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Removing Surface Contaminants from Silicon Wafers to Facilitate EUV Optical Characterization

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Removing Surface Contaminants from Silicon Wafers to Facilitate EUV Optical Characterization

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Key Words: Substrate cleaning
Strippable coating

Silicon cleaning
UV/ozone cleaning

ABSTRACT

The extreme ultraviolet (EUV) is becoming increasingly important. Principal applications include orbital space-based astronomy and lithography for integrated circuit computer chips. A 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 often contaminated with foreign material, especially organic compounds, when exposed to laboratory air. Several cleaning techniques were evaluated, namely: 1) strippable solid optical cleaner (Opticlean®); 2) oxygen plasma etch; 3) high energy UV light/ozone; 4) strippable coating followed by oxygen plasma etch, 5) strippable coating followed by high intensity UV light and, 6) exposure to cold pressurized carbon dioxide (CO₂ snow). These processes are compared experimentally based on effectiveness, cleaning time and ease of use. DADMAC (polydiallyldimethyl-ammonium chloride), which forms a layer of known, uniform thickness on silicon wafers is used as a "stand in" for organic contamination. Effectiveness is judged on how well the surface is cleaned. Ellipsometry is used to determine the thicknesses of surface layers. XPS (X-ray Photoelectron Spectroscopy) is used to look for trace contaminants, particularly carbon from the DADMAC. We find that the strippable cleaning coat leaves a residue. Oxygen plasma rapidly removes contaminants, but can quickly oxidize the silicon surface. Exposure to the UV light/ozone for five minutes leaves the surface clean with little additional oxidation. Oxygen plasma or UV light effectively removes the strippable coat residue. Exposure to cold pressurized carbon dioxide has reduced oxide level in one case. The recommended procedure for cleaning bare silicon wafers is strippable coat application followed by 2.5 minutes of exposure to high intensity UV light.

INTRODUCTION

The BYU XUV group has been researching the optical properties of metals in the EUV (10-100 nm) since the late 1990's. The most significant and comprehensive work has been done in the study of uranium compounds. We study these materials by analyzing thin films which have been deposited onto

various substrates: silicon test wafers, quartz slides, TEM grids, etc. Our efforts have been concentrated on characterizing the optical constants for materials in the EUV by taking measurements at varying angles and wavelengths of our thin films.

Difficulties arise when working with light of such small wavelength. High vacuum must be maintained or the light will be absorbed in air. Because of these and other factors, the optical constants of many materials in the EUV are not well known.

Our research requires us to have an accurate composition of our thin films. The buildup of airborne hydrocarbons on the surface of the thin films is a challenge in making accurate measurements. As a film is exposed to the atmosphere, the natural accumulation of organic material essentially creates an additional layer. If this layer is not removed, its effect will be mistakenly credited to uranium, introducing a significant error. Moreover, as seen in Figure 1, reflectance decreases as the thickness of hydrocarbon contaminants increases.

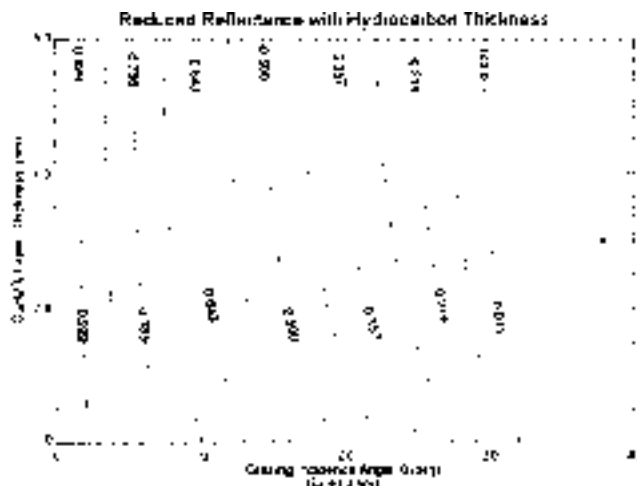


Figure 1: Reduced Reflectance with Hydrocarbon Thickness. Theoretical change in reflectance versus grazing angle and hydrocarbon thickness (at $\lambda=40.0$ nm). Plot calculated using IMD [1].

In an attempt to estimate the thickness of organic contaminants, a short study was performed. Spectroscopic ellipsometry was first used to model uncontaminated silicon wafers as a single silicon dioxide layer on a silicon substrate. The wafers were then exposed to contaminants in a number of ways. Another set of ellipsometry measurements was made and then compared to the first. The apparent change in thickness is attributed to a new hydrocarbon layer.

Table 1: Results from Contamination Tests. Short-(10s) and long-term (18 day) contamination experiments performed on a silicon substrate.

Description of Exposure	Exposure Time	Apparent Thickness (nm)
Spittle [2]	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 paper 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

Our focus was on examining them for center EUV optics and nanofabrication cleaning applications. The materials used and how they are used for these applications are sufficiently different than standard industrial applications that these properties of the techniques need to be investigated. This data show the detrimental effects and rapid buildup of organic contaminants. This paper focuses on five methods of cleaning by hydrocarbon removal. These procedures are evaluated with respect to ease, effectiveness, duration of treatment, and safety to the films. In attempting to find a solution to the hydrocarbon contamination problem, we have researched five contaminant cleaning methods.

The first cleaning method involves applying Opticlean®, an industrial optical dust remover, to the silicon wafer samples. After the Opticlean® cures, it is peeled off. The peeled layer takes with it the larger that is its contaminant particles that were on the surface. In the second method, a plasma etching system uses 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 and ozone breaks up many of the hydrocarbon bonds, forming smaller molecules which then evaporate. Fourth, the sample was initially cleaned with Opticlean® and then exposed to oxygen plasma etching. Finally, the fifth method combines Opticlean® with subsequent exposure to a UV lamp. This article reports the experimentally determined effectiveness, cleaning time, and ease of cleaning of each method from the point of view of preparing surfaces for EUV and soft x-ray measures.

METHODOLOGY

Two questions were asked to ascertain whether the cleaning method in question was an effective cleaning method. First, did the cleaning process damage the thin film surface? Second, was the hydrocarbon layer removed?

For all five methods, a spectroscopic ellipsometer was used to measure the change of apparent thickness of the contaminant layer before and after cleaning. Before and after cleaning, the contaminated test wafers were measured. The layer thicknesses were modeled by spectroscopic ellipsometry with a J.A. Woollam Co., Inc. Multi-Wavelength Ellipsometer (model number M1000 with a UV optimization package from 1.24 to 6.5 eV). The layers were modeled with the ellipsometer's VASE® software as a silicon dioxide layer over a silicon substrate. After cleaning, we re-measured and modeled our sample in the same manner. We used the same model for the wafer before and after cleaning, because very thin layers of arbitrary hydrocarbon contaminants (<5 nm) on top of silicon dioxide cannot be distinguished from a single silicon dioxide. The simplest model then assumes that the hydrocarbon layer contaminant is only additional silicon oxide. The thickness trade-off is close to one-to-one. This same method was used in the contamination study presented in the introduction. Ellipsometric measurements were taken before and after exposure to the contamination process and modeled as described above.

After cleaning, x-ray photoelectric spectroscopy (XPS) was used to determine whether the cleaning methods had actually removed the hydrocarbons. Our XPS system uses K- α x-rays from aluminum (1487.7 eV) to remove electrons and then plots their binding energies. These binding energies correspond to specific elements. Thus, the presence of carbon can be used as a test as to whether the hydrocarbon layer has been removed (thus answering question 1).

Both XPS and scanning electron microscopy (SEM) were used to detect whether the Opticlean® method damaged our thin films. We applied the polymer to several 10-30 nm thick thin films of uranium, scandium, and vanadium that had been sputtered onto three different test wafers. (These are thin films commonly studied in our research group). Then we removed the polymer and examined the surface that had been in contact with coated wafer surface. XPS was used to test for the presence of uranium, scandium, or vanadium on the removed Opticlean® polymer layer. An SEM fitted with an energy-dispersive x-ray spectroscopy (EDS) [3] was also used detect the presence of the thin film metals on the removed cleaning polymer. 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. Neither XPS nor the SEM detected any uranium, vanadium, or scandium on the removed Opticlean®

layer. The SEM was also used to examine the thin film surface to detect whether the surface had visibly been damaged.

A standard hydrocarbon contaminant was needed for the cleaning methods described. This allows for the effects of the cleaning method in question to be separated from the effects arising from variations in contamination. For these studies, we selected DADMAC (polydiallyldimethyl-ammonium chloride) as our standard material. DADMAC is a well-characterized polymer used in nanotechnology due to 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 polymer chains.

The thickness of the polymer layer is limited by the fact that each DADMAC molecule acquires a positive charge when dissolved in water. 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.

Several test wafers can be coated without precision equipment because after an initial period of rapid film growth, the thickness of the DADMAC layer is only minorly dependent on time in solution. 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.

In the oxygen plasma and UV studies, we used DADMAC as the standard contaminant. We used a 1 milli-mol solution of DADMAC and 100 milli-mol of salt in this study. This produces an apparent equilibrium thickness after 15-30 minutes of about 1 nm, as measured by ellipsometry. This thickness is a reasonable approximation of accumulated contamination. The surfaces of clean silicon wafers quickly acquire a coating 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 via ellipsometry DADMAC. The thickness of DADMAC is determined by subtracting the measurable oxide thickness from the post DADMAC thickness. This thickness is referred to as being the apparent thickness because, as was discussed be-

fore, ellipsometry is unable to distinguish between the DADMAC and the silicon dioxide underneath. So, two facts are seen as contributing to this situation. First, the silicon dioxides on the wafer and DADMAC have very similar indices of refraction over the 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 the thicknesses of both the polymer and silicon dioxide layers are fitted by the 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.

Opticlean® Method

Specifically, we were concerned with first determining whether Opticlean® would leave behind a residue, and if the application and removal process would damage our thin films, by pulling off pieces of our film, for example.

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. Theoretically, the contaminants and dust on the surface will bind to the polymer and be removed with it.

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 [4]. 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.

The etching process most often includes the production of hydrogen, oxygen or fluoride plasmas (atomic ions and free electrons). The etching cleans samples by bombarding the surface with the high-energy particles 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 2.

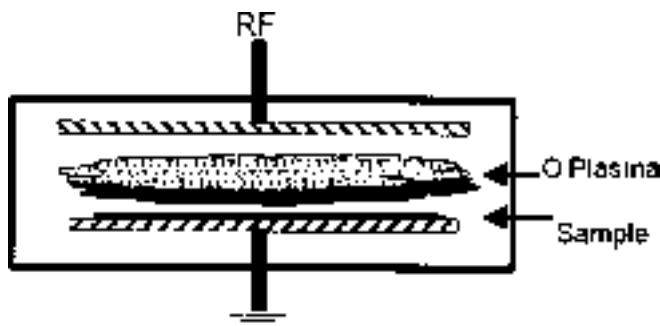


Figure 2: Sketch of O Plasma Etch. The applied radio frequency voltage (RF) causes the oxygen to ionize, bombarding the sample with high energy oxygen ions and free electrons.

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.

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 above, and again measured the apparent thickness of the silicon dioxide layer with ellipsometry at the center of the sample. The change in the apparent thickness of the silicon dioxide layer is attributed to the DADMAC thickness as above. After applying DADMAC and re-measuring thickness, we broke each wafer up into nine roughly rectangular fragments. From each wafer two pieces were kept as controls and were 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 post-process contamination.

The plasma etch system was pre-cleaned by three times for a total of four minutes prior to loading the pre-cleaned wafer fragments. Three DADMAC-coated wafer fragments were loaded on top of a silicon wafer, and the wafer was placed into the wafer boat in the etcher. The etcher was programmed with gas flow, pressure, radio frequency (RF) power, and plasma run time. When the program is initiated, the etcher automatically removes the wafer from the boat and places it in the plasma chamber afterwards as the system is evacuated. After the prescribed pressure is reached, RF power is applied for the programmed time. The 38 fragments were exposed to plasma for various amounts of time. The system was programmed for an RF power of 250 Watts, 0.120 Torr of pressure, and an oxygen flow of 0.75 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.

UV Lamp

The third cleaning method we investigated was an ultraviolet/ozone clean. We wanted to determine if the UV lamp would remove organic contaminants from samples and the time required to remove them. A commercial Eximer™ UV lamp, housed in a plexiglas demonstration unit, was used for this study. The lamp is gas cooled and if an oxygen containing gas is used, unhealthy levels of ozone will be generated in the cooling gas.

Ultraviolet light from the UV lamp cleans the surface through two processes. First, the high-energy light interacts directly with the hydrocarbon bonds. The UV light has sufficient energy to break the hydrocarbon chains into smaller segments. The smaller segments are more volatile species, and some will leave the surface. Second, the UV light interacts with the oxygen in the air tube, above the wafer breaking up oxygen molecules, forming oxygen atoms which react with O₂ to create ozone O₃. In the presence of UV, this ozone then reacts with the hydrocarbon contaminants and oxidizing them, and, to volatile species which evaporate into the air. One drawback to this method is that the ozone is a very strong oxidizer and may quickly oxidize some surface beyond what air normally does. Results are discussed below in the data section.

Our UV/ozone tests followed the protocol map employed by it for the plasma cleaning described above. One difference is that the wafers were plasma etched and then measured prior to DADMAC application. After applying the layer of DADMAC, we broke each wafer into nine pieces. We then measured the thickness of the layer on each of the nine fragments. Determining the thickness of the DADMAC layer on each piece from the difference in the surface layer before and after 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 so that the center of each wafer fragments was less than 1.5 cm below the lamp tube.

Opticlean® UZ/Ozone Plus Atomistic Cleaning: Fourth Process

After we conducted the Opticlean® cleaning test described previously, it was clear 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 other plasma etching or UZ/ozone would effectively remove the residue, so we employed the two processes described above on silicon wafer pieces “cleaned” by Opticlean®. Our theory was that Opticlean® would remove the dust and

larger hydrocarbons, and that the atomistic techniques would remove the hydrocarbon residue.

**Opticlean® Plus Cold, Pressurized Carbon Dioxide:
Fifth Process**

Finally, the last method that we analyzed was exposure to cold, pressurized CO₂ snow. Pressurized CO₂ is passed through a *CO₂ Snow Cleaning Solenoid Unit* pressurized CO₂ gun by Applied Surface Technologies, where it is frozen into CO₂ “snow”. The handheld unit is aimed at the sample, and the stream of snow freezes the hydrocarbon layer and breaks it off due to erosion.

RESULTS

Opticlean®

We had two concerns with the Opticlean® process. First, did the Opticlean® polymer leave a residue, and second, as stated above, did Opticlean® damage the surface of our thin film samples? Through previous use in cleaning optical surfaces, we knew that Opticlean® was effective in removing larger contaminants. Therefore, our first tests measured whether Opticlean® left a residue. On two separate tests, we saw an increase in the ellipsometric thickness the surface layer of 1.7 and 2.0 nm with ellipsometry. Thus, we concluded that Opticlean® does leave behind an organic layer.

Our second concern was tested with as described previously with SEM and XPS. After reviewing the EDS results from the SEM, we saw no 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 none 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 bulk contaminants safely from our metal oxide thin films. However, due to the residue it leaves on the surface, Opticlean® by itself is not a suitable cleaning method for our thin films.

Oxygen Plasma

In Figure 4, we found that the DADMAC was removed extremely rapidly. The shortest time used removed all the DADMAC. The very reactive ionized oxygen and the physical collisions of the sputtering (oxygen atoms impacting the surface) evidently remove the contaminants very effectively.

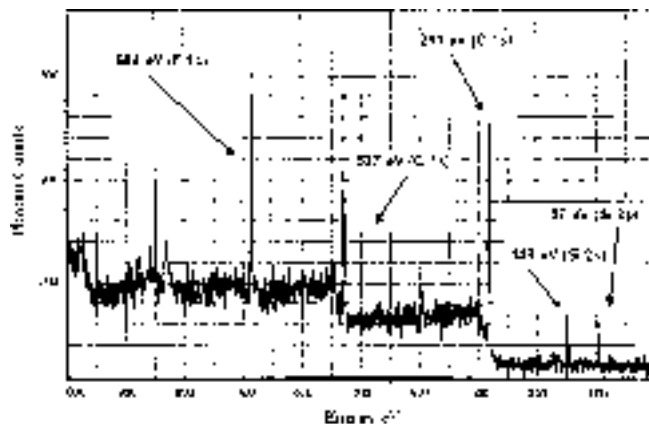


Figure 3: XPS results of removed Opticlean® polymer. Photoelectron count versus photon energy (eV). (The unit eV (electron volt) is inversely proportional to wavelength, so higher energy means shorter wavelength). Notice that XPS revealed the components of Opticlean®.

Results of O₂ Plasma Exposure

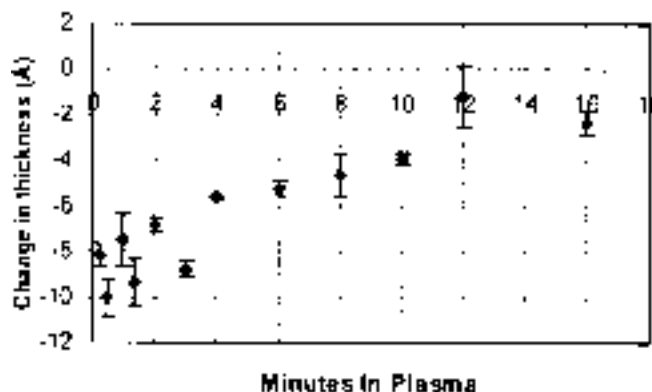


Figure 4: Results of O₂ Plasma Exposure. Change in apparent thickness with exposure to oxygen plasma.

The three points in the lower left hand corner of Figure 4 merit comment. It appears to show an upper and lower trend lines. This may be due to the time the samples spent in a petri dish before being measured. The 15 second, 80 second and three minute samples (the lower points) 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 transit between etching and ellipsometric measurement.

We also found that, with increased exposure to the plasma, the “apparent oxide” thickness increases. This trend is clearly evident in Figure 4. Could it be that the free oxygen reacts with the surface to produce additional silicon dioxide? This is not necessarily the case. It is also possible that contaminants from the plasma chamber are accumulating on the surface. We used XPS to test the possibilities. XPS results in Figure 5 clearly show only oxygen (532.7 eV) and silicon (150.5 eV). The peaks around 750, 880 and 580 eV are thought to be phantoms from the detector and have no physical significance. Carbon at 281 eV is not present. 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. However, no detectable sodium (500 eV and 50 eV) is present on the surface.

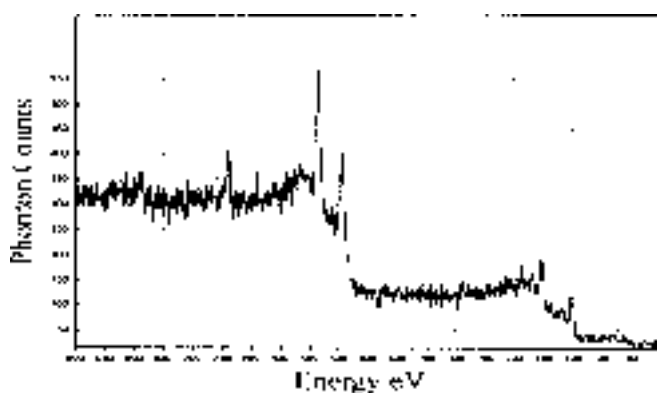


Figure 5: XPS of Si wafer cleaned in O₂ Plasma. No carbon found.

The most important result of Figure 5 is that no carbon (281 eV) was found on the surface of plasma-treated wafers, indicating that the DADMAC was completely removed and that the increase in “apparent oxide” thickness is not attributable to contamination, but must be due to oxide growth. This is a significant observation. Many applications, from gates in ULSI to nanofabrications, depend critically on the Dub nanometer (atomic level) changes in oxides. O₂ plasma processes is too aggressive for its use in general organic cleanup for our applications and may be so for others.

UV Lamp

The wafers were measured before and after the DADMAC application to calculate the thickness of the hydrocarbon layer. The DADMAC for this test was approximately 4.5 Å thick. Figure 6 shows that the DADMAC was removed rapidly. Within about five minutes of exposure, the “apparent oxide thickness” had returned to its value before the DADMAC deposition, and it appears that all of the organic contamination is removed.

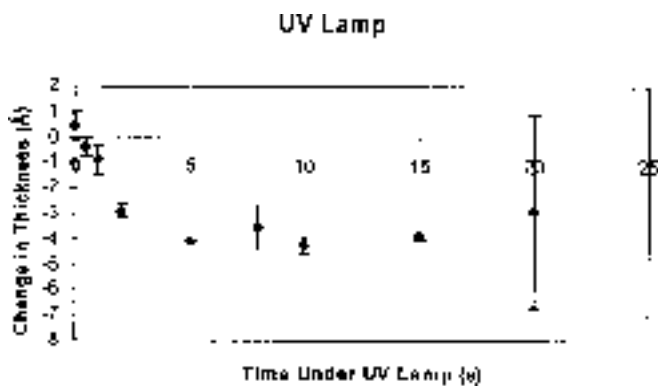


Figure 6: Results of UV lamp exposure. Change in apparent thickness versus exposure time of UV lamp.

XPS analysis on a DADMAC-coated sample exposed to UV for five minutes (Figure 7) shows exactly this. No carbon is present. The 1000 eV and 550 eV lines are spurious lines. 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 interpreted to mean that contaminant levels are much below the detection limits. The data point for the 20-minute samples displayed suggests that one of the samples was adulterated.

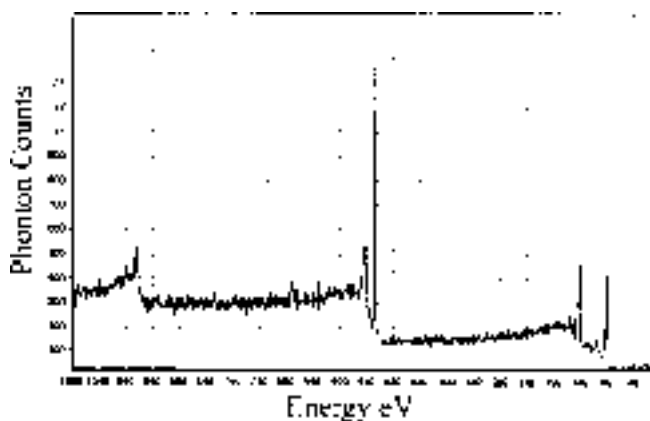


Figure 7: XPS Spectrum of UV cleaned sample. Only oxygen (532.8 eV) and silicon (150.8 eV, 97 eV) are present. The 1000 eV and 550 eV peaks are detector artifacts.

Opticlean®

As stated above, the Opticlean® atomistic cleaning process left an organic residue approximately 2 nm thick. We investigated whether either plasma etching, or UV/ozone would remove this hydrocarbon residue.

One of the samples was measured with ellipsometry to have 2.2 nm of residue. We placed this 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. Therefore, we concluded that oxygen plasma etching effectively removes the residue left from the Opticlean® cleaning process. We suggest that when Si wafers require a rigorous cleaning, Opticlean® followed by oxygen plasma etching provides a good method for a combination of large (dust particles) and small contaminant cleaning. Because of its rapid, strong oxidizing character, however, its use on metal films will have to be investigated on a case-by-case basis.

Opticlean® + UV Lamp

We took four pieces of a silicon test wafer and measured the apparent silicon dioxide thickness with ellipsometry. The change in thickness after Opticlean® application is recorded in Table 2.

Table 2: Change in SiO₂ Thickness Due to Opticlean® Residue.

Sample	Initial SiO ₂ Thickness (Å)	Final SiO ₂ Thickness (Å)	Change in SiO ₂ Thickness (Å)
C1	27.767	42.519	14.752
C2	29.758	43.446	13.688
C3	26.098	43.331	17.233
C4	24.21	40.717	16.507

After applying and removing the Opticlean®, the samples were exposed to the UV/ozone lamp. Figures 8 and 9 show how the apparent silicon dioxide thickness decreases with UV exposure time for samples C1 and C3, respectively. The sample C1 was exposed to the lamp in 60 second intervals between which ellipsometric measurements were taken. The apparent silicon oxide thickness becomes negative because the silicon wafers were not completely clean when the initial thicknesses were measured. From the plot, we can deduce that the wafer initially had about 5 Å of contaminant before cleaning. This is the value that the plot is asymptotically approaching.

Sample C3 was initially exposed to 60 seconds of UV light and then to 15 second exposures with intermittent ellipsometric measurements. Once again, we found that after approximately 2.5 minutes, nearly all of the Opticlean® residue had been removed.

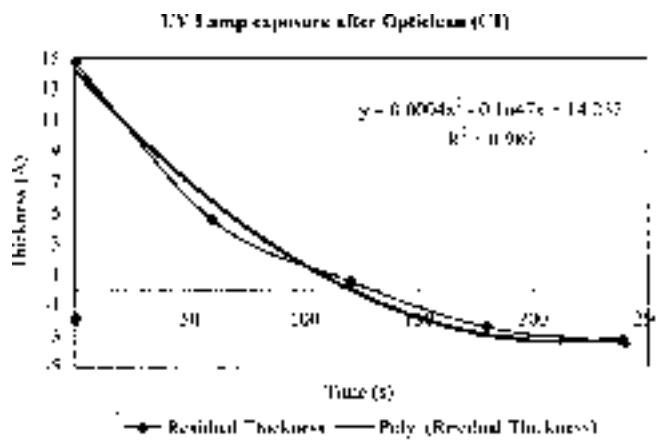


Figure 8: Decrease in apparent silicon oxide thickness with exposure to UV lamp. The silicon samples with Opticlean® residue were exposed at 60 second intervals. The negative thickness is due to the original natural contamination layer present before Opticlean® application.

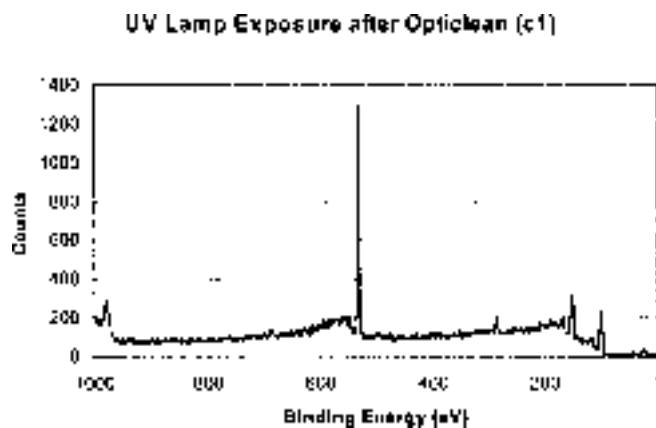


Figure 9: Energy levels present after UV lamp exposure. This shows the elements present in the sample after UV cleaning. There is no fluorine, indicating that most of the Opticlean® was removed. Oxygen (532 eV), silicon (99 and 103 eV) and minute amounts of carbon are present.

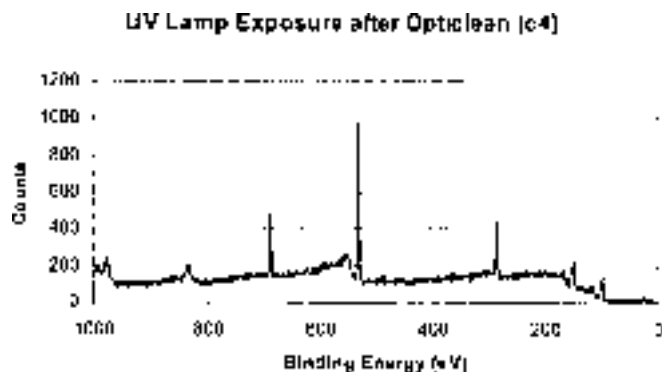


Figure 10: Elements present before UV lamp exposure, in addition to silicon and oxygen carbon at 275 eV and fluorine at 690 eV can be seen.

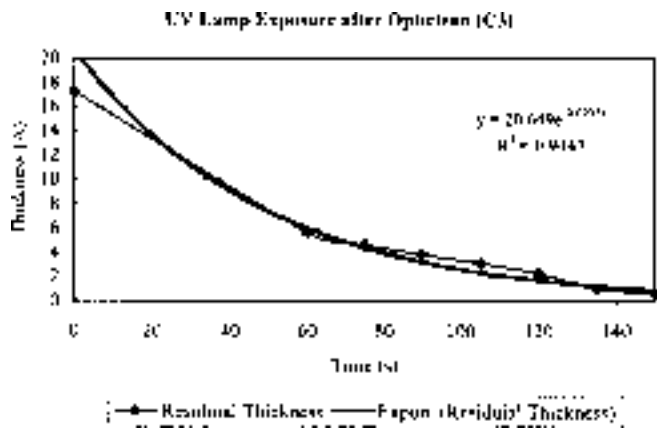


Figure 11: Decrease in apparent silicon oxide thickness with exposure to UV lamp. The silicon sample with Opticlean residue was exposed initially to 60 seconds of UV light and then in subsequent 15 second intervals.

Opticlean® Plus Cold, Pressurized Carbon Dioxide

Instead of using DADMAC, we took several relatively clean samples, cleaned them using the Opticlean®, measured the apparent oxide thickness, cleaned the samples with the CO₂ snow jet, and then measured the oxide thickness again. This told us how much hydrocarbon/Opticlean residue was taken off. In each case, the Opticlean® left a residue of about 2 nm. The change in thickness is recorded in Table 3.

Table 3: Apparent oxide thickness due to cold, pressurized CO₂ snow jet.

Sample #	Exposure time to Co ₂ (seconds)	Thickness before Opticlean®	Thickness Residue Å	Thickness after Co ₂ Exposure (Å)
1	0	25.93	46.32	46.67
2	0	25.27	47.98	47.72
3	5	26.82	41.69	40.68
4	5	25.19	42.77	38.48
5	10	24.82	42.39	42.00
6	10	25.75	46.93	21.05

The effectiveness of the gun was obviously different between the two 10 second cases. This is probably due to the nature of the gun itself. First, it cleans macroscopically, not atomistically. Second, the gun was handheld so the distance and the angle between the gun and the sample varied between cleanings.

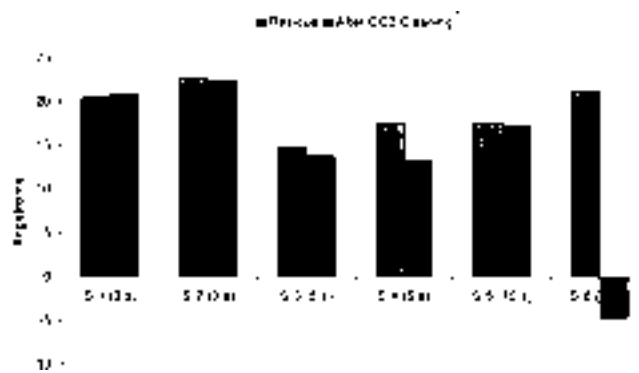


Figure 12

CONCLUSION

Recommended Cleaning Procedure

We have examined three different methods of cleaning surfaces of thin films, one bulk method, Opticlean®, and two atomistic methods, oxygen plasma on silicon and UV/ozone. Additionally, we investigated two-step cleaning, using Opticlean® followed by one of the atomistic methods. During the experiments, DADMAC was substituted for natural contaminants. The factors considered were effectiveness, ease of use and cleaning time. Table 4 summarizes the experimental results.

Based upon the experimental trials conducted for this study, the Opticlean® plus Eximer UV lamp is the best cleaning process for silicon wafers. It is the simplest process to use with the fewest side effects. Due to the fact that UV lamp exposure has been shown to rapidly oxidize many metallic thin film coatings, further tests are being conducted as to the optimal exposure time. The recommended exposure time for bare silicon wafers is 1.5 to 5 minutes. This exposure time results in a clean surface with very little additional surface oxidation.

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Table 4: Comparison of Cleaning Methods.

Method	Effectiveness	Cleaning Time	Ease of Use	Notes
Opticlean®	Left residue.	Must wait for polymer to cure.	Can be difficult peel off.	Good for dust, large particles, 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.	Good for removing larger contaminants and hydrocarbons.
Opticlean® + UV Lamp	Removes all Opticlean® residue and preexisting contaminant.	Cure time for Opticlean® + exposure time, 2.5 minutes.	Very easy, only skill required is peeling off Opticlean®.	Less silicon dioxide buildup and Opticlean® removes large contaminants.
Opticlean® + CO ₂ snow jet	In question – possibly works with exposure of 10 seconds or longer	Fastest of all methods	Potentially the easiest to use	Cleans macroscopically, so even under good conditions cleaning might be non-uniform

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