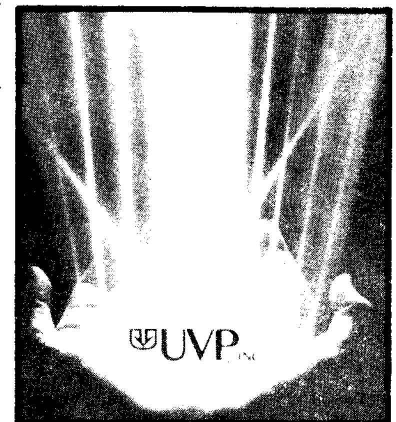
Paper #1009

UV/Ozone Cleaning

-A Description-

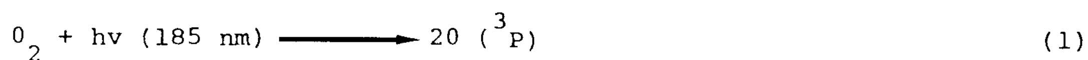


UV/OZONE CLEANING - A DESCRIPTION

Introduction

UV/Ozone cleaning is an effective method for removing organic contaminants from surfaces where cleanliness is critical. Properly precleaned surfaces placed within a few millimeters of a low pressure mercury UV light source producing 185 nm and 254 nm emissions are cleaned to the last atomic layer of contaminant. The method is a simple, dry process which takes place in normal, surrounding air at ordinary room temperature. Only absorbed UV energy is effective in producing these photochemical changes. The specific wavelengths of UV light are important in this photochemical process including wavelengths absorbed by both oxygen (from air) and ozone.

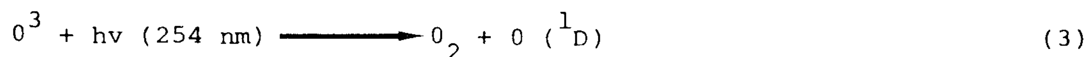
The ozone is produced in a two-step photochemical process initiated by the photolysis of ambient oxygen at 185 nm.



$$0_2 + hv \text{ (185 nm)} \longrightarrow 20\ (^3P) \qquad (1)$$

$$0\ (^3P) + 0_2 \longrightarrow 0_3 \qquad (2)$$

The ozone is then photo-decomposed by absorption of UV radiation at 254 nm, producing excited state ^1D oxygen atoms. (Equation (3)).



$$0^3 + hv \text{ (254 nm)} \longrightarrow 0_2 + 0\ (^1D) \qquad (3)$$

The 254 nm wavelength does not contribute to ozone generation, and it can be absorbed by many hydrocarbons as well as by ozone. The absorption of 254 nm UV by ozone is principally responsible for the destruction of ozone. When both of the above wavelengths are present, ozone is continuously being formed and destroyed. The result is the formation of atomic oxygen - a very strong

oxidizing agent. Very simply, the free radicals produced by dissociation of the contaminant organic molecules react further with atomic oxygen to form simpler molecules such as water and carbon dioxide. These are volatile gases which leave readily the surface, leaving it contaminant free.

Experimentation

Ultraviolet radiation has been known to decompose organic molecules, but it has only been within the past decade that this phenomenon, together with ozone photochemistry, has been utilized as a means for cleaning organic matter from surfaces.

In 1972, Bolon and Kunz[1] successfully depolymerized photoresist films of several thousand angstrom thickness with UV radiation in less than an hour. The major products of depolymerization were found to be water and carbon dioxide. Examination by Auger Electron Spectroscopy showed their substrates to be free of carbonaceous residue. The use of a Pyrex filter, or a nitrogen atmosphere rather than oxygen, hindered depolymerization. It was recognized then that oxygen and UV wavelengths shorter than 300 nm played an important role in depolymerization using UV radiation.

In 1974, Sowell et. al.[2] described UV cleaning of absorbed hydrocarbons from glass and gold surfaces in air and in a vacuum. During the cleaning of gold surfaces in a vacuum at 10^{-4} torr of oxygen, the partial pressure of 0_2 decreased while that of CO_2 and H_20 increased.

These authors also noted surface cleanliness could be maintained indefinitely by storage under UV light.

Also in 1974, Vig et. al. 3-5 described a series of experiments to determine optimum conditions for UV/Ozone cleaning in the removal of hydrocarbon contaminant on quartz resonator crystals. It was shown that UV/Ozone Cleaning, under proper conditions, was capable of producing clean surfaces in less than ten minutes. Because gross contamination has to be eliminated as a prerequisite to UV/Ozone processing, the Vig work implemented a preclean procedure. At these early development stages five steps were suggested for high quartz cleaning of quartz. These are:

1. Scrub sample with swab while immersed in ethyl alcohol,
2. Ultrasonic agitation in fresh ethyl alcohol,
3. Boil in fresh ethyl alcohol following with ultrasonic agitation, and
4. Rinse in freshly prepared, running ultrapure (18 MegOhm) water.

Prior to this procedure, the steam test and contact angle measurements indicated surface contamination. However, exposure to UV/Ozone followed by the same test for contamination invariably indicated clean surfaces. The cleanliness of such UV/Ozone cleaned surfaces has been verified by Auger Electron Spectroscopy and, ESCA (Electron Spectroscopy for Chemical Analysis) on numerous occasions. (Ref. 1,3,4,6,7,8).

Typical tests for cleanliness after UV/Ozone cleaning are:

Auger Electron Spectroscopy

Electron Spectroscopy for Chemical Analysis

Ion Scattering Spectroscopy

Secondary Ion Mass Spectroscopy

The previous experimentation with UV/Ozone cleaning clearly demonstrates the viability of combined UV radiation and ozone as a cleaning procedure most beneficial to the electronics industry. UV/Ozone cleaning is especially practical for surfaces requiring specialized coatings such as treatments for microlithography and lens manufacture. Special equipment made of glass and quartz resonator crystals will also benefit.

CONTAMINANTS

A series of eleven contaminants more or less typical to wafer production as well as to the electronics manufacturing industry in general were tested by Vig et. al. under UV/Ozone cleaning. These were applied to clean polished quartz wafers. The wafers were precleaned and exposed to the UV/Ozone cleaning process. After 60 seconds exposure, the steam test and Auger Electron Spectroscopy indicated all traces of contamination were removed.

The Contaminants were:

Human Skin Oils	DC 704 Sil. Diff. Pump Oil
Absorbed Air Contaminants	DC 705 Sil. Diff. Pump Oil
Cutting Oil	Silicone Vacuum Grease
Lapping Vehicle	An Acid Solder Flux
Beeswax/Resin Mixture	Rosin Core Lead-Tin Solder Flux
Mech. Vac. Pump Oil	

It is interesting to note that Auger Electron Spectroscopy could not differentiate between the silicon peaks due to quartz and those due to the silicon contaminants. Therefore, silicone diffusion pump fluids were tested on Alzak and gold, which normally have a silicon-free oxide surface. On both metals, Auger Electron Spectroscopy showed no traces of silicon residue present, indicating that organo-silanes of lower molecular weight were produced and volatilized off the surface.

UV/Ozone cleaning is also particularly effective for removing solvent residues that have been used in a chemical preclean. The nature of the organic solvent used is dependent on the nature of the organic residue expected and the desired process results. These clean times are expected to be on the order of 4-6 minutes for air dried samples.

Variables Associated with UV/Ozone Cleaning

There are several variables to be considered in the UV/Ozone cleaning process. As an example: Vig cleaned a number of quartz wafers by UV/Ozone which were then thoroughly contaminated with human skin oil, one of the more difficult contaminants to remove. The wafers were precleaned again and divided into groups. Each group was exposed to one of four different UV/Ozone cleaning combinations. The combinations were:

1. 254 nm UV + 185 nm UV + Ozone
2. 254 nm UV + Ozone
3. 254 nm UV only
4. Ozone only

The wafer group exposed to 254 and 185 nm UV + Ozone were cleaned in 20 seconds. Samples exposed to 254 nm UV plus Ozone were cleaned in 90 seconds. The samples exposed only to 254 nm UV and Ozone alone required from one to ten hours before monotomically clean surfaces were obtained. The demonstrated conclusion then is the combination of 254 and 185 nm UV plus Ozone is the most practical for fast and efficient cleaning where human skin oil contamination is the concern.

The distance separating the sample and the UV source is another variable. The intensity of UV radiation decreases as distance from the light source increases. Small samples should be placed as close to the UV source as possible.

More recently, Zafonte and Chiu [9] demonstrated that this liquid films on the surface can enhance the organic removal rate on silicon semiconductor wafers by almost an order of magnitude. Their use of hydrogen peroxide and water was prompted by the requirement that the decomposition product of the liquid be volatile and residue free. The presence of bulk liquid in a solid phase/liquid phase reaction led to the higher cleaning rates. The process was accompanied by the formation of a 20-40 Angstrom formation of silicon dioxide which acted to protect the surface from further oxidation.

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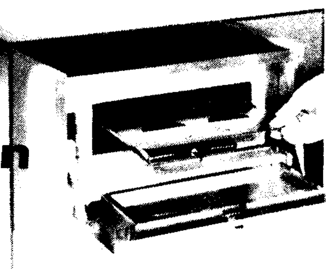

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