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Eliminating carbon contamination on oxidized Si surfaces using a VUV excimer lamp

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Abstract

In the VUV spectrum we see a significant decrease in reflection due to organic contamination on the surface of mirrors. To study VUV mirrors it is requisite to have calibration standards. Such standards are useless as calibration tools if the surface has organic contamination. For our standard, we use a thermally oxidized silicon wafer with a 27 nm oxide overlayer. We found that silicon wafer samples capped with native oxide acquire 0.1 to 0.2 nm of organic contamination within two hours of being cleaned with stored in closed, but nonvacuum, conditions. After a week there is an additional 0.2 to 0.5 nm deposition after which no further significant deposition is measured up to 90 days. We place the samples in air within one cm of a xenon excimer lamp that radiates 7.2 eV photons which remove half of the remaining contamination every minute. Five minutes exposure is sufficient to clean both fresh and stored samples. Data are determined using spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS). Additionally this paper addresses the need to ensure that these characterization tools are not a source of organic contamination. We determined that the antechamber of our XPS was contaminating samples at a rate of 0.6 nm/30 min as they waited for transfer to the analysis chamber. This contamination was virtually eliminated by attaching an oxygen radical source (ORS) device (Evactron® C De-Contaminator RF Plasma Cleaning System) directly to the antechamber.

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1. Introduction

Surface contamination, even if extremely thin, can have dramatic effects. Many are aware of the problems associated with environmental (organic) surface contamination on silicon [1,2], because of how it can interfere with device fabrication [3]. Even if the films are extremely thin, in the vacuum and extreme ultraviolet (VUV/EUV), surface contamination can significantly reduce reflection. Calculations of reflectance vs. angle of incidence (Fig. 1) show that a layer of carbon as thin as 2 nm on a silicon surface decreases reflectance dramatically. Reflectance at 41.3 nm is expected to be a full 10 percentage points (or 30% relative) less at 30° by 2 nm of carbon. Contrast the triangles to the diamonds in Fig. 1. This effect has also

been seen experimentally in the normal incidence reflectance of mirrors for space applications [5].

To make meaningful reflectance measurements of EUV mirrors, researchers must have calibration mirrors for aligning and checking optical equipment. Furthermore, there must be ways of cleaning and maintaining such calibration standards.

We have investigated techniques suitable for cleaning and storing an EUV reflectance standard consisting of a stable, smooth, thermally-oxidized silicon wafer. We use a (100) Si wafer with a 27 nm oxide overlayer for the EUV standard (for the 10 to 30 nm range) [6]. An oxide overlayer with a thickness in the 20 to 40 nm range produces reflectance interference fringes as a function of angle for wavelengths near 20 nm. We needed to ensure that the method of storing the sample produced the minimum contamination, furthermore, a suitable method for eliminating hydrocarbon contamination without destroying the surface needed to be found. We used native oxide (1.8 nm SiO₂) silicon wafer pieces to develop the techniques, but have shown that they work as well for the 27 nm thermal oxide standard.

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2. Experimental

We addressed these four tasks: understanding the surface contamination, finding ways to remove it while preserving the integrity of the standard, investigating different ways of storing samples and studying how quickly carbon contamination returns.

To study cleaning treatment effectiveness we needed suitable measurement techniques. We chose spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS). The first was a quick two minute way of detecting that an adventitious layer had formed on the sample and that it was increasing in thickness. The second allowed us to investigate chemical identity and bonding in the adventitious carbon-containing overlayer.

The test samples were cleaved from (100) silicon wafers. Prior to cleaning, these wafers were stored in a variety of conditions; however the vast majority of them were cut from wafers that were stored vertically in the original factory packaging. By the time they were measured by SE all test pieces had several angstroms of surface contamination. We deduced this from the fact that all samples started with an “apparent” oxide thickness as measured by SE [J.A. Woollam spectroscopic ellipsometer (M2000)] thicker than that of the 1.83 nm native oxide there. All had at least 2.1 nm initially, with an average thickness of 2.27 ± 0.15 nm for 55 samples, however in every case the native oxide layer was only 1.83 ± 0.03 nm thick when the samples were remeasured after adequate excimer lamp cleaning. XPS indicated that these samples had the lowest carbon contamination signal.

Since we were interested in carbon elimination it would seem more intuitive to measure that layer's thickness directly rather than from the thickness of an “apparent” oxide. The adventitious layer was so thin, however, that the ellipsometer

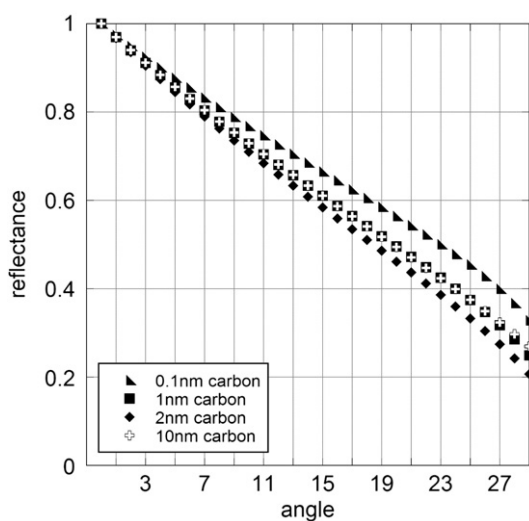


Fig. 1. Calculated reflectance for 41.3 nm light on a silicon wafer with a 1.8 nm oxide overlayer. Note how the reflectance decreases as the thickness of the adventitious carbon overlayer increases to a minimum at 2 nm. (Reflectance is measured relative to the grazing angle as is common in EUV and X-ray optics.) [4].

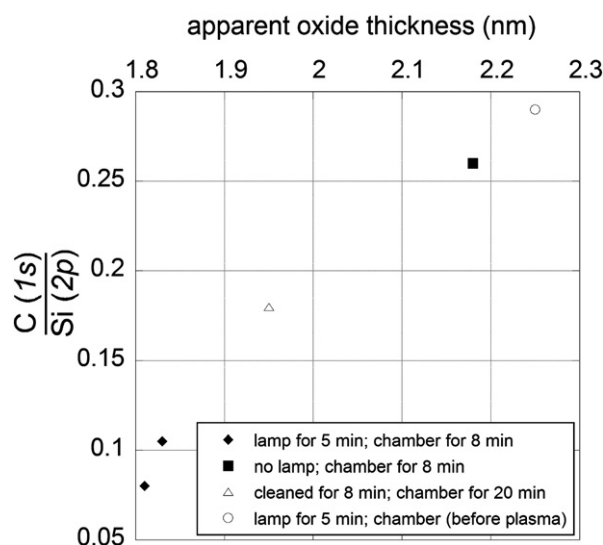


Fig. 2. Apparent oxide thickness (SE) increases as contamination rises as determined by XPS.

(using wavelengths of light from 191.72 to 989.29 nm) could not reliably distinguish between the oxide and the organic on top. Despite the ellipsometer's inability to distinguish such ultrathin layers, we knew that the contamination was there because we detected carbon with XPS and furthermore, we observed that its signal increased monotonically with the apparent oxide thickness as measured by SE. (See Fig. 2 and accompanying discussion.)

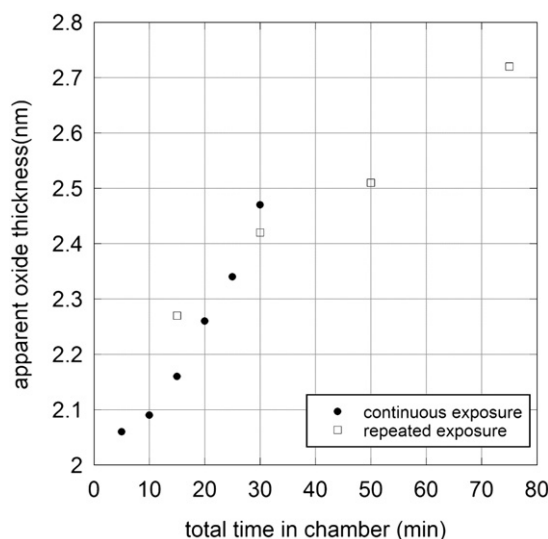


Fig. 3. Contamination deposition rate in the XPS antechamber. The thickness of the apparent oxide layer (and thus the contamination layer) increases with the time a sample sits in the chamber. Any increase in the “apparent” oxide thickness above 1.83 nm native oxide is contamination that XPS showed to be mostly carbon. Prior to installation of the Evactron-C the contamination increased steadily as an initially clean sample sat in the chamber. Interrupting the exposure has an effect. Note that samples which spent the same total amount of time in the chamber do not necessarily experience the same rate of carbon growth. Samples that were repeatedly exposed to the chamber (open squares) show a marked difference in the growth rate from the samples that were exposed for one continuous run (closed circles).

As a practical matter, we forced the ellipsometer to “detect” and quantify the carbon by measuring the thickness of the apparent oxide layer. We modeled the combination as a single “oxide layer” on top of a silicon substrate so that the program calculated a thickness for that “layer”. After cleaning, we again used the ellipsometer to determine the new thickness of the “oxide” layer. The “thickness” of the adventitious layer is the difference between the two thicknesses. XPS confirmed that the decrease in the apparent oxide thickness corresponded with a decrease in the carbon to silicon ratio (Fig. 3).

X-ray photoelectron spectroscopy characterization was performed using a SSX-100 ESCA Spectrometer with a conventional Al K_{α} anode. All measurements were taken at better than 2×10^{-8} Torr. The system was regularly calibrated using the Cu($2p$ 3/2) and Cu($3s$) peaks along with the Au ($4f$ 5/2) and Au ($4f$ 2/7) peaks. Binding energies were referenced based on this calibration. We discovered as we used it in these studies that our XPS's antechamber was a source of substantial surface contamination. The carbon 1s peak was very pronounced in the XPS spectra. The antechamber is pumped down using a Balzers rotary vane roughing pump and a Pfeiffer TPU 170 turbomolecular pump. During the 30 min pump-down/holding time required by the former operating procedure, the XPS antechamber deposited ~ 0.6 nm of carbon-containing contamination onto samples' surfaces while they awaited transfer to the XPS chamber (Fig. 3). Looking at the figure we see that the increase was largest in the first 5 min and that after about ten minutes the increase became linear, rising at a rate of 0.02 nm/min for 30 min.

This situation was ameliorated by the installation of an oxygen radical source (ORS), the Evactron[®] C De-Contaminator RF Plasma Cleaning System (Fig. 4). This device was designed to employ neutral oxygen radicals to remove hydrocarbon contamination from electron microscope chambers, particularly those of scanning electron microscopes [7]. We operated the Evactron when the antechamber pressure was

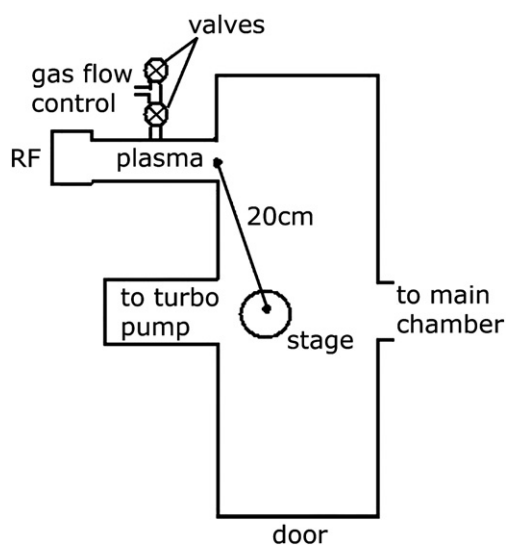


Fig. 4. Schematic of the XPS antechamber with the addition of the Evactron system. The volume of the antechamber is 22L.

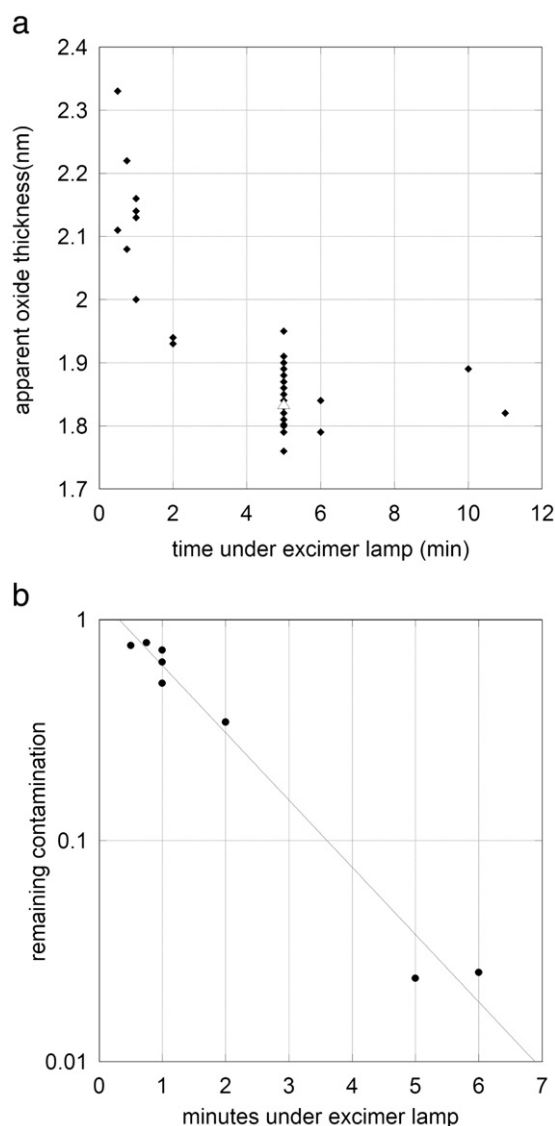


Fig. 5. a) Apparent oxide thickness of 59 samples that were cleaned exclusively with the excimer lamp. The white triangle on the graph represents the mean five-minute thickness for 45 samples. (30 of the 45 samples lie at or below the mean). The decrease is most rapid at the outset, falling asymptotically toward the 1.83 nm thickness of native oxide. After five minutes under the lamp it is difficult to see any further changes. b) The relative fraction of remaining contamination follows an exponential decrease. Here the log of $[(t - 1.82 \text{ nm}) / (t_0 - 1.82 \text{ nm})]$ is plotted vs time exposure where t is apparent oxide thickness measured after cleaning and t_0 is the initial thickness. Like Fig. 5a this graph demonstrates the cleaning-effectiveness of the excimer lamp on the organic contamination. Further this suggests that the final contamination layer thickness is only $\sim 2\%$ of the uncleaned thickness. The data point at five minutes is the mean thickness of 45 samples (the white triangle in 5a). Data for points beyond six minutes are not included because there was not adequate data to achieve the needed accuracy.

at ~ 0.4 Torr. This pressure was stabilized by adjusting the flow rate from the ORS device to balance the pumping speed of the antechamber's turbo pump. The RF power was set at 12 W. We did not find it necessary to use the optional nitrogen purge mode. We varied the time that we cleaned the chamber with the ORS. We used the plasma-cleaning method on the chamber and on the stage before we introduced the samples. Samples

previously cleaned with the excimer lamp were then introduced to the antechamber for various holding times. The increase of the amount of apparent oxide was an order of magnitude less than before.

We used a variety of techniques to clean the samples (i.e., reduce the apparent oxide thickness to ~ 1.83 nm). We chose green, gentle approaches to cleaning: detergent and water and alcohol where needed, with the last step gaseous cleaning based on atomic oxygen from our VUV lamp. For our applications, HF containing liquids are not a viable option for cleaning because they would eliminate the oxide which is required for the standard's optical performance and would attack one or more layers in most EUV mirrors. Our approach also eliminates the need to dispose of waste chemicals inherent with techniques commonly used in industry such as the RCA clean [8]. It is also intrinsically gentler than plasma processing. The ion bombardment component could roughen the standard's surface, which is impermissible. For this research VUV light (7.2 eV) from a xenon excimer lamp (Resonance LTD) was the critical last step [9]. A typical sample was cleansed of its last 0.5 to 1 nm of contamination with about five minutes of light exposure in air at ambient pressure.

The combination of cleaning techniques varied depending on what the storage conditions for the sample were. Some were washed using soap and water, then rinsed with ethanol. After each liquid cleaning step the sample was "blown-dry" with a clean, dry inert gas. The last step was to clean sample with the excimer lamp. Other samples were cleaned with methanol only, others with the lamp only, and some with a combination of the two. We varied the amount of time the samples spent under the lamp. All lamp-exposed samples were placed 1 cm from the excimer lamp. It was operated in a hood in air, and cooled with nitrogen gas. Samples with an initial apparent oxide layer of 2.3 ± 0.3 nm need a minimum of five minutes under the lamp.

3. Results and discussion

Samples that have less than 1 nm of organic overlayer must be cleaned with the excimer lamp for at least 5 min to reach an apparent oxide thickness of 1.8 nm. (See Fig. 5a and b). A straight line is drawn from the upper left corner to the lower right corner of 5b. This suggests that the thickness of the contamination falls off exponentially with time. The time for halving is about one minute. The mechanism may be pseudo first-order, depending only on the amount of organic on the surface. The limiting factor is the fraction of the surface covered with organic. That is, there may be enough atomic oxygen to oxidize organics if an atom happens to strike an organic molecule on the surface, but if it does not strike oxidizable material then it (re)combines to give a less active oxidizer.

As the apparent oxide thickness decreases the carbon to silicon ratio decreases (Fig. 3). The carbon to silicon ratio was determined by an analysis package provided by Surface Physics. An untreated sample with an apparent oxide thickness of 2.17 ± 0.02 nm had a carbon to silicon ratio of 26.2 to 73.8. The sample exposed to the lamp had an apparent oxide thickness of 1.81 ± 0.03 nm and had a carbon to silicon ratio of

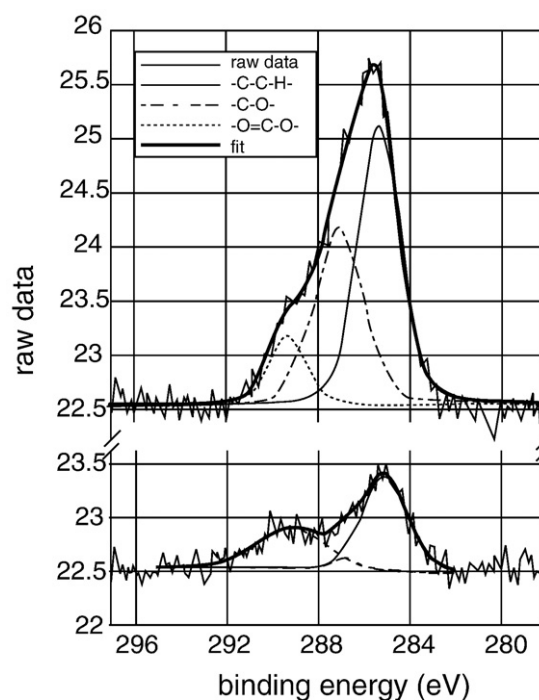


Fig. 6. C (1s) peak for an untreated SiO₂ on Si sample show higher levels of adventitious carbon contamination (upper curve). From the peak fit for this sample we see that the carbon-only type bonds are the dominate feature. We also see two statistically significant peaks of the OC type. The lower curve is the C (1s) peak for a sample exposed to the excimer lamp. The carbon peak is significantly reduced. Statistically speaking, the peak fit only recognizes the carbon-only peak and the peak which corresponds to an organic acid (carboxyl) type.

8.4 to 91.6. In general, we see that the C (1s) peak decreases relative to the silicon peak for a sample exposed to the excimer lamp.

The peak fitting and line shape analysis of the C (1s) peak reveals how the excimer lamp's cleaning treatment effects the adventitious carbon (AC) on the sample surface (see Fig. 6). We fit using a Shirley background and the peak fitting package supplied by Surface Physics. To provide statistical analysis of the peak fit, we used the Mathematica 6.0 fitting package and fit the data to Gaussian and Lorentzian models. The position and shape of the C (1s) peak also provides information about the chemical nature of the overlayer. Peak fitting the carbon peak on a dirty sample suggests, as expected, that C–H or carbon-only type bonds are the dominate feature [2]. There is also always some oxidized adventitious carbon present. Cleaning with the lamp significantly decreases the carbon-only AC and the oxidized carbon (lower curve in Fig. 6). We refer to the overlayer as organic (or hydrocarbons) because organic compounds have characteristics that match the characterization data. They are ubiquitous in the environment, are carbon-containing, have the correct peak shifts. Furthermore they possess sufficient volatility to move as a gas but can also condense on surfaces. For the contamination on the samples exposed to the antechamber before the installation of the ORS, the antechamber pump oil is a likely contamination culprit and fits the data. We note that the carbon exhibits evidence of

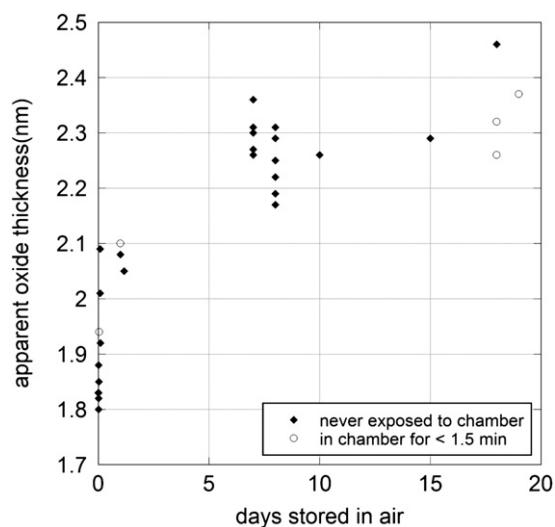


Fig. 7. This storage data come from 37 samples that were cleaned with the excimer lamp prior to being stored in air. Five samples were exposed to the organic contamination in the XPS chamber for less than 1.5 min; thus they started storage with an apparent oxide of about 1.9 ± 0.5 nm. 32 samples were never exposed to the antechamber; the apparent oxide was initially 1.83 ± 0.03 nm thick. Storage time varied from ten minutes to nineteen days. Of the 37 samples, all but six had an apparent oxide thickness ≤ 1.84 nm at the time the storage study started.

significant oxygen content. Gaussian peaks fitted to match the data are indicated as solid, dotted and dashed lines under the collected data. The largest peak is due to C–C and/or C–H bonds. In Fig. 6 the first peak dotted under the data to the left of this peak is due to C=O (carbonyl) or an ether (C–O–C). The peak on the far left is due to an organic acid group (O=C–O). There is good evidence that the organic contaminants are polar. Acids are especially polar. This may lead to stronger bonding to the substrate for the first layer that accumulates.

Lastly, we turn to the question of storage. Standards and mirrors cannot always be stored under vacuum. We found that with nonvacuum storage conditions, after two hours of being cleaned, 0.1 to 0.2 nm of hydrocarbon reappear on the surface. After a week there is an additional 0.2 to 0.5 nm deposition. Between the time span of a week and 90 days, we saw no further significant hydrocarbon overlayer deposition (see Fig. 7). The amount of contamination is thus comparable to what was on the samples when the wafers were removed from their factory

packaging. We cleaned the stored samples with the excimer lamp and found the same behavior observed for fresh samples.

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References

- [1] Researchers refer to the mostly carbon-containing contamination layer which settles on surfaces as an environmental, organic, molecular, hydrocarbon, carbon or adventitious layer. (We use the word “carbon” as a stand-in for organic films or unknown composition since carbon is the species in the contamination layer detected by XPS and can be the dominant EUV absorber.) Adventitious means, extrinsic, associated with something by chance rather than as an integral part.
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- [7] Although somewhat unusual, use of the Evactron on an XPS system is not unprecedented. In 2001 two posters were presented at the Microscopy and Microanalysis conference where the Evactron was used with XPS systems.
- [8] The RCA clean was developed by Werner Kern in 1965 while working for RCA (Radio Corporation of America). It consists of two steps. First, there is an organic cleaning where insoluble organic contaminants are removed with 5:1:1 H₂O:H₂O₂:NH₄OH. Then ionic and heavy metal atomic contaminants are removed with a 6:1:1 H₂O:H₂O₂:HCl. See for example. W. Kern, *J. Electrochem. Soc.*, 137, (1990) 1887–1892.
- [9] The excimer lamp creates ozone and oxygen radicals by exposing oxygen to 172 nm photons. These products oxidize the adventitious carbon on the samples thus freeing the sample of its organic contamination. Excimer lamp cleaning is thought to rely on atomic oxygen rather than ozone; this is in contrast with earlier low-pressure mercury discharge lamps (photon at 6.6 eV, 187 nm).