UV/ozone cleaning of surfaces

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The ultraviolet (UV)/ozone surface cleaning method is reviewed. The UV/ozone cleaning procedure is an effective method of removing a variety of contaminants from surfaces. It is a simple-to-use dry process which is inexpensive to set up and operate. It can rapidly produce clean surfaces, in air or in a vacuum system, at ambient temperatures. By placing properly precleaned surfaces within a few millimeters of an ozone producing UV source, the process can produce clean surfaces in less than 1 min. The technique is capable of producing near-atomically clean surfaces, as evidenced by Auger electron spectroscopy, ESCA, and ISS/SIMS studies. Topics discussed include: the variables of the process, the types of surfaces which have been successfully cleaned, the contaminants which can be removed, the construction of a UV/ozone cleaning facility, the mechanism of the process, UV/ozone cleaning in vacuum systems, rate enhancement techniques, safety considerations, effects of UV/ozone other than cleaning, and applications.

I. INTRODUCTION

The ability of ultraviolet (UV) light to decompose organic molecules has been known for a long time, but it is only during the past decade that UV cleaning of surfaces has been explored.

In 1972, Bolon and Kunz1 reported the ability of UV light to depolymerize a variety of photoresist polymers. The polymer films were enclosed in a quartz tube, the tube was evacuated, then backfilled with oxygen. The samples were irradiated with UV light from a medium pressure mercury lamp which generated ozone. The polymer films, which had been several thousand angstroms thick, were successfully depolymerized in less than 1 h. The major products of depolymerization were found to be water and carbon dioxide. Subsequent to depolymerization, the substrates were examined by Auger electron spectroscopy (AES) and were found to be free of carbonaceous residues. Only inorganic residues such as tin and chlorine were found. When a Pyrex filter was placed between the UV light and the films, or when a nitrogen atmosphere was used instead of oxygen, the depolymerization was hindered. Thus, Bolon and Kunz recognized that oxygen and wavelengths shorter than 300 nm played a role in the depolymerization.

In 1974, Sowell et al.2 described UV cleaning of adsorbed hydrocarbons from glass and gold surfaces, in air and in a vacuum system. A clean glass surface was obtained after 15 h of exposure to the UV radiation in air. In a vacuum system at 10⁻⁴ Torr of oxygen, clean gold surfaces were produced after about 2 h of UV exposure. During cleaning, the partial pressure of O₂ decreased, while that of CO₂ and H₂O increased. The UV also desorbed gases from the vacuum chamber walls. In air, gold surfaces which had been contaminated by adsorbed hydrocarbons could be cleaned by “several hours of exposure to the UV radiation.” Sowell et al. also noted that by storing clean surfaces under UV radiation it was possible to maintain the surface cleanliness indefinitely.

Starting in 1974, Vig et al.3-5 described a series of experiments aimed at determining the optimum conditions for producing clean surfaces by UV irradiation. The variables of cleaning by UV irradiation were defined, and it was shown that, under the proper conditions, UV/ozone cleaning was capable of producing clean surfaces in less than 1 min.

II. THE VARIABLES OF UV/OZONE CLEANING

A. The wavelengths emitted by the UV sources

To study the variables of the UV cleaning procedure, Vig and LeBus5 constructed the two UV cleaning boxes shown in Fig. 1. Both were made of aluminum and contained low-
pressure mercury discharge lamps and an aluminum stand with Alzak\(^6\) reflectors. The two lamps produced nearly equal intensities of short wavelength UV light, about 1.6 mW/cm\(^2\) for a sample 1 cm from the tube. Both boxes contained room air (in a clean room) throughout these experiments. The boxes were completely enclosed to reduce contamination by air circulation.

Since only the light which is absorbed can be effective in producing photochemical changes, the wavelengths emitted by the UV sources are important variables. The low-pressure mercury discharge tubes generate two wavelengths of interest, 184.9 and 253.7 nm. The 184.9 nm wavelength is important because it is absorbed by oxygen, and it thus leads to the generation of ozone.\(^7\) The 253.7 nm radiation is not absorbed by oxygen; it therefore does not contribute to ozone generation. However, it is absorbed by most hydrocarbons\(^8,9\) and also by ozone.\(^7\) The absorption by ozone is principally responsible for the destruction of ozone in the UV box. Therefore, when both wavelengths are present, ozone is continually being formed and destroyed. An intermediate product of both the formation and destruction processes is atomic oxygen, which is a very strong oxidizing agent.

The tube of the UV lamp\(^10\) in box 1 consisted of 91 cm of "hairpin-bent" fused quartz, which transmits both the 253.7 and 184.9 nm lines. The lamp emitted about 0.1 mW/cm\(^2\) of 184.9 nm radiation, measured at 1 cm from the tube.

The lamp in box 2 had two straight and parallel, 46 cm long, high-silica glass tubes. The glass was Corning UV Glass No. 9823 which transmits at 253.7 nm but not at 184.9 nm. Since this lamp generated no measurable ozone, a separate Siemens-type ozone generator\(^11\) was built into box 2. This ozone generator did not emit UV light. Ozone was produced by a "silent" discharge when high-voltage ac was applied across a discharge gap formed by two concentric glass tubes, each of which was wrapped in aluminum foil electrodes. The ozone-generating tubes were parallel to the UV tubes, approximately 6 cm away.

UV box 1 was used to expose samples, simultaneously, to 253.7 nm, 184.9 nm, and the ozone generated by the 184.9 nm radiation. UV box 2 permitted the options of exposing samples to 253.7 nm plus ozone, 253.7 nm only, or ozone only.

Vig et al. used contact angle measurements, wettability tests, and Auger electron spectroscopy (AES) to evaluate the results of cleaning experiments. Most of the experiments were conducted on polished quartz wafers, the cleanliness of which could be evaluated by the "steam test," a highly sensitive wettability test.\(^2,12,15\)

A "black-light" long wavelength UV source, which emitted wavelengths above 300 nm only, was also tried. It produced no noticeable cleaning even after 24 h of irradiation.

It was found early in the studies of Vig et al. that samples could be cleaned consistently by UV irradiation only if gross contamination was first removed from the surfaces. Their precleaning procedure consisted of the following steps:

1. Scrub the samples with a swab while it is immersed in ethyl alcohol.
2. Degrease ultrasonically in a good solvent.
3. Boil in fresh ethyl alcohol, then agitate ultrasonically.
4. Rinse in running ultrapure (18 M cm) water.
5. Spin-dry immediately after the running water rinse.

Subsequent to this precleaning procedure, the steam test and contact angle measurements invariably indicated that the surfaces were contaminated. However, after exposure to UV/ozone in box 1, the same tests always indicated clean surfaces. On numerous occasions the cleanliness of such UV/ozone cleaned surfaces has been verified in the author's laboratory, and elsewhere by AES and electron spectroscopy for chemical analysis (ESCA).\(^1,3,4,13-15\) The effectiveness of UV/ozone cleaning has also been confirmed by ion scattering spectroscopy/secondary ion mass spectroscopy (ISS/SIMS).\(^16\)

A number of quartz wafers were precleaned and exposed to the UV light in box 1 until clean surfaces were obtained. Each of the wafers was then thoroughly contaminated with human skin oil which has been a difficult contaminant to remove. The wafers were precleaned again, groups were exposed to each of the four UV/ozone combinations mentioned earlier, and the time to attain a clean surface, as indicated by the steam test, was measured. In each UV box, the wafers were placed within 5 mm of the UV source (where the temperature was about 70 °C).

The wafers exposed to 253.7 nm + 184.9 nm + ozone in UV box 2 became clean in 20 s. The samples exposed to 253.7 nm + ozone in UV box 2 reached the clean condition in 90 s. Samples exposed to 253.7 nm without ozone and to ozone without UV light took about 1 h and 10 h, respectively, before clean surfaces were obtained.

The conclusion one can draw is that, while both UV light without ozone and ozone without UV light can produce a slow cleaning effect in air, the combination of both short wavelength UV light and ozone, such as is obtained from a quartz UV lamp, produces a clean surface orders of magnitude faster. Although the 184.9 nm radiation is also absorbed by many hydrocarbons, it was not possible from these experiments to isolate the cleaning effect of the 184.9 nm radiation. The ozone concentrations had not been measured. As is discussed below, the concentrations vary within each box with distance from the UV source.

B. Distance between sample and UV source

Another variable which can greatly affect the cleaning rate is the distance between the sample and the UV source. Because of the shapes of the UV tubes and of the Alzak reflectors above the tubes and below the samples, the lamps in both boxes were essentially plane sources. Therefore, one might have expected that the intensity of UV light reaching a sample would be nearly independent of distance. This was not so, however, when ozone was present, because ozone has a broad absorption band\(^7,17,18\) centered at about 260 nm. At 253.7 nm, the absorption coefficient of ozone is 130 cm\(^-1\) atm\(^-1\). The intensity \(I\) of the 253.7 nm radiation reaching a sample therefore decreases as

\[
I = I_0e^{-130pd},
\]

where \(p\) is the average ozone pressure between the sample and the UV source in atmospheres at 0 °C, and \(d\) is the dis-
tance to the sample in centimeters. When a quartz UV tube is used, both the ozone concentration and the UV radiation intensity decrease with distance from the UV source.

Two sets of identically precleaned samples were placed in UV box 2. One set was placed within 5 mm of the UV tube, the other, at the bottom of the box, about 8 cm from the tube. With the ozone generator off, there was less than a 30% difference in the time it took for the two sets of samples to attain a minimal contact angle (about 60 min vs 75 min). When the experiment was repeated with the ozone generator on, the samples near the tube became clean nearly ten times faster (about 90 s vs 13 min). Similarly, in UV box 1, samples placed within 5 mm of the tube were cleaned in 20 s vs 20–30 min for samples placed near the bottom of the box, 13 cm away. Therefore, to maximize the cleaning rate, the samples should be placed as close to the UV source as possible.

C. Contaminants

Vig et al. tested the effectiveness of the UV/ozone cleaning procedure on a variety of contaminants. Among the contaminants were: human skin oils, contamination adsorbed during prolonged exposure to air, a cutting oil,19 a beeswax and rosin mixture, a lapping vehicle,20 a mechanical vacuum pump oil,21 DC 704 silicone diffusion pump oil,22 DC 705 silicone diffusion pump oil,22 a silicone vacuum grease,22 an acid (solder) flux,23 and a rosin flux from a rosin core lead–tin solder. The contaminants were applied to clean, polished quartz wafers. After contamination, the wafers were precleaned, then exposed to UV/ozone by being placed within a few millimeters of the tube in UV box 1. After a 60 s exposure, the steam test and AES indicated that all traces of the contaminants had been removed.

Since AES could not differentiate between the silicon peaks due to quartz and those due to the silicon containing contaminants, the removal of silicone diffusion pump fluids was also tested on Alzak, which normally has a silicon-free oxide surface, and on gold. AES examination of the Alzak and gold surfaces following UV/ozone cleaning showed no traces of silicon present.

During the course of their studies, Vig et al. learned from colleagues working on ion implantation for integrated circuits that the usual wet-cleaning procedures (with hot acids) failed to remove the photoresist from silicon wafers which had been exposed to radiation in an ion-implantation accelerator, presumably because of crosslinking of the photoresist. Ion-implanted silicon wafers, each with approximately 1 μm coating of exposed Kodak Micro Resist 747,24 were placed within a few millimeters of the source in UV box 1. After an overnight (~ 10 h) exposure to UV/ozone, all traces of the photoresist were removed from the wafers, as confirmed by AES.

Films of carbon, vacuum deposited onto quartz to make the quartz surfaces conductive for study in an electron microscope, were also successfully removed by exposure to UV/ozone. Inorganic contaminants such as dust and salts cannot be removed by UV/ozone. Such contaminants should be removed in the precleaning procedure.

UV/ozone has also been used for waste-water treatment and for destruction of highly toxic compounds.25–28 Experimental work in connection with these applications has shown that UV/ozone can convert a wide variety of organic and some inorganic species to relatively harmless, mostly volatile products such as CO₂, CO, H₂O, N₂, etc. Compounds which have been successfully destroyed in water by UV/ozone include: ethanol, acetic acid, glycine, glycerol, palmitic acid; organic nitrogen, phosphorous and sulfur compounds; potassium cyanide; complexed Cd, Cu, Fe, and Ni cyanides; photographic wastes, medical wastes, secondary effluents; plus chlorinated organics and pesticides such as pentachlorophenol, dichlorobenzene, dichlorbutane, chloroform, malathion, Baygon, Vapam, and DDT. It has also been shown that the combination of UV and ozone is more effective in destroying microbial contaminants in water, such as E. coli and streptococcus faecalis, than UV or ozone alone.

D. The precleaning

Although UV/ozone is able to remove contaminants such as thick photoresist coatings and carbon films, without any precleaning, the procedure cannot, in general, remove gross contamination. For example, when a clean quartz wafer was coated thoroughly with human skin oils and placed in UV box 1 (Fig. 1) without any precleaning, even prolonged exposure to UV/ozone failed to produce a low-contact-angle surface. This is possibly due to the fact that human skin oils contain materials, such as inorganic salts, which cannot be removed by photosensitized oxidation.

The UV/ozone removed silicones from surfaces which had been precleaned, as described earlier, and also from surfaces which had been just wiped with a cloth to leave a thin film. However, when the removal of a thick film was attempted, the UV/ozone removed most of the film upon prolonged exposure; but it also left a hard cracked residue on the surface. This may be due to the fact that many chemicals respond to radiation differently, depending on whether or not oxygen is present. In the presence of oxygen many polymers, for instance, degrade when irradiated; whereas, in the absence of oxygen (as would be the case for the bulk of a thick film) these same polymers crosslink. In the study of the radiation degradation of polymers in air, the "results obtained with thin films are often markedly different from those obtained using thick specimen."

For the UV/ozone cleaning procedure to work reliably, the surfaces must be precleaned: first, to remove contaminants such as dust and salts which cannot be changed to volatile products by the oxidizing action of UV/ozone, and, second, to remove thick films the bulk of which could be transformed into a UV resistant film by the crosslinking action of the UV light that penetrates the surface.

E. The substrate

The UV/ozone cleaning process has been successfully used on a variety of surfaces including: glass, quartz, mica, sapphire, ceramics, metals, semiconductors, and a conductive polyimide cement.

Quartz and sapphire are especially easy to clean with UV/ozone, since these materials are transparent to short wavelength UV. For example, when a pile of thin quartz plates, a
couple of centimeters deep, was cleaned by UV/ozone, both sides of all the blanks, even the ones at the bottom of the pile, were cleaned by the process. Since sapphire is even more transparent, it too could probably be cleaned the same way. When flat quartz plates were placed one on top of the other so that there could have been little or no ozone circulation between the plates, the UV/ozone cleaning was able to clean both sides of these plates also. (There is evidence in the literature\(^{31}\) that photocatalytic oxidation of hydrocarbons, without the presence of gaseous oxygen, can occur on some oxide surfaces.)

When white alumina ceramic substrates were cleaned by UV/ozone, the surfaces could be cleaned properly. However, the sides facing the UV turned yellow, probably due to the production of (UV-induced) color centers. After several days at room temperature, or a few minutes at high temperatures, the white color returned.

Metal surfaces could be cleaned by UV/ozone without any problems as long as the UV exposure was limited to the time required to produce a clean surface. (This time should generally be about 1 min or less for surfaces which have been properly precleaned.) However, prolonged exposure of oxide-forming metals to UV light can produce rapid corrosion. Silver samples, for example, turned black in UV box 1 within 1 h. Experiments with sheets of Kovar, stainless steel (type 302), gold, silver, and copper showed that, upon extended UV irradiation, the Kovar, the stainless steel, and the gold appeared unchanged; the silver and copper oxidized on both sides, but the oxide layers were darker on the sides facing away from the UV source than on the sides facing the UV. When electroless gold-plated nickel parts were stored under UV/ozone for several days, a black powdery coating gradually appeared on the parts. Apparently, nickel diffused to the surface through pinholes in the gold plating, and the oxidized nickel eventually nearly completely covered the gold. The corrosion was observed even in UV box 2, when no ozone was being generated. The rate of corrosion increased substantially when a beaker of water was placed in the UV boxes to increase the humidity. Even Kovar showed signs of corrosion under such conditions.

The corrosion may possibly be explained by the fact that, as is known in the science of air-pollution control, in the presence of short wavelength UV light, impurities in air, such as oxides of nitrogen and sulfur, combine with water vapor to form a corrosive mist of nitric and sulfuric acids. The use of controlled atmospheres in the UV box should, therefore, minimize the corrosion problem.

Since UV/ozone dissociates organic molecules, it may be useful for cleaning some organic materials just as etching and electropolishing are sometimes useful for cleaning metals. The process has been used successfully to clean quartz crystal resonators which have been bonded with silver-filled polyimide cement.\(^{32}\) Teflon (TFE) tape exposed to UV/ozone in UV box 1 for 10 days experienced a weight loss of 2.5\%.\(^{33}\) Also, the contact angles measured on clean quartz plates increased after a piece of Teflon was placed next to the plates in a UV box.\(^{34}\) Similarly, Viton shavings taken from an O ring experienced a weight loss of 3.7% after 24 h in UV box 1. At the end of the 24 h, the Viton surfaces had become sticky.\(^{33}\)

Semiconductor surfaces have been successfully UV/ozone-cleaned without adversely affecting the functioning of the devices. For example, after a 4K static RAM integrated circuit was exposed to UV/ozone for 120 min in a commercial UV/ozone cleaner, the device continued to function without any change in performance. (This IC has been made using n-channel silicon gate technology, with 1 to 1.5 \(\mu\)m junction depths.\(^{35}\))

F. Rate enhancement techniques

UV/ozone cleaning “rate enhancement” techniques have been investigated by Zafonte and Chiu.\(^{36}\) Experiments on gas phase enhancement techniques included a comparison of the cleaning rates in dry air, dry oxygen, moist air, and moist oxygen. The moist air and moist oxygen consisted of gases that had been bubbled through water. Oxygen that had been bubbled through hydrogen peroxide was also tried. Experiments on liquid-enhancement techniques consisted of drop-wise addition of either distilled water or of hydrogen peroxide solutions of various concentrations to the sample surfaces. Most of the sample surfaces consisted of various types of photosresist on silicon wafers.

The gas phase “enhancement” techniques resulted in negligible to slight increases in the rates of photosresist removal (3–20 Å/min without enhancement vs 3–30 Å/min with enhancement). The water and hydrogen peroxide liquid phase enhancement techniques both resulted in significant rate enhancements (100–200 Å/min) for non-ion implanted resists. The heavily ion implanted resists (10\(^{15}\)–10\(^{16}\) atoms/cm\(^2\)) were not significantly affected by UV/ozone, whether “enhanced” or not.

III. THE MECHANISM OF UV/OZONE CLEANING

The available evidence indicates that UV/ozone cleaning is primarily the result of photosensitized oxidation processes, as is represented schematically in Fig. 2. The contaminant molecules are excited and/or dissociated by the absorption of short wavelength UV light. Simultaneously, atomic oxygen and ozone\(^{17,18}\) are produced when \(O_2\) is dissociated by the absorption of UV with a wavelength less than 245.4 nm. Atomic oxygen is also produced\(^{17,18}\) when ozone is dissociated by the absorption of the UV and longer wavelengths of radiation. The excited contaminant molecules, and the free radicals produced by the dissociation of con-

![Fig. 2. Simplified schematic representation of UV/ozone cleaning process.](image-url)
taminant molecules, react with atomic oxygen to form simpler volatile molecules, such as \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{N}_2 \), etc.

The energy required to dissociate an \( \text{O}_2 \) molecule into two ground state \( \text{O} \) atoms corresponds to 245.4 nm. However, at and just below 245.4 nm the absorption of \( \text{O}_2 \) is very weak.\(^7\)\(^11\)\(^18\) The absorption coefficient increases rapidly with decreasing wavelengths. A convenient wavelength for producing \( \text{O} \) is the 184.9 nm emitted by low-pressure Hg discharge lamps in fused quartz envelopes. Similarly, since most hydrocarbons have a strong absorption band between 200 and 300 nm, the 253.7 nm wavelength emitted by the same lamps is useful for exciting or dissociating contaminant molecules. The energy required to dissociate ozone corresponds to 1140 nm. The absorption by ozone reaches a maximum near the 253.7 nm wavelength. The actual photochemical processes occurring during UV/ozone cleaning are more complex than shown in Fig. 2. For example, the rate of production of ozone by 184.9 nm photons is promoted by the presence of other molecules, such as \( \text{N}_2 \) and \( \text{CO}_2 \).

As described earlier, the combination of short wavelength UV light and ozone produced clean surfaces about 200 to 2000 times faster than UV light alone or ozone alone. Similarly, Prengle et al.\(^{25}\)\(^28\) had found in their studies of wastewater treatment that UV enhances the reaction with ozone 10\(^3\)-fold to 10\(^3\)-fold, and the products of the reactions are materials such as \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and \( \text{N}_2 \). Increasing the temperature was found to increase the reaction rates. Mattox\(^{37}\) has also found that mild heating increases the UV/ozone cleaning rates. Bolon and Kunz,\(^7\) on the other hand, had found that the rate of UV/ozone depolymerization of photoresists did not change significantly between 100 and 300 °C. The rate of destruction of microorganisms was similarly insensitive to a temperature increase from room temperature to 40 °C.\(^{29}\)

### V. SAFETY CONSIDERATIONS

In the construction of a UV cleaning facility, one should be aware of the safety hazards associated with short wavelength UV light. Exposure to intense short wavelength UV light can cause serious skin and eye injury within a short time. For the UV boxes used in the Vig et al. experiments, switches are attached to the doors in such a manner that when the doors are opened, the UV lamps are shut off automatically. If the application demands that the UV lamps be used without being completely enclosed (for example, as might be the case if an UV cleaning facility is incorporated into a thermostatic vacuum chamber), then proper clothing and eye protection should be worn to prevent skin burns and eye injury.

Another safety hazard is ozone, which is highly toxic. In setting up a UV cleaning facility, one must ensure that the ozone levels to which people are exposed do not exceed 0.1 ppm, the OSHA standard.\(^{38}\) Ozone is also a potential hazard in a cryopumped vacuum system because cryopumped ozone can become explosive under certain conditions.\(^{39}\)

One method of minimizing the hazards associated with ozone is to use two types of short wavelength ultraviolet sources for UV/ozone cleaning.\(^{40}\) One, an ozone generating UV lamp, e.g., a low-pressure mercury light in a fused quartz envelope. The other, a UV lamp that does not generate ozone but one which emits one or more wavelengths that are strongly absorbed by ozone, e.g., a low-pressure mercury light in a high silica glass tube, which emits primarily at 253.7 nm. Such a nonozone generating UV source can be used as an “ozone killer.” For example, in one cryopumped vacuum system it was found that after the UV/ozone cleaning, in up to 20 Torr of oxygen, was completed and the ozone generating UV lamp was turned off, 10 min of “ozone killer” UV light reduced the concentration of ozone to less than 0.01 ppm, a level that is safe for immediate cryopumping.\(^{41}\) With the ozone killer lamp, ozone concentrations were reduced by at least a factor of 100 within 10 min. Without the ozone killer lamp, the half life of ozone is 3 days at 20 °C.\(^{42}\)

### VI. UV/OZONE CLEANING FACILITY CONSTRUCTION

The material chosen for the construction of a UV/ozone cleaning facility should be one which is not corroded by extended exposure to UV/ozone. One material that can be used is polished aluminum with a relatively thick anodized oxide layer, such as Alzak.\(^6\) Such materials are resistant to corrosion, have a high thermal conductivity which helps to prevent heat buildup, and are also good reflectors of short wavelength UV. Most other metals, including silver, are poor reflectors in this range.

Vig et al. initially used ordinary, shop variety aluminum sheet for UV box construction. After a while, however, it was noticed that a thin coating of a white powder (probably aluminum oxide particles) appeared at the bottom of the boxes. Even in a UV box made of standard Alzak, after a couple of years’ usage white spots started appearing on the Alzak. To avoid the possibility of particles being generated inside the UV/ozone cleaning facility, the facility should be
inspected periodically for signs of corrosion. The use of "class M" Alzak may also help, since this material has a much thicker oxide coating. It is made for "exterior marine service," instead of the "mild interior service" specified for standard Alzak. Commercially available UV/ozone cleaners are constructed of stainless steel. To date, no corrosion problems have been reported with such cleaners.

Organic materials should not be present in the UV cleaning box. For example, the plastic insulation usually found on the leads of UV lamps should be replaced with inorganic insulation, such as glass or ceramic. The box should be enclosed so as to minimize recontamination by circulating air, and to prevent accidental UV exposure.

The most widely available sources of short wavelength UV light are mercury arc lamps. Low-pressure mercury lamps in pure, fused quartz envelopes operate near room temperature, emit approximately 90% at 253.7 nm, and generate sufficient ozone for effective surface cleaning. Approximately 5% of the output of these lamps is at 184.9 nm. Medium and high-pressure UV lamps generally have a much higher output in the short wavelength UV range. These lamps also emit a variety of additional wavelengths below 253.7 nm, which may enhance their cleaning action. However, they operate at high temperatures (the envelopes are near red hot), have a shorter lifetime, a higher cost, and present a greater safety hazard. The mercury tubes can be fabricated in a variety of shapes to fit different applications. In addition to mercury arc lamps, microwave-powered mercury vapor UV lamps are also available.

Other good sources of short wavelength UV, such as xenon lamps and deuterium lamps, are also available. These lamps must also be in an envelope transparent to short wavelength UV, such as quartz. In setting up a UV cleaning facility, one should choose a UV source which will generate enough UV/ozone to allow for rapid photosensitized oxidation of contaminants; however, too high an output at the ozone generating wavelengths can be counterproductive because a high concentration of ozone will absorb most of the UV light before it reaches the samples. The samples should be placed as close to the UV source as possible to maximize the intensity reaching the samples. In the UV cleaning box 1 of Vig et al., the parts to be cleaned are placed on an Alzak stand, the height of which can be adjusted to bring the parts close to the UV lamp. The parts to be cleaned can also be placed directly onto the tube if the box is built so that the tube is on the bottom of the box.43

VII. APPLICATIONS

The UV/ozone cleaning procedure has found numerous applications during the past several years. A major use is substrate cleaning prior to thin-film deposition as is widely used in the quartz crystal industry during the manufacture of quartz crystal resonators. There is probably no other device of which the performance is so critically dependent on surface cleanliness. For example, the aging requirement for a 5 MHz resonator is that the frequency change no more than two parts on 1010 per week, whereas adsorption or desorption of a monolayer of contamination from such a device changes the frequency by about one part in 106. The surface cleanliness must therefore be such that the rate of transfer of contamination within the (hermetically sealed) resonator enclosure is less than 10−4 monolayers per week! In the author's quartz resonator fabrication laboratory, UV/ozone is used at several points during the fabrication sequence, such as for cleaning and storing metal tools, masks, resonator parts, and storage containers.

The process is also being applied in a hermetic sealing method which relies on the adhesion between clean surfaces in an ultrahigh vacuum.44,45 It has been shown that metal surfaces will weld together under zero-zero forces if the surfaces are atomically clean. A gold gasket between gold metallized (UV/ozone cleaned) aluminum oxide sealing surfaces is currently providing excellent hermetic seals in the production of ceramic flatpack-enclosed quartz resonators. The feasibility of achieving good hermetic seals by pressuring a clean aluminum gasket between two clean, unmetallized aluminum oxide ceramic surfaces has also been shown.44,45

The same adhesion phenomenon between clean (UV/ozone cleaned) gold surfaces has been applied to the construction of a novel surface contaminant detector.47,48 The rate of decrease in the coefficient of adhesion between freshly cleaned gold contacts is used as a measure of the gaseous condensable contaminant level in the atmosphere.

The process has also been applied to improve the reliability of wire bonds, especially at reduced temperatures. It has been shown,49,50 for example, that the thermocompression bonding process is highly temperature dependent when organic contaminants are present on the bonding surfaces. The temperature dependence can be eliminated by UV/ozone cleaning of the surfaces just prior to bonding. In a study of the effects of cleaning methods on gold ball bond shear strength, UV/ozone cleaning was found to be the most effective method of cleaning contaminants from gold surfaces.51 UV/ozone is also being used for cleaning alumina substrate surfaces during the processing of thin-film hybrid circuits.52

When the nonuniform appearance of thermal/flash protective electro-optic goggles was traced to organic contaminants on the electro-optic wafers, a number of cleaning methods were tested. UV/ozone proved to be the most effective method for removing these contaminants, and thus it was chosen for use in the production of the goggles.53

Other applications which have been described are photoresist removal,1,5,12 the cleaning of: vacuum chamber walls,7 photomasks,54 silicon wafers (for enhancing photore sist adhesion),54 lenses,53 mirrors,54 solar panels,54 sapphire (before the deposition of HgCdTe),54 cold-rolled steel (for paint and zinc coating adhesion improvement),54 surface acoustic wave and other fine linewidth devices,54,55 inertial guidance subcomponents (glass, chromium-oxide surfaced gas bearings, and beryllium),55 and gallium arsenide wafers.57 Since short wavelength UV can generate radicals and ions, a side benefit of UV/ozone cleaning of insulator surfaces can be the neutralization of static charges.58

UV/ozone cleaning of silicon substrates in silicon molecular beam epitaxy (MBE) has been found to be effective in producing near-defect-free MBE films.59 By using UV/ozone cleaning, the above 1200°C temperatures required for removing surface carbon in the conventional method can be
lowered to below 1000 °C. The slip lines resulting from thermal stresses and thermal pits that are often produced by the high temperature treatment are minimized in the lower temperature processing. Impurity redistribution in the substrate is also reduced.

VIII. EFFECTS OTHER THAN CLEANING

Short wavelength UV, ozone, and the combination of the two, can have effects other than surface cleaning. Among the more significant of these effects are the following:

A. Oxidation

Ozone’s oxidation power is second only to that of fluorine. Ozone can oxidize most inorganic compounds to their final oxidative state. For most substrates, UV/ozone cleaning for the minimum time necessary to obtain a clean surface will not cause a significant amount of oxidation. However, extended storage under UV/ozone may be detrimental for some oxidizable surfaces. In some cases, the enhanced oxide formation may be beneficial. For example, whereas the “native” oxide on GaAs is only about 30 Å thick, UV/ozone produces an oxide layer that is 100 to 300 Å thick, i.e., UV/ozone can produce a clean, enhanced oxide “passivated” surface. 10 min of UV/ozone cleaning increased the oxide thickness on silicon substrates from 0.9 to 1.2 nm. Similarly, the native UV/ozone produced oxide layer at the interface of HgCdTe–SiO₂ has been found to enhance the interface properties. Solar radiation and atmospheric ozone have been found to markedly enhance the sulfidation of copper. Extended exposure to UV/ozone has been found to significantly increase the oxide layer thickness on aluminum surfaces. Whereas the oxide thickness on air exposed aluminum surfaces is normally limited to about 50 Å, after 10 min of UV/ozone exposure, the oxide thickness was found to be 90 Å, and after 60 min, 200 Å.

B. UV-enhanced outgassing

Short wavelength UV has been found to enhance the outgassing of glasses. The UV light produced evolution of significant quantities of hydrogen, and also water, carbon dioxide, and carbon monoxide. The hydrogen evolution was proportional to the amount of radiation incident onto the samples. For UV-opaque glasses, the evolution occurred from the side exposed to the UV; for high transmission samples, the gas evolved from both sides.

C. Other surface/interface effects

Energetic radiation such as UV and γ-radiation has been reported to produce dehydration and the formation of free radicals on silica surfaces. However, dehydrated (or siloxinated) silica surfaces are hydrophobic, whereas UV/ozone cleaned silica (quartz) surfaces exhibit a very low (less than 4°) contact angle, thus indicating that the UV/ozone cleaning does not dehydrate the surfaces, nor does it modify surface silanol groups the way high-temperature vacuum baking does. Short wavelength UV has also been found to produce a bleaching effect in Si–Si₂ interfaces with thin oxides, and has also been found to produce yellowing (color centers) during the cleaning of aluminum oxide ceramics. The yellowing can be readily bleached by heating the sample.

D. Etching

Short wavelength (193 nm) UV laser irradiation of biological and polymeric materials has been shown to be able to etch the materials with great precision, via “ablative photodecomposition,” and without significant heating of the samples. Linewidths 5 µm wide have been etched onto a plastic film to demonstrate the capability of this technique. Oxygen does not appear to have the same significance in this process as it does in UV/ozone cleaning. The etch depth versus fluence in vacuum and air were found to be the same. The UV/ozone has been found to etch Teflon and Viton, and will likely etch other organic materials as well.

IX. SUMMARY AND CONCLUSIONS

The UV/ozone-cleaning procedure has been shown to be a highly effective method of removing a variety of contaminants from surfaces. It is a simple-to-use dry process which is inexpensive to set up and operate. It can produce clean surfaces at room temperature, either in a room atmosphere or in a controlled atmosphere.

The variables of the UV cleaning procedure are: the contaminants initially present, the precleaning procedure, the wavelengths emitted by the UV source, the atmosphere between the source and sample, the distance between the source and sample, and the time of exposure. For surfaces which are properly precleaned and placed within a few millimeters of an ozone-producing UV source, the process can produce a clean surface in less than 1 min. The combination of short wavelength UV light plus ozone produces a clean surface substantially faster than either short wavelength UV light without ozone or ozone without UV light. Clean surfaces will remain clean indefinitely during storage under UV/ozone, but prolonged exposure of oxide-forming metals to UV/ozone in room air can produce rapid corrosion.

The cleaning mechanism seems to be a photosensitized oxidation process in which the contaminant molecules are excited and/or dissociated by the absorption of short wavelength UV light. Simultaneously, atomic oxygen is generated when molecular oxygen is dissociated and when ozone is dissociated by the absorption of both short and long wavelengths of radiation. The products of the excitation of contaminant molecules react with atomic oxygen to form simpler molecules, such as CO₂ and H₂O₂, which desorb from the surfaces.
