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UV/OZONE CLEANING OF SURFACES

JOHN R. VIG
ELECTRONICS TECHNOLOGY AND DEVICES LABORATORY

MAY 1986

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The UV/ozone method, which is reviewed in this report, 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. Placing properly precleaned surfaces within a few millimeters of an ozone-producing UV source can produce clean surfaces in less than one minute. The technique can produce near-atomically clean surfaces, as evidenced by Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), and ion scattering spectroscopy/secondary ion mass spectroscopy (ISS/SIMS) studies. Topics discussed include the variables of the process, the types of surfaces which have been cleaned successfully, the contaminants that can be removed, the construction of a UV/ozone cleaning facility, the mechanism of the process, UV/ozone cleaning in vaccum systems, rate-enhancement techniques, safety considerations, effects of UV/ozone other than cleaning, and applications.

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1. SUMMARY

The (UV)/ozone surface-cleaning method, which is reviewed in this report,* 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. Placing properly precleaned surfaces within a few millimeters of an ozone-producing UV source can produce clean surfaces in less than one minute. The technique can produce 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 cleaned successfully, the contaminants that can be removed, the construction of an 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.

2. INTRODUCTION

The capability 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 Kunz(1) reported that UV light had the capability to depolymerize a variety of photoresist polymers. The polymer films were enclosed in a quartz tube that was evacuated and then backfilled with oxygen. The samples were

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*This report was originally prepared in response to an invitation from K. L. Mittal for a chapter on UV/ozone cleaning for the forthcoming Treatise on Clean Surface Technology. Dr. Mittal is the Treatise Editor. The Treatise is to be published by Plenum Publishing Corp.

irradiated with UV light from a medium pressure mercury lamp that generated ozone. The several-thousand-angstroms-thick polymer films were successfully depolymerized in less than one hour. 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 hours 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 two hours of UV exposure. During cleaning, the partial pressure of O_2 decreased, while that of CO_2 and H_2O 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 storing clean surfaces under UV radiation maintained the surface cleanliness indefinitely.

During the period 1974-1976, 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 light were defined, and it was shown that, under the proper conditions, UV/ozone cleaning has the capability of producing clean surfaces in less than one minute. Since 1976, use of the UV/ozone cleaning method has grown steadily. UV/ozone cleaners are now available commercially.

3. THE VARIABLES OF UV/OZONE CLEANING

3.1 The Wavelengths Emitted by the UV Sources

To study the variables of the UV cleaning procedure, Vig and LeBus(5) constructed the two UV cleaning boxes shown in Figure 1. Both were made of aluminum, and both 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 recontamination by air circulation.

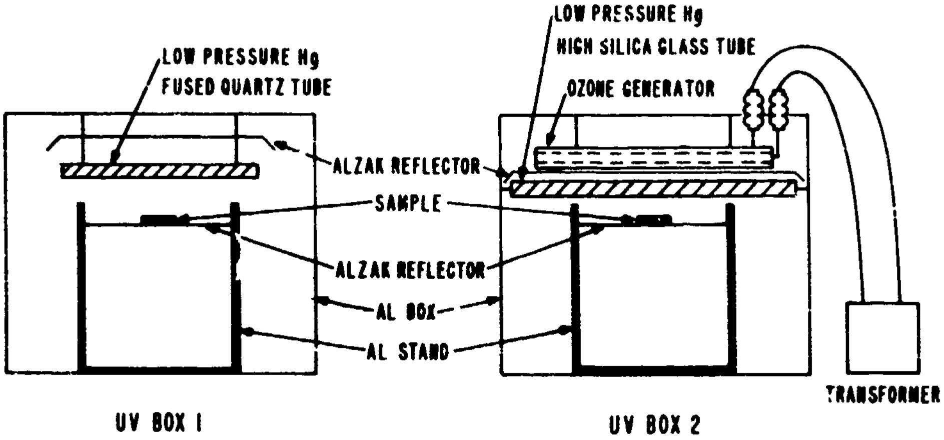


Figure 1. Apparatus for UV/ozone cleaning experiments.

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 nm and 253.7 nm. Whether or not these wavelengths are emitted depends upon the lamp envelopes. The emissions through the three main types of envelopes are summarized in Table 1.

Table 1. Principal wavelengths of low-pressure Hg discharge lamps.

	LAMP ENVELOPE		
WAVELENGTH	QUARTZ	HIGH SILICA GLASS	GLASS
184.9 nm	T	0	0
253.7 nm	T	T	0
>300.0 nm	T	T	T

T = Transparent, 0 = Opaque

The 184.9 nm wavelength is important because it is absorbed by oxygen, thus leading to the generation of ozone.(7) The 253.7 nm radiation is not absorbed by oxygen, therefore, it does not contribute to ozone generation, but is absorbed by most organic molecules (8,9) and 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, both of the formation and of the 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 tubing. The fused quartz transmits both the 253.7 nm and the 184.9 nm wavelengths. The lamp emitted about 0.1 mW/cm^2 of 184.9 nm radiation measured at 1 cm from the tube.

The absorption spectrum of oxygen is shown in Figure 2 and that of ozone in Figure 3. The effects of the principal wavelengths generated by low-pressure mercury discharge lamps are summarized in Table 2.

Table 2. Effects of the principal wavelengths generated by low-pressure Hg discharge lamps.

WAVELENGTH	EFFECTS
184.9 nm	● Absorbed by O_2 and organic molecules ● Creates atomic oxygen and ozone ● Breaks contaminant molecule bonds
253.7 nm	● Absorbed by organic molecules and O_3; not absorbed by O_2 ● Destroys ozone ● Breaks contaminant molecule bonds

The lamp in box 2 had two straight and parallel 46 cm long high-silica glass tubes made of 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

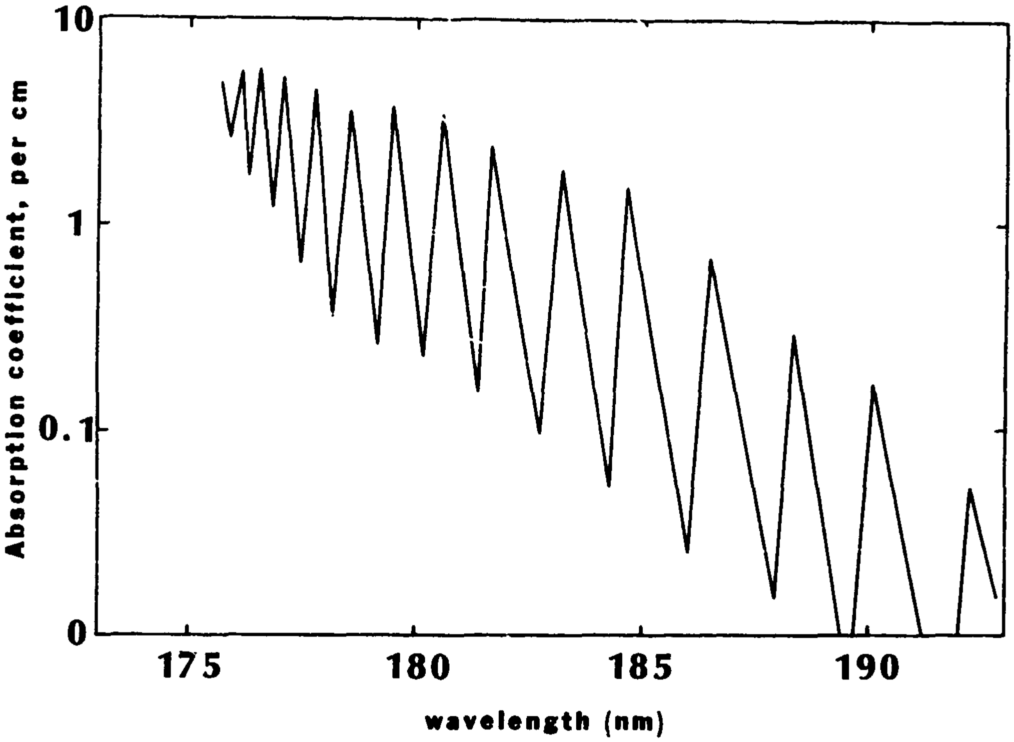


Figure 2. Absorption spectrum of oxygen.

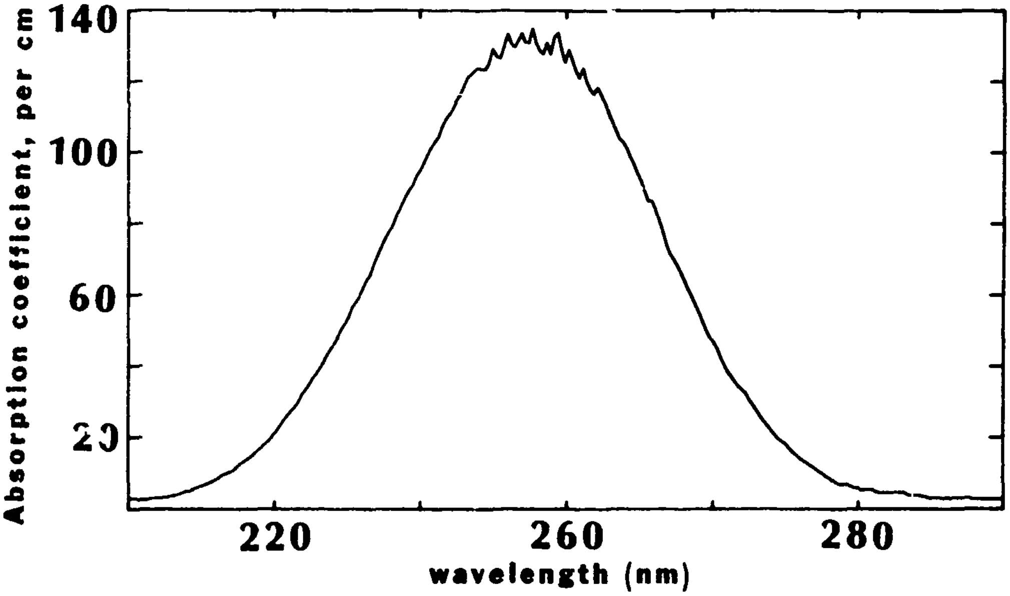


Figure 3. Absorption spectrum of ozone.

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 and were spaced approximately 6 cm apart.

UV box 1 was used to expose samples, simultaneously, to the 253.7 nm and 184.9 nm wavelengths and to the ozone generated by the 184.9 nm wavelength. 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.(5,12,15) Contact angle measurements and the steam test can detect fractional monolayers of hydrophobic surface contamination.

Also tested was a "black-light" long-wavelength UV source that emitted wavelengths above 300 nm only. This UV source produced no noticeable cleaning, even after 24 hours of irradiation.

In the studies of Vig et al., it was found 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) scrubbing with a swab while the sample was immersed in ethyl alcohol,
(2) degreasing ultrasonically in a solvent such as trichlorotrifluoroethane,
(3) boiling in fresh ethyl alcohol, then agitating ultrasonically,

(4) rinsing in running ultrapure (18ΩM cm) water,

(5) spinning 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. The cleanliness of such UV/ozone-cleaned surfaces has been verified on numerous occasions, in the author's laboratory and elsewhere, by AES and electron spectroscopy for chemical analysis (ESCA).(1,3,4,13-16) Figure 4 shows Auger spectra before and after UV/ozone cleaning.(16)

Ten minutes of UV/ozone cleaning reduced the surface contamination on an aluminum thin film to below the AES detectability level, about one percent of a monolayer. The effectiveness of UV/ozone cleaning has also been confirmed by ion scattering spectroscopy/secondary ion mass spectroscopy (ISS/SIMS).(17)

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 skin oil was applied by rubbing the wafer on the forehead of one of the researchers.) The wafers were precleaned again, groups of wafers were exposed to each of the four UV/ozone combinations mentioned earlier, and the time needed to attain a clean surface was measured, as indicated by the steam test. In each UV box, the samples 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 1 became clean in 20 s. The samples exposed to 253.7 nm + ozone in

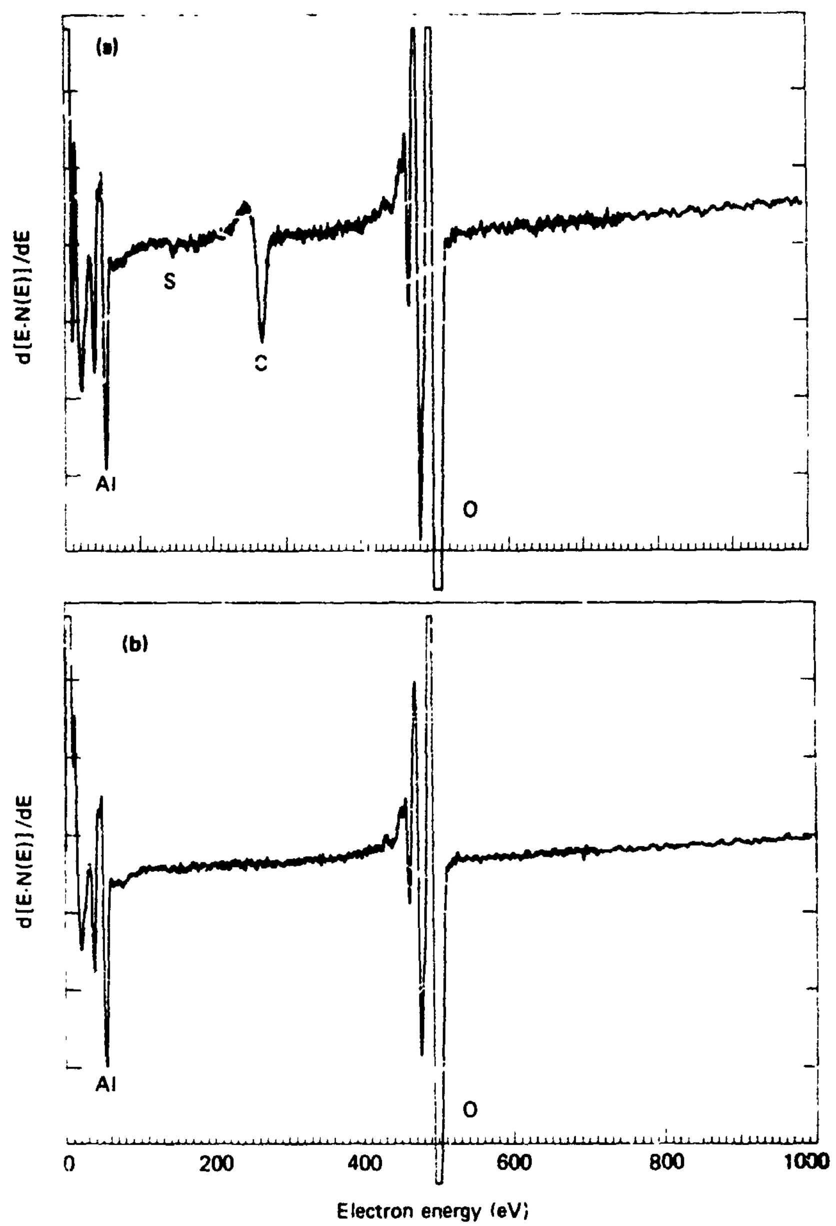


Figure 4. Auger spectra of evaporated aluminum film on silicon substrate: (a) before UV/ozone cleaning; (b) after UV/ozone cleaning.

UV box 2 reached the clean condition in 90 s. Samples exposed to 253.7 nm without ozone were cleaned within one hour, and samples exposed to ozone without UV light were cleaned within ten hours. The results are summarized in Table 3.

Table 3. Exposure types vs. cleaning times.

Exposure Type	Cleaning Time
"Black light" (>300 nm)	No cleaning
O_3, no UV	10 hours
253.7 nm, no O_3	1 hour
253.7 nm + O_3	90 sec
253.7 nm + 184.9 nm + O_3	20 sec

Therefore, one may conclude that, while both UV light without ozone and ozone without UV light can produce a slow cleaning effect in air, the combination of short-wavelength UV light and of 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 organic molecules, 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, within each box the ozone concentrations vary with distance from the UV source.

3.2 Distance Between the Sample and UV Source

Another variable that 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 may conclude that the intensity of UV light reaching a sample would be nearly independent of distance. However, this is not so when ozone is present, because ozone has a broad absorption band(7,18,19) centered at about 260 nm, as is shown in Figure 3. At 253.7 nm, the absorption coefficient is 130 cm^{-1} atm^{-1}. The intensity I of the 253.7 nm radiation reaching a sample therefore decreases as

$$I = I_0 e^{-130pd}$$

where p is the average ozone pressure between the sample and the UV source in atmospheres at 0°C, and d is the distance 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 was placed at the bottom of the box about 8 cm from the tube. With the ozone generator off, there was less than a 30 percent difference in the time it took for the two sets of samples to attain a minimal (~4°) contact angle, about 60 min versus 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 versus 13 min). Similarly, in UV box 1, samples placed within 5 mm of the tube were cleaned in 20 s versus 20-30 min for samples placed near the bottom of the box at a distance of 13 cm. Therefore, to maximize the cleaning rate, the samples should be placed as close as practicable to the UV source.

3.3 The Contaminants

Vig et al. tested the effectiveness of the UV/ozone cleaning procedure on a variety of contaminants. Among the contaminants were:

(1) human skin oils (wiped from the forehead of one of the researchers),

(2) contamination adsorbed during prolonged exposure to air,

(3) cutting oil,(20)

(4) beeswax and rosin mixture,

(5) lapping vehicle,(21)

(6) mechanical vacuum pump oil,(22)

(7) DC 704 silicone diffusion pump oil,(23)

(8) DC 705 silicone diffusion pump oil,(23)

(9) silicone vacuum grease,(23)

(10) acid (solder) flux,(24)

(11) rosin flux from a rosin core lead-tin solder

(12) cleaning solvent residues, including acetone, ethanol, methanol, isopropyl alcohol, trichloroethane, and trichlorotrifluoroethane.

The contaminants were applied with swabs to clean, polished quartz wafers. The amount of contamination was not measured. However, each time a swab was used in the application, it was obvious to the unaided eye that the samples had been thoroughly contaminated. After contamination, the wafers were precleaned, then exposed to UV/ozone by placement 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.

Using AES, no differentiation could be made between the silicon peaks due to quartz and those due to the silicon-containing contaminants. The removal of silicone diffusion pump fluids was, therefore, also tested on Alzak, which normally has a silicon-free oxide surface, and on gold. Following UV/ozone cleaning, AES examination both of the Alzak and the gold surfaces showed no presence of silicon.

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 that had been exposed to radiation in an ion-implantation accelerator, presumably because of cross-linking of the photoresist. Ion-implanted silicon wafers, each with approximately a 1 μm coating of exposed Kodak Micro Resist 747,(25) 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 and should be removed in the precleaning procedure.

UV/ozone has also been used for waste-water treatment and for destruction of highly toxic compounds.(26-29) 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 CO_2, CO, H_2O, and N_2. Compounds which have been destroyed successfully 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; chlorinated organics and pesticides such as pentachlorophenol, dichlorobenzene, dichlorbutane, chloroform, malathion, Baygon, Vapam, and DDT. It has also been shown(30) that using the combination of UV and ozone is more effective than using either one alone in destroying microbial contaminants (E. coli and streptococcus faecalis) in water.

3.4 The Precleaning

Contaminants such as thick photoresist coatings and pure carbon films can be removed with UV/ozone, without any precleaning, but, in general, gross contamination cannot be removed without precleaning. For example, when a clean quartz wafer was coated thoroughly with human skin oils and placed in UV box 1 (Figure 1) without any precleaning, even prolonged exposure to UV/ozone failed to produce a low-contact-angle surface, because 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 simply been 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, possibly because many chemicals respond to radiation in various ways, depending upon whether or not oxygen is present. For instance, in the presence of oxygen, many polymers 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... "(31)

For the UV/ozone cleaning procedure to perform reliably, the surfaces must be precleaned: first, to remove contaminants such as dust and salts, which cannot be changed into 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.

3.5 The Substrate

The UV/ozone cleaning process has been used with success on a variety of surfaces, including: glass, quartz, mica, sapphire, ceramics, metals, silicon, gallium arsenide, 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, approximately two centimeters deep, was cleaned by UV/ozone, both sides of all the plates, even those 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 on top of each other so that there could have been little or no ozone circulation between the plates, it was possible to clean both sides of the plates by the UV/ozone cleaning method. (Reference 32 shows 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 were cleaned properly. However, the sides facing the UV became yellow, probably due to the production of UV induced color centers. After a few minutes at high temperatures (>160°C), the white color returned.

Metal surfaces could be cleaned by UV/ozone without any problems, so long as the UV exposure was limited to the time required to produce a clean surface. (This time should be approximately one minute 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, blackened within one hour in UV box 1. 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. When electroless gold-plated nickel parts were stored under UV/ozone for several days, a powdery black coating gradually appeared on the parts. Apparently, nickel diffused to the surface through pinholes in the gold plating and the oxidized nickel eventually covered the gold nearly completely. The corrosion was also observed in UV box 2 when no ozone was being generated. The rates 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 as follows: 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. Therefore, the use of controlled atmospheres in the UV box may minimize the corrosion problem.

Since UV/ozone dissociates organic molecules, it may be a useful means of cleaning some organic materials, just as etching and electropolishing are sometimes useful for cleaning metals. The process has been used successfully to clean quartz resonators which have been bonded with silver-filled polyimide cement.(33) Teflon (TFE) tape exposed to UV/ozone in UV box 1 for ten days experienced a weight loss of 2.5 percent.(34) 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.(35) Similarly, Viton shavings taken from an O-ring experienced a weight loss of 3.7 percent after 24 hours in UV box 1. At the end of the 24 hours, the Viton surfaces had become sticky. 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 had been made using n-channel silicon gate technology, with 1 to 1.5 μm junction depths.)(36)

3.6 Rate Enhancement Techniques

UV/ozone cleaning "rate enhancement" techniques have been investigated by Zafonte and Chiu.(37) 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 a drop-wise addition either of distilled water or of hydrogen peroxide solutions of various concentrations to the sample surfaces. Most of the sample surfaces consisted of various types of photoresist on silicon wafers.

The gas phase "enhancement" techniques resulted in negligible to slight increases in the rates of photoresist 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 (to 100 to 200 Å/min) for non-ion implanted resists. The heavily ion implanted resists (10^{15} to 10^{16} atoms/cm^2) were not significantly affected by UV/ozone, whether "enhanced" or not.

Photoresist removal rates of 800 to 900 Å/min for positive photoresists and 1500-1600 Å/min for negative photoresists(38) were reported by one manufacturer of UV/ozone cleaning equipment.(38) The fast removal rate was achieved at 300°C by using a 253.7 nm source of UV, a silent discharge ozone generator, a heater built into the cleaning chamber, and by using oxygen from a gas cylinder to generate the ozone. A schematic drawing of this UV/ozone cleaner is shown in Figure 5.

The photoresist stripping rate vs. substrate temperature for three different photoresists is shown in Figure 6.

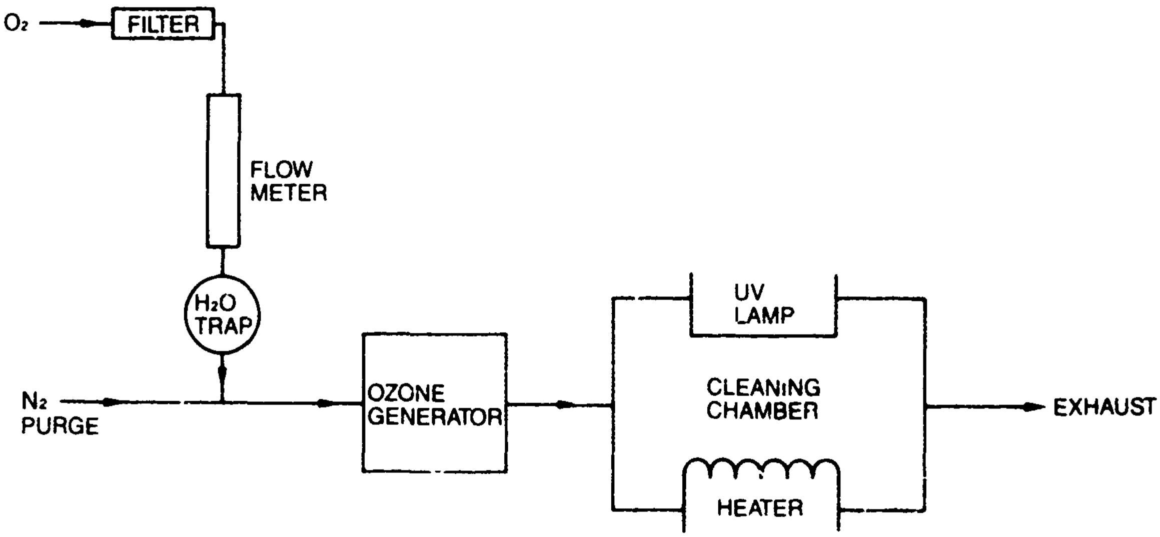


Figure 5. Schematic drawing of a UV/ozone cleaner that uses a silent-discharge ozone generator.

4. 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 Figure 7. The contaminant molecules are excited and/or dissociated by the absorption of short wavelength UV light. Atomic oxygen and ozone(18,19) are produced simultaneously when O_2 is dissociated by the absorption of UV with wavelengths less than 245.4 nm. Atomic oxygen is also produced(18,19) when ozone is dissociated by the absorption of the UV and longer wavelengths of radiation. The excited contaminant molecules and the free radicals produced

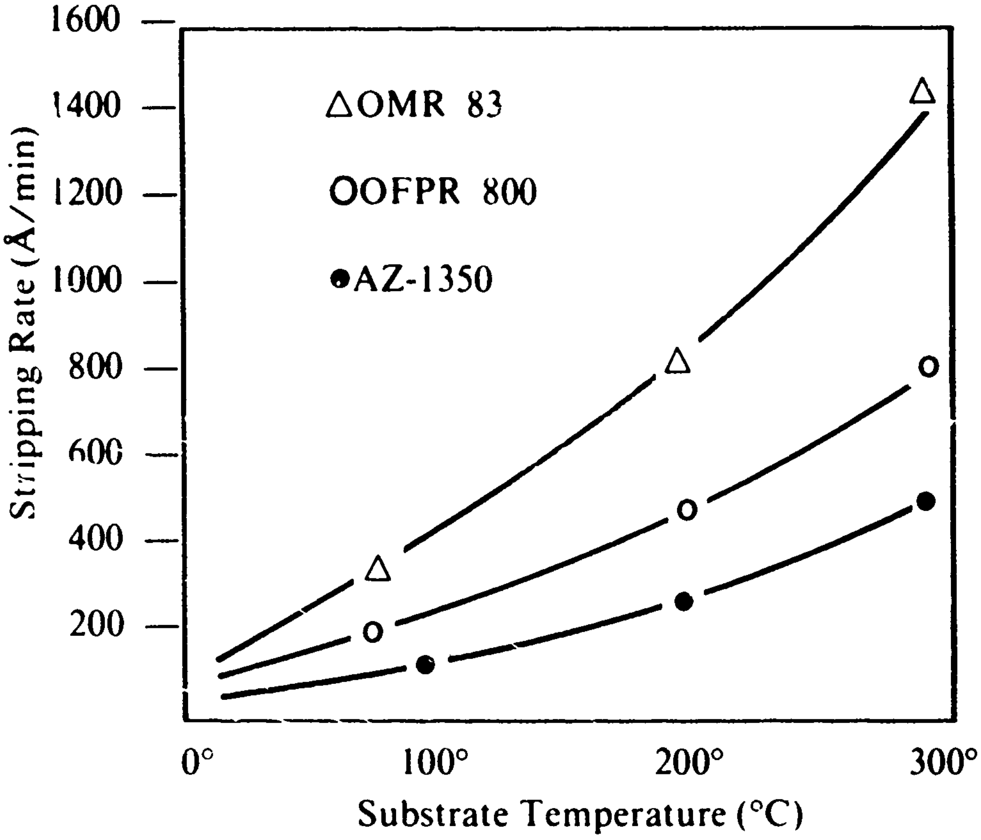


Figure 6. Photoresist stripping rate vs. substrate temperature for three types of photoresists.

by the dissociation of contaminant molecules react with atomic oxygen to form simpler, volatile molecules, such as CO_2, H_2O, and N_2.

The energy required to dissociate an O_2 molecule into two ground state O atoms corresponds to 245.4 nm. However, at and just below 245.4 nm the absorption of O_2 is very weak.(7,18,19) The absorption coefficient increases rapidly below 200 nm with decreasing wavelengths, as is shown in Figure 2. For producing O_3, a convenient wavelength is the 184.9 nm emitted by low-pressure Hg discharge lamps in fused quartz envelopes. Similarly, since most organic molecules have a strong absorption band between 200 nm and 300 nm, the 253.7 nm wavelength emitted by the same lamps is useful for exciting or

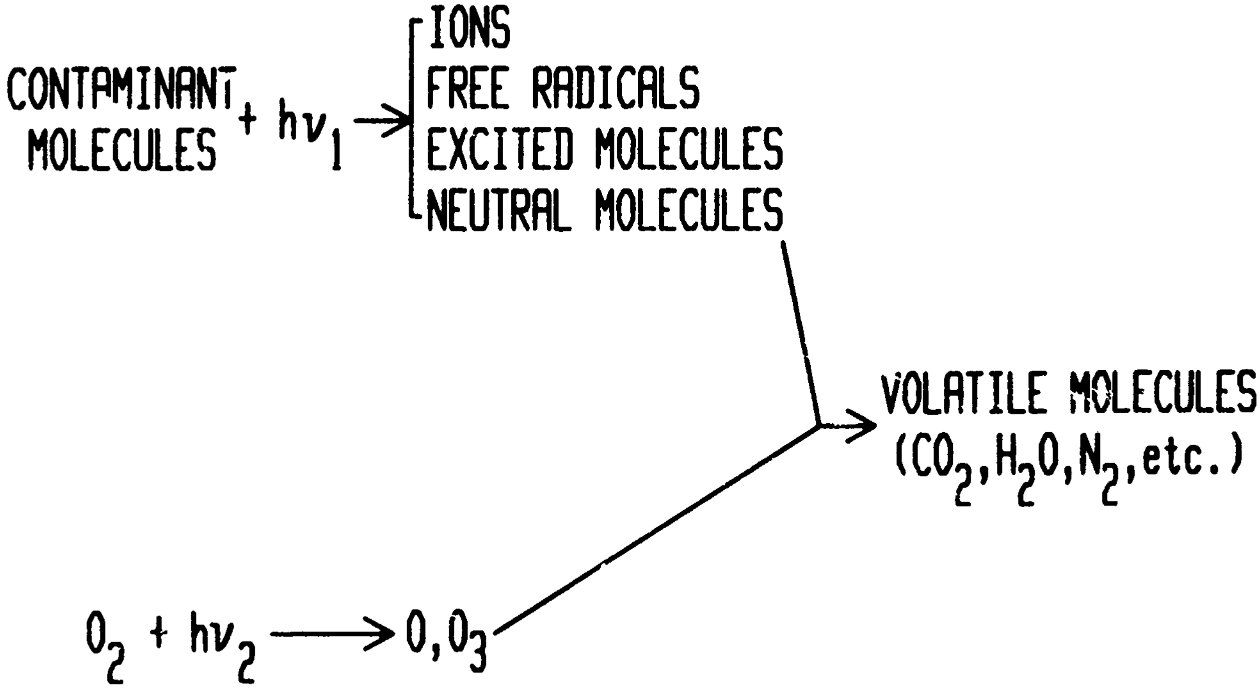


Figure 7. Simplified schematic representation of UV/ozone cleaning process.

dissociating contaminant molecules. The energy required to dissociate ozone corresponds to 1,140 nm; however, the absorption by ozone is relatively weak above 300 nm. The absorption reaches a maximum near the 253.7 nm wavelength, as is shown in Figure 3. The actual photochemical processes occurring during UV/ozone cleaning are more complex than that shown in Figure 7. For example, the rate of production of ozone by 184.9 nm photons is promoted by the presence of other molecules, such as N_2 and CO_2.

As was described previously, the combination of short wavelength UV light and ozone produced clean surfaces about 200 to 2,000 times faster than UV light alone or ozone alone. Similarly, in their studies of wastewater treatment, Prengle et al.(26,29) had found that UV enhances the reaction with ozone 10^2 to 10^4-fold, and the products of the reactions are materials such as CO_2, H_2O, and N_2. Increasing the temperature increased the reaction rates. Mattox(39) also found that mild heat increases the UV/ozone cleaning rates.

Bolon and Kunz,(1) on the other hand, had found that the rate of ozone depolymerization of photoresists did not change significantly between 100°C and 300°C. The rate of destruction of microorganisms was similarly insensitive to a temperature increase from room temperature to 40°C.(30) One manufacturer of UV/ozone cleaning equipment claims that the rate of photoresist stripping by UV/ozone increases severalfold as the temperature is raised from 20°C to 300°C.(38)

5. UV/OZONE CLEANING IN VACUUM SYSTEMS

Sowell et al.(2) reported that, when 10^{-4} torr pressure of oxygen was present in a vacuum system, short-wavelength UV desorbed gases from the walls of the system. During UV irradiation, the partial pressure of oxygen decreased, while that of CO_2 and H_2O increased.

One must exercise caution in using a mercury UV source in a vacuum system because, should the lamp envelope break or leak, mercury can enter and ruin the usefulness of the system. Mercury has a high vapor pressure; its complete removal from a vacuum chamber is a difficult task. Other types of UV sources, such as xenon or deuterium lamps, may be safer to use in vacuum systems. The UV light can also be radiated into systems through sapphire or quartz windows, or through deep-UV fiber optic bundles. A small partial pressure of oxygen should be present during UV cleaning.

Caution must also be exercised when using UV/ozone in a cryopumped vacuum system, since cryopumped ozone is potentially explosive,(40) particularly during regeneration of the cryopump. A convenient method of dealing with this potential hazard is to use two kinds of UV sources, one an ozone-generating source, the other an "ozone killer" source.(41) (See next section.)

6. SAFETY CONSIDERATIONS

In constructing a UV/ozone cleaning facility, one should be aware of the safety hazards associated with exposure to short-wavelength UV light which can cause serious skin and eye injury within a short time. In the UV boxes used by Vig et al., 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 a UV cleaning facility is incorporated into a wire bonder), then proper clothing and eye protection (e.g., UV safety glasses with side flaps) should be worn to prevent skin and eye damage.

Short-wavelength UV radiation is strongly absorbed by human cellular DNA. The absorption can lead to DNA-protein crosslinks, and can result in cancer, cell death, and cell mutation. It is now well known that solar UV radiation is the prime causative factor in human skin cancer,(42,43) and is a significant risk factor in eye cancer.(44) The 290-320 nm portion of solar UV radiation has been found to be the most effective wavelength region for causing skin cancer. Because the atmosphere filters out the shorter wavelengths, humans are not normally exposed to wavelengths as short as 254 nm. However, in a study of the effects of UV radiation on skin cancer rates, it was found that the 254 nm wavelength was many times more effective in causing cell mutations than were the above-300 nm wavelengths. Therefore, it is essential that personnel not be exposed to the short wavelengths needed for UV/ozone cleaning because even low doses of these wavelengths can cause significant damage to human cells.

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.(45) Ozone is a potential hazard in a cryopumped vacuum system because cryopumped ozone can become explosive under certain conditions.(40)

One method of minimizing the hazards associated with ozone is to use two types of short-wavelength ultraviolet sources for UV/ozone cleaning(41): 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 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 at 253.7 nm but not at 184.9 nm. Such a non-ozone generating UV source can be used as an "ozone killer." For example, in one cryopumped vacuum system, UV/ozone cleaning was performed in up to 20 torr of oxygen. After the cleaning was completed and the ozone-generating UV lamp was turned off, ten minutes of "ozone killer" UV light reduced the concentration of ozone to less than 0.01 ppm, a level that is safe for cryopumping.(46) Therefore, with the "ozone killer" lamp, ozone concentrations were reduced by at least a factor of 100 within ten minutes. Without the "ozone killer" lamp, the half-life of ozone is three days at 20°C.(47)

The decomposition of ozone can also be greatly accelerated through the use of catalysts. For example, prior to 1980, in high-flying aircraft, ozone was found to be a causative factor for flight personnel and passengers experiencing headaches, eye, nose and throat irritations and chest pains. Passing the aircraft cabin air through a precious metal catalytic converter reduced the ozone concentration from the 1 ppm to 2 ppm level present in the troposphere to the low levels required for passenger comfort and safety.(48)

7. UV/OZONE CLEANING FACILITY CONSTRUCTION

The materials chosen for the construction of a UV/ozone cleaning facility should remain uncorroded by extended exposure to UV/ozone. Polished aluminum with a relatively thick anodized oxide layer, such as Alzak,(6) is one such material. It is resistant to corrosion, has a high thermal conductivity, which helps to prevent heat buildup, and is also a good reflector of short wavelength UV. Most other metals, including silver, are poor reflectors in the UV range.

Initially, Vig et al. used an ordinary shop-variety aluminum sheet for UV box construction, which was found not to be a good material because, in time, a thin coating of 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 appeared on the Alzak, probably due to pinholes in the anodization. To avoid the possibility of particles being generated inside the UV/ozone cleaning facility, the facility should be inspected periodically for signs of corrosion. Using "Class M" Alzak may also aid in avoiding particle generation, since this material has a much thicker oxide coating, and is made for "exterior marine service," whereas standard Alzak is for "mild interior service." Some commercially available UV/ozone cleaners are now constructed of stainless steel.(49,50) 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 and ozone escape.

The most widely available sources of short-wavelength UV light are the mercury arc lamps. Low-pressure mercury lamps in pure fused quartz envelopes operate near room temperature, emit approximately 90 percent at the 253.7 nm wavelength, and generate sufficient ozone for effective surface cleaning. Approximately five percent of the output of these lamps is at 184.9 nm. Medium- and high-pressure UV lamps(7) 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, 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 lamps are also available.(51)

Other available sources of short-wavelength UV include xenon lamps and deuterium lamps. These lamps must also be in an envelope transparent to short-wavelength UV, such as quartz or sapphire, if no separate ozone generator is to be used. 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 can 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.(52)

An alternative to using low-pressure mercury lamps in fused quartz envelopes is to use an arrangement similar to that of box 2, shown in Figure 1. Such a UV/ozone cleaner, now also available commercially,(38) uses silent-discharge-generated ozone and a UV source that generates the 253.7 nm wavelength, as is shown in Figure 5. The manufacturer of this cleaner claims a cleaning rate that is much faster than that which is achievable with UV/ozone cleaners that do not contain separate ozone generators. This cleaner also uses oxygen from a gas cylinder and a built-in sample heater that may further increase the cleaning rate.

8. APPLICATIONS

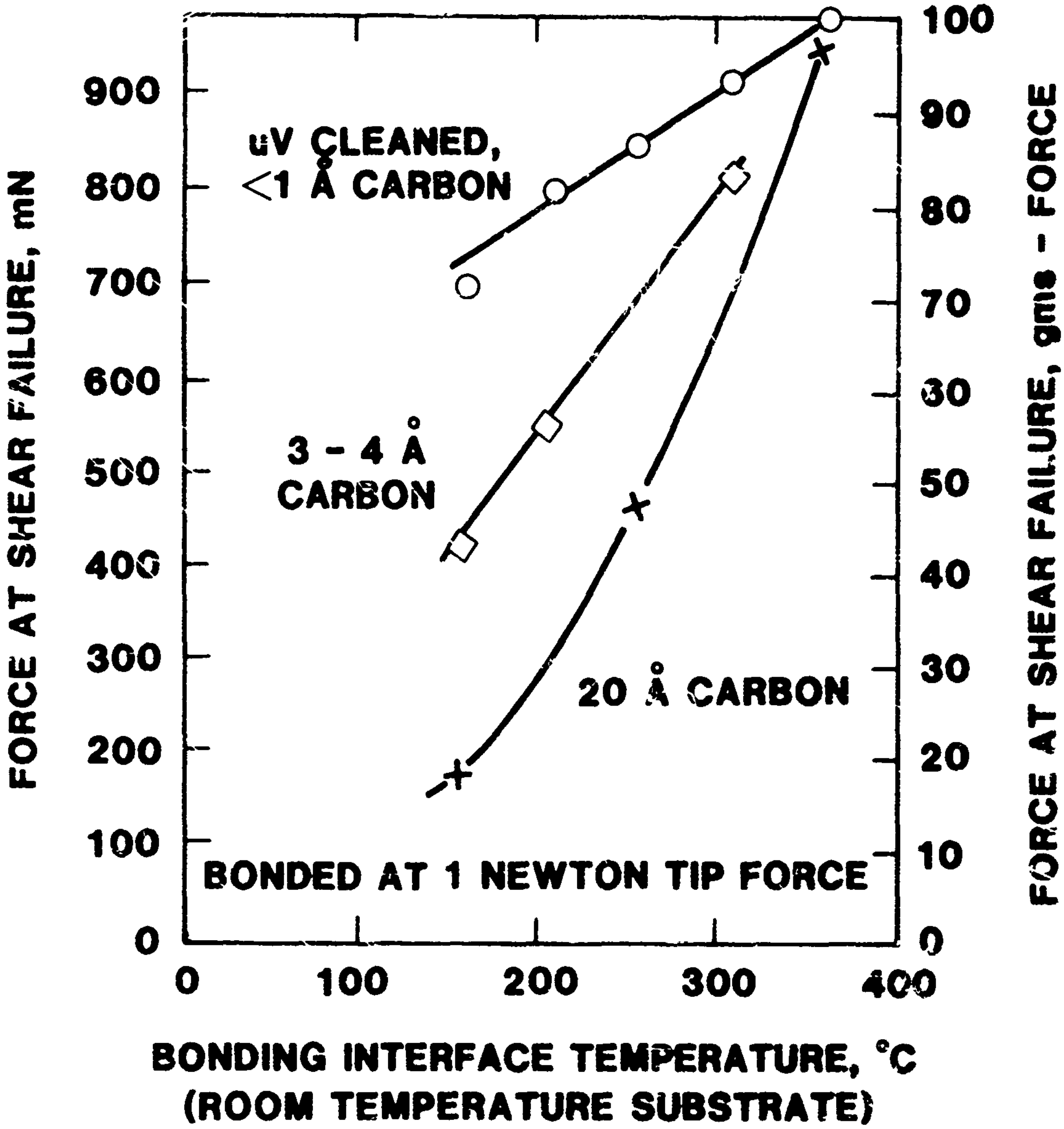
The UV/ozone cleaning procedure is now used in numerous applications. A major use is substrate cleaning prior to thin film deposition, as is widely used in the quartz crystal industry during the manufacture of quartz crystal resonators for clocks and frequency control. There is probably no other device of which the performance is so critically dependent upon surface cleanliness. For example, the aging requirement for one 5 MHz resonator is that the frequency change no more than two parts on 10^{10} per week, whereas adsorption or desorption of a monolayer of contamination from such a device changes the frequency by about one part in 10^6. The surface cleanliness must therefore be such that the rate of contamination transfer within the hermetically sealed resonator enclosure is less than 10^{-4} monolayers per week! In the author's quartz resonator fabrication laboratory, UV/ozone has been 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.(14,53-55) It has been shown that metal surfaces will weld together under near-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 a ceramic flatpack enclosed quartz resonator. It has also been shown(53-55) that it is feasible to achieve hermetic seals by pressing a clean aluminum gasket between two clean, unmetallized aluminum oxide ceramic surfaces.

The same adhesion phenomenon between clean (UV/ozone cleaned) gold surfaces has been applied to the construction of a novel surface contaminant detector.(56,57) 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. For example, it has been shown(58,59) that the thermocompression bonding process is highly temperature dependent when organic contaminants are present on the bonding surfaces. The temperature dependence can be greatly reduced by UV/ozone cleaning of the surfaces just prior to bonding, as is shown in Figure 8. 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.(60) UV/ozone is also being used for cleaning alumina substrate surfaces during the processing of thin film hybrid circuits.(61)

A number of cleaning methods were tested when the nonuniform appearance of thermal/flash protective electrooptic goggles was traced to organic contaminants on the electrooptic wafers. 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.(62)



DATA ARE FOR t/c BALL BONDS OF 25μm DIA. GOLD WIRE BONDED TO GOLD - CHROMIUM METALLIZATION

Figure 8. Effect of UV/ozone cleaning on gold-to-gold thermocompression bonding.

Other applications which have been described are: photoresist removal,(1,5,13,38) the cleaning of vacuum chamber walls,(2) photomasks,(63) silicon wafers (for enhancing photoresist adhesion),(63) lenses,(63) mirrors,(63) solar panels,(63) sapphire(63) (before the deposition of HgCdTe) and other fine linewidth devices,(63,64) inertial guidance subcomponents (glass, chromium-oxide surfaced-gas bearings, and beryllium),(63,65) gallium-arsenide wafers,(66) the cleaning of stainless steel for studying a milk-stainless steel interface,(67) and the cleaning of adsorbed species originating from epoxy adhesives.(68) 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.(68)

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.(69) 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.

In the processing of semiconductor wafers, a single UV/ozone exposure has been found to be capable both of "descumming" and of stabilizing.(70) After developing and rinsing the photoresist pattern, the UV/ozone removes the thin layers of organic photoresist residue (scum) from the "clear" regions. The photoresist stabilization is believed to be due to crosslinking produced by the short wavelength (deep) UV radiation.(71) The stabilization rate is accelerated by increasing the temperature. For example, UV/ozone exposure times of 10 to 30 minutes from a 25 cm X 25 cm low pressure mercury grid lamp at 100°C yields satisfactory results. The stabilized photoresist pattern exhibits: 1) improved adhesion to the substrate, 2) improved ability to maintain geometrical shape under thermal stress, and 3) improved ability to withstand exposure to the etchants and solvents used to create the desired patterns in the circuit coatings.(70)

9. 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:

9.1 Oxidation.

Ozone's oxidation power is second only to that of fluorine. Ozone can oxidize most inorganic compounds to their final oxidative state.(47) 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 Å to 300 Å thick,(72) i.e., UV/ozone can produce a clean, enhanced "oxide passivated" surface. Ten minutes of UV/ozone cleaning increased the oxide thickness on silicon substrates from 0.9 nm to 1.2 nm.(69) Similarly, the native UV/ozone-produced oxide layer at the interface of HgCdTe-SiO_2 has been found to enhance the interface properties.(73) Solar radiation and atmospheric ozone have been found to markedly enhance the sulphidation of copper.(74) Extended exposure to UV/ozone has been found to significantly increase the oxide layer thickness on aluminum surfaces.(75) Whereas the oxide thickness on air-exposed aluminum surfaces is normally limited to about 50 Å, UV/ozone exposure increased the oxide layer thickness significantly beyond the "normal" 50 Å limit, as is shown in Table 4.

9.2 UV-enhanced Outgassing.

Short-wavelength UV has been found to enhance the outgassing of glasses.(76) The UV light produced the evolution of

Table 4. UV/ozone exposure vs. oxide thickness on aluminum.

Substrate Treatment	Oxide Thickness (Å)
Evaporate 1 μm of aluminum	47
10 minute UV/ozone cleaning	90
60 minute UV/ozone cleaning	200

significant quantities of hydrogen, and, also, water, carbon dioxide, and carbon monoxide. The hydrogen evolution was proportional to the amount of radiation incident to 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.

9.3 Other Surface/Interface Effects.

Energetic radiation such as UV and gamma radiation has been reported to produce dehydration and the formation of free radicals on silica surfaces.(77) However, dehydrated (or siloxinated) silica surfaces are hydrophobic,(78,79) whereas UV/ozone-cleaned silica (quartz) surfaces exhibit a very low (less than 4°) water contact angle, thus indicating that the UV/ozone does not dehydrate the surfaces, nor does it modify surface silanol groups the way high temperature vacuum baking does.(80) Short-wavelength UV has also been found to produce a bleaching effect in $Si-Si_3$ interfaces with thin oxides,(81) and has also been found to produce yellowing (color centers) during the cleaning of aluminum oxide ceramics.(34) The yellowing can be readily bleached by heating the sample to above 160°C.

9.4 Etching.

Short wavelength (193 nm) UV laser irradiation of biological and polymeric materials has been shown to be capable of etching the materials with great precision, via "ablative photodecomposition," and without significant heating of the samples. Linewidths 5 m wide have been etched onto a plastic film to demonstrate the capability of this technique.(82) Oxygen does not appear to have the same significance in this process as it does in UV/ozone cleaning. The etch depth vs. fluence in vacuum and in air were found to be the same.(83) UV/ozone has been found to etch Teflon,(34,35) and Viton,(34) and will likely etch other organic materials as well.(84,85) The susceptibility of polymers to degradation by ozone can be reduced by various additives and through the elimination of "the offending double bonds from the backbone structure of the polymers."(86)

10. 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 one min. The combination of short-wavelength UV light plus ozone produces a clean surface substantially faster than 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 short and long wavelengths of radiation. The products of the excitation of contaminant molecules react with atomic oxygen form simpler molecules, such as CO_2 and H_2O, which desorb from the surfaces.

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