy	Less silicon dioxide buildup then plasma.
Opticlean [®] + Oxygen Plasma	Effective Possible 1 Å residue or oxide	Long, plasma setup and polymer cure time.	Complex clean room equipment and skill needed to peel	

Table 1: Summary of cleaning method comparison.

Based upon the experimental trials conducted for this study the Eximer UV lamp is the best cleaning process. It is the simplest to use process with the fewest side effects. The recommended exposure time is 5 minutes. This exposure time results in a clean surface with very little additional surface oxidation.

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APPENDIX

Appendix A: Diagnostic Methods

A.1 Ellipsometry

A.1.1 Theory

An ellipsometer projects polarized light onto a sample and then analyzes the reflected light. Light is considered elliptically polarized when its electric field rotates around in an elliptical pattern. Circular polarized light is a special case of elliptically polarized. In Figure 8, shows a light source which projects elliptically polarized light onto a sample (which sits on the sample stage). The reflected light's polarization changes according to the properties of the sample. These include the chemical composition of the different layers and their thicknesses.

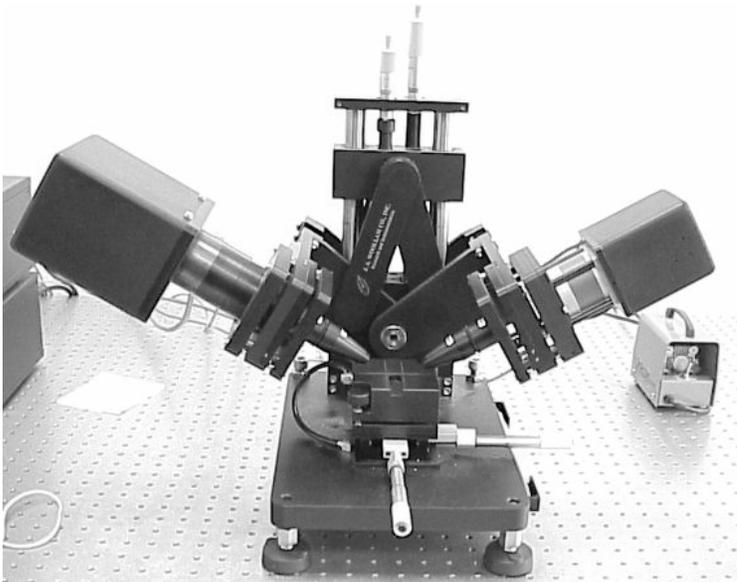


Figure 8: The J.A. Woollam Ellipsometer Inc, Multi-Wavelength Ellipsometer model number M1000 with a UV optimization package from 1.24 to 6.5 eV (J. A. Woollam Co.)

On the right, the ellipsometer has a light detector/analyzer which interprets the change in the polarization. This information is then processed according to:

$$\tan(\Psi)e^{i\Delta} = R_p / R_s \quad (\text{A.1})$$

where R_p and R_s are the reflectance constants relating to different polarizations.

A.1.2 Usefulness

Analyzing the ellipsometric data with a computer, allows us to determine the sample's optical properties, or its composition. If part of the composition is known, then various physical models can be used to extrapolate information about the other parts. With a simple silicon wafer, we know we have about 1mm of silicon on the bottom of our sample, but we do not know how much silicon dioxide we have on top. An ellipsometer can tell us the thickness of layers if we know 1) the chemical composition and structure of the sample and 2) its optical properties.

A.1.3 Limitations

Ellipsometry does have major limitations. Ellipsometers can tell us thickness or optical constants, but not both. When we have a sample of numerous layers, like the ones in our real mirrors, then this dilemma becomes much bigger. Accurately, we can only isolate one unknown per layer. In order to accurately determine all of the unknowns in the sample, we need to know the information before we start modeling the ellipsometric data.

A.1.4 Use in this study

In all of our cleaning methods, ellipsometric data was taken before and after cleaning so that we could see how the cleaning method affected the apparent thickness of the contaminant layer

A.2 XPS

A.2.1 Theory

XPS utilizes Einstein's photoelectric effect. He demonstrated that when light shines on a metallic surface, atoms in the metal absorb quantized packets of light or *photons* and then eject electrons. The photoelectric effect states that the energy of the ejected electron, K_{max} , is given by:

$$K_{max} = hf - \phi \quad (\text{A.2})$$

where h is Planck's constant ($h=6.63 \times 10^{-34}$ J*s), f is the frequency of the light incident on the metal, and ϕ is the work function or binding energy of the ejected electron.³ These emitted electrons are called *photoelectrons*. Samples are bombarded with high-energy x-rays causing them to emit these photoelectrons. In the BYU chemistry department's XPS system, K- α x-rays from aluminum (1487.7 eV) or magnesium (1253.6 eV) are used. As shown in equation (A.2), the binding energy of the emitted photoelectron is found by taking the difference between the energy of the incoming light (hf) and the kinetic energy of the emitted photoelectron (K_{max}). This information is then compared against the known binding energies of elements and chemical compounds.

A.2.2 Usefulness

In the EUV group, we use XPS to give us "information on the nature of chemical bonds and the valence states" of our samples.⁴ By comparing the binding energy of the emitted photoelectron to the known binding energy, XPS can determine the presence of elements, the chemical makeup, and relative chemical abundance of its samples.

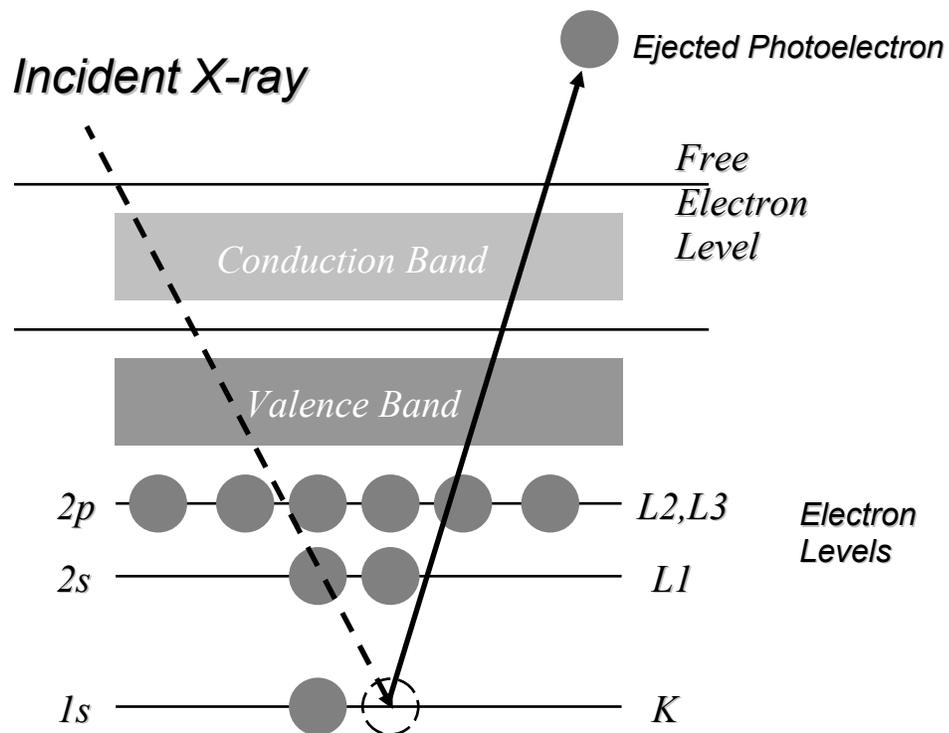


Figure 8: How x-rays eject photoelectrons from the K shell of samples. XPS analyzes the kinetic energy of these ejected electrons to determine their binding energies and thus the existence of different elements in the samples.[5]

A.2.3 Limitations

One of the major difficulties of using XPS is calibrating the system regularly to assure accuracy. Shannon Lunt, a recent Master's degree graduate from BYU describes how the surface of many materials may become charged due to the removal of electrons during the XPS process⁴. This can affect the measured kinetic energy by 3-10 eV.

A.2.4 Use in this study

XPS was used in our studies to determine the chemical composition of our samples, as well as the chemical makeup of the contaminants. In some cases, XPS was used to test whether samples had contamination.

A.3 SEM

A.3.1 Theory

Instead of using light waves to see smaller specimens, the scanning electron microscope uses electrons. It emits a beam of high energy electrons that scan the specimen. When the beam hits the sample, secondary electrons are emitted from the surface of the specimen. These electrons are counted and sent to an amplifier where they are built up into an image.¹

A.3.2 Usefulness

The use of electrons to build the images allows the SEM to show microscopic structures in greater detail. It also allows the composition of a structure to be determined by monitoring the secondary x-rays that are produced when the electron beam hits the specimen.

A.3.3 Limitation

Images can become distorted because of the way that the electrons interact with the specimen. When the surface charge increases, details become unclear and there is a possibility that the specimen could be damaged. SEM is also limited because it cannot look directly at the specimen. The image created by the electrons may not accurately reflect the actual object.

A.3.4 Use in this study

SEM was used in this study to analyze the composition of the material. It was useful in determining the purity of the material by allowing us to see if it had a layer of contamination. This allowed us to measure the effectiveness of each cleaning process.

APPENDIX B: SOURCES OF CONTAMINATION

Before analyzing the cleaning methods under scrutiny, we first wanted to understand the contaminant's nature. We needed to know how easily contaminants condensed on the samples, their thickness and how they affected the sample's reflectance. We conducted several experiments to determine these values.

B.1 Determining contamination thickness and rate

To see how everyday activities affected the thickness of contaminants on surfaces we subjected 3-inch silicon test wafers to a series of tests. Before exposing the test wafers to contaminants, spectroscopic ellipsometry was used to model the thickness of the layers, using a J. A. Woollam Co., Inc Multi-Wavelength Ellipsometer (model number M1000 with a UV optimization package from 1.24 to 6.5 eV). For a more detailed discussion on ellipsometry see appendix A. They were modeled with the ellipsometer's VASE[®] software as a silicon dioxide layer over a silicon substrate. After exposure, we re-measured and modeled our sample in the same manner. We used the same model for the wafer before and after contamination, because the thin layers of contaminants (<20 nm) make it difficult for our models to distinguish between silicon dioxide and an arbitrary hydrocarbon. The simplest model assumes that the hydrocarbon contaminant is only additional silicon oxide. We compared this modeling method to a model with a layer of hydrocarbon on top of silicon dioxide all on a silicon substrate. We found that the ellipsometry software could not tell the difference. The contamination tests produced the results in Table 2:

<u>Results from Short (10s) and Long Term (18 day) Exposure Tests</u>		
Description of Exposure	Exposure Time	Apparent Δ Thickness (nm)
Spit on Sample	NA	45.0
Touched with bare fingers	10 s	14.3
Dipped in deionized water	10 s	1.8
Touched with latex gloves	10 s	1.6
Placed in Kim wipe	427.92 hrs	1.0
Placed in a letter envelope	428.85 hrs	1.2
Left in open air (surface up)	425.5 hrs	2.1
Touched with latex glove and left in air	427.23 hrs	4.6
Stored in clean, dry sample holder	428.96 hrs	~0

Table 2: Results from Contamination Tests. Short and long term contamination experiments performed on a silicon substrate.

These tests simulate contamination possibilities in a common lab setting (spitting on a sample might resemble a mistaken contamination due to speaking).

B.2 How contamination affects reflectance

To further illustrate the effects of contamination, we modeled the reflectivity of silicon substrate with 2.1 nm of oxide and a variable thickness of $C_{10}H_8O_4$ with respect to grazing incidence angle. We used a computer simulated reflectance modeling program called IMD⁶ to project how reflectance might change with hydrocarbon buildup.

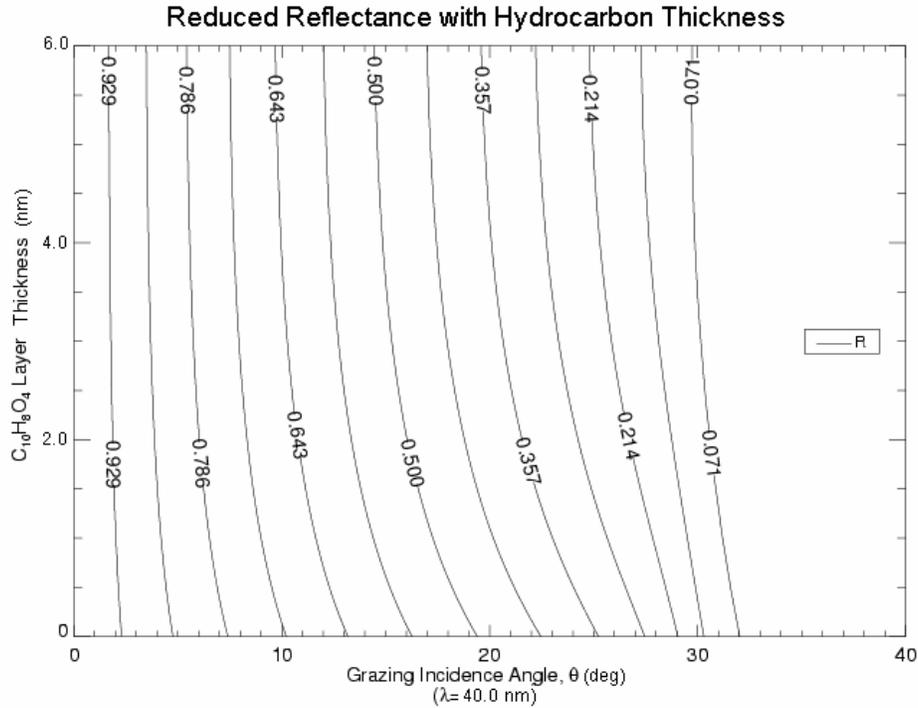


Figure 10: Reduced Reflectance with Hydrocarbon Thickness. Theoretical change in reflectance versus grazing angle and hydrocarbon thickness (at $\lambda=40.0$ nm)

The simulations described above are displayed in Figure 10. From this generated data, we expect to see the following decreases from initial reflectance due to buildup of 18 days:

- *46% of initial reflectance due to leaving in ambient air*
(Corresponds to 2.0 nm of buildup)
- *36% of initial reflectance due to touching with a latex glove*
(Corresponds to 4.6 nm of buildup)

From this analysis, we found that in characterizing the optical constants of metal oxide thin films, we need to be concerned about the amount of contaminant that is on and between our layers. This interlayer contamination might occur if we were to remove a sample from the vacuum chamber and later sputter a layer on top.

C. Procedure to apply the DADMAC:

A helpful hint is to not write on the back of the wafer with pen prior to DADMAC application. The solution will loosen or dissolve the ink spreading it out all over the wafer.

1. Clean the sample wafers.
2. Measure Oxide thickness using ellipsometry.
3. Place each wafer polished side up in a new clean Petri dish.
4. Pour sufficient DADMAC solution to cover wafer.
5. Cover and gyrate to spread evenly.
6. Allow to stand for 20 minutes.
7. Remove wafer with forceps.
8. Rinse wafer with DI. (deionized water)
9. Blow dry wafer with dry Nitrogen gas.
10. Measure new apparent oxide thickness.
11. Solution remaining in the Petri dish can be neutralized with a citric acid solution and rinsed down the drain.