

Ultraviolet-Ozone Surface Treatment

1. Summary

The production process for all components includes one or more cleanings, and the quality of the cleaning significantly influences the improvements in the yield.

With the recent development of micromachining technology in electronics, conventional cleaning methods are increasingly inadequate in many fields; thus, several new cleaning methods have been developed.

However, newly developed cleaning apparatuses each have advantages and disadvantages, and at present cannot be regarded as prevalent. The ultraviolet-ozone

cleaning (hereinafter referred to as "UV-O₃ cleaning") apparatus described herein seems not to affect the object to be cleaned, and seems to enable easy precision cleaning in a relatively wide range.

Currently, the various cleaning techniques are used, and their methods can be broadly classified into two types: wet cleaning and dry cleaning. The UV-O₃ cleaning method has the characteristics of dry cleaning.

Table 1 shows examples of the dry-cleaning methods.

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Dry cleaning ⊙	1) Laser and X-ray cleaning	Cleaning by thermal action
	2) Plasma cleaning	Cleaning by the collision energy of gas molecules and the chemical action on contaminants
	3) Cleaning by ion milling	Cleaning by surface etching
	4) UV-O ₃ cleaning	Cleaning by the decomposition of contaminants by ultraviolet irradiation and the chemical action of oxidation by O ₃

Table 1. Examples of dry cleaning method

In general, contaminants are classified into the organic and inorganic types. Organic contaminants include machine oils, vacuum-pump oils, and human sebum, and inorganic ones include dusts, metal powder, tobacco smoke, and salts.

Table 2 shows examples of organic contaminants.

1) Cutting oils 2) Mixtures of beeswax and pine resin 3) Lapping agents 4) Vacuum-pump oils, silicon diffusion-pump oils 5) Silicon vacuum greases 6) Soldering fluxes 7) Human sebum 8) Contaminants attached during long-term air exposure 9) Carbon thin films formed by vacuum deposition

Table 2. Examples of organic contaminants¹⁾

UV-O₃ cleaning is generally effective for removing organic contaminants, though it may be ineffective for removing inorganic contaminants. Therefore, as preliminary cleaning, inorganic contaminants must be removed in advance using pure water, solvents, or the like before UV-O₃ cleaning is conducted.

2. UV-O₃ cleaning technique

The decomposition of carbohydrates by ultraviolet irradiation has been known, but surface cleaning by ultraviolet irradiation and its applicability to the manufacture of electronic components have not been studied until recently.

In 1972, Bolon and Kuns succeeded in decomposing photoresist polymers by ultraviolet irradiation.¹⁾ This enabled the achievement of very clean surfaces. J.R. VIG used UV-O₃ cleaning to clean the surface of crystal oscillators.¹⁾ Even monolayer contamination will significantly affect the frequency change of the oscillators.

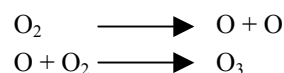
2-1. Principle of UV-O₃ cleaning

The principle of UV-O₃ cleaning is as follows: organic compounds are converted into volatile

substances (e.g., water, carbon dioxide, nitrogen) by decomposition by ultraviolet rays and by strong oxidation during the formation and decomposition of O₃, and are removed from the contaminated surface.

The major wavelengths of the ultraviolet rays radiated from a well-known low-pressure mercury vapor lamp are 184.9 nm and 253.7 nm. When atmospheric oxygen O₂ is irradiated with ultraviolet rays with a wavelength of 184.9 nm, the oxygen absorbs the ultraviolet rays to form O₃ by the following reaction:

Ultraviolet rays with a wavelength of 189.4 nm



Ozone O₃ irradiated with ultraviolet rays with a wavelength of 253.7 nm absorbs the ultraviolet light to decompose O₃. During the process of formation or decomposition of O₃, atomic oxygen O having a strong oxidizing ability is generated.

Then, contaminant organic compounds are irradiated with ultraviolet rays, and absorb the ultraviolet rays to cause photolysis and generate the following substances:

Organic compounds irradiated with ultraviolet rays

- ⎧ Ions
- Free radicals
- Excited molecules
- Neutral molecules

The energy E per mol of an electromagnetic wave has a relationship with the wavelength λ as expressed by the following formula:

$$E = Nhc/\lambda \times 10^5 \text{ KJ} \cdot \text{mol}^{-1}$$

Where

h is Planck's constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{Sec}$),

c is the velocity of light ($2.998 \times 10^{10} \text{ cm} \cdot \text{Sec}^{-1}$),

λ is the wavelength (cm), and

N is Avogadro's constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).

The energy E per mol of ultraviolet rays with a wavelength of 184.9 nm is

$$E_{(1849)} = \frac{6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.998 \times 10^{10}}{1849} \times 10^5 \text{ KJ} \cdot \text{mol}^{-1} = 647 \text{ KJ} \cdot \text{mol}^{-1}$$

In a like manner, the energy $E_{(2537)}$ per mol of ultraviolet rays with a wavelength of 253.7 nm is:

$$E_{(2537)} = 472 \text{ KJ} \cdot \text{mol}^{-1}$$

Table 3 shows the bond energies of various molecules of organic compounds. Organic compounds can be decomposed by irradiating them with energy stronger than the bond energy. These excited contaminants, or the free radicals of the contaminants formed by photolysis, react with atomic oxygen to form simple molecules such as CO_2 , H_2O , N , and O_2 , which are removed from the surface.

2-2. Evaluation of cleanliness

Currently, surface cleanliness is evaluated based on the contact angle (θ) with water, a steam test in which the adhesion condition of steam is observed, and analytical methods such as Auger electron

spectroscopy (AES) and photoelectron spectroscopy (ESCA).

A clean surface has high surface energy, while a contaminated surface has low surface energy. Therefore, water droplets dropped on each surface in the same amount spread widely on the clean surface and have a small contact angle, while they do not spread so widely on the contaminated surface and have a large contact angle.

Table 4 shows the correlation between the contact angle, steam test, and cleanliness.

2-3. Application of UV- O_3 cleaning

This section provides a few examples of the recent applications of UV- O_3 cleaning in various fields.

In the manufacture of crystal oscillators, surface contamination significantly affects the performance of the oscillators.

The frequency change of a crystal oscillator with a frequency of 5 MHz must be $2/10^{10}$ or less in a week, but the adsorption or desorption of monolayer contamination on the surface causes a frequency change of $1/10^6$.

Therefore, contaminations equal to or less than monolayer or smaller must be removed; UV- O_3 cleaning has been used for this purpose.¹⁾

UV- O_3 cleaning is highly effective in removing organic contaminants from gold surfaces, and significantly decreases the temperature dependency of thermo-compression wire bonding.¹⁾ Thus, this cleaning method is used to improve the reliability of wire bonding at low temperatures.

Bond	Bond energy (KJ/mol)	Bond	Bond energy (KJ/mol)
O - O	138.9	C = C	607
O = O	490.4	C \equiv C	828
O - H	462.8	C = O	724
C - C	347.7	C - Cl	328.4
C - H	413.4	H - F	563.2
C - N	291.6	C - F	441.0
C \equiv N	791	H - Cl	431.8
C - O	351.5	N - H	309.8

Table 3. Chemical-bond energy ²⁾

Results of the steam test	Conditions of steam condensation on polished quartz	Contact angle	Contaminant monolayer
Excellent interference fringes	Uniform rainbow fringes during both condensation and evaporation	4°	< 0.1
Good interference fringes	Uniform ray fringes during condensation, irregular fringes during evaporation	4°	< 0.1
Bad interference fringes	Irregular fringes during condensation	4°	≤ 0.1
Orange peel	Colorless, water droplets, transparent	5° to 10°	0.1 to 1
Mist	Translucent due to many small water droplets	> 10°	1

Table 4. Correlation between the contact angle, steam test, and cleanliness¹⁾

This cleaning method has also been used for removing the following materials in pretreatment for coating of a photoresist, and for improving the adhesive force of adhesives.

- 1) Glass plates
- 2) Chrome masks
- 3) Nesa films
- 4) Semiconductors (e.g., silicon wafers)
- 5) Metals (e.g., copper, aluminum, SUS, nickel)
- 6) Ceramic plates

The following uses are suggested for the application of UV-O₃ cleaning:

- 1) Surface treatment prior to coating, plating, or vaporization
- 2) Clean oxidation of metal and semiconductor surfaces
- 3) Modification of polymer surfaces
- 4) Peeling and etching of photoresist thin films
- 5) Others

2-4. Contaminants removable by UV-O₃ cleaning

1. Cutting oils
2. Mixtures of beeswax and pine resin
3. Lapping agents
4. Vacuum-pump oils
5. Silicon diffusion-pump oils
6. Silicon vacuum greases
7. Soldering fluxes
8. Human sebum
9. Contaminants adsorbed during long-term air exposure
10. Carbon thin films formed by vacuum evaporation

3. UV-O₃-cleaning experimental apparatus

As an experimental apparatus for UV-O₃ cleaning,

a stainless-steel apparatus as shown in Fig. 1 (a) and (b) was manufactured.

In Fig. 2 (a), a sample was irradiated with ultraviolet rays with wavelengths of 184.9 nm and 253.7 nm, and then O₃ was formed in the apparatus. In (b), an ozoneless quartz plate was placed between the sample and the light source, the sample was irradiated with ultraviolet rays with a wavelength of 253.7 nm only, and no O₃ was formed in the apparatus.

In apparatus (a), contaminants were exposed to O₃ and ultraviolet rays with wavelengths of 184.9 nm and 253.7 nm, while in apparatus (b) they were exposed to ultraviolet rays with a wavelength of 253.7 nm only. The irradiation distance assumed to be approximately 5 mm.

The results of the two experiments are described below.

In apparatus (a), the contact angle with water droplets of the sample exposed to 184.9 nm + 253.7 nm + O₃ decreased from 35° before treatment to 4° less within 20 seconds to 60 seconds.

In apparatus (b), the sample exposed to 253.7 nm could not achieve a contact angle of 4° or less even after one to several hours.

These experiments showed that the irradiation of ultraviolet rays only cannot achieve an immediate and sufficient and cleaning effect.

Fig. 2 shows the results of the ESCA analysis of the surface of the quartz glass plate that had achieved a contact angle of 4° or less. Few carbon peaks were detected on the cleaned surface, indicating the effect of UV-O₃ cleaning.

Additionally, in the results of the AES analysis of the gold surfaces before and after UV-O₃ cleaning (Fig. 3), few carbon peaks were detected on the cleaned surface.

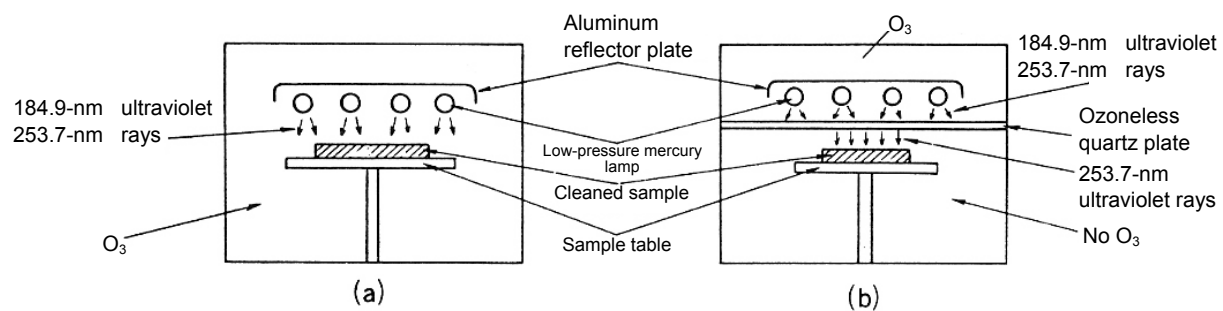
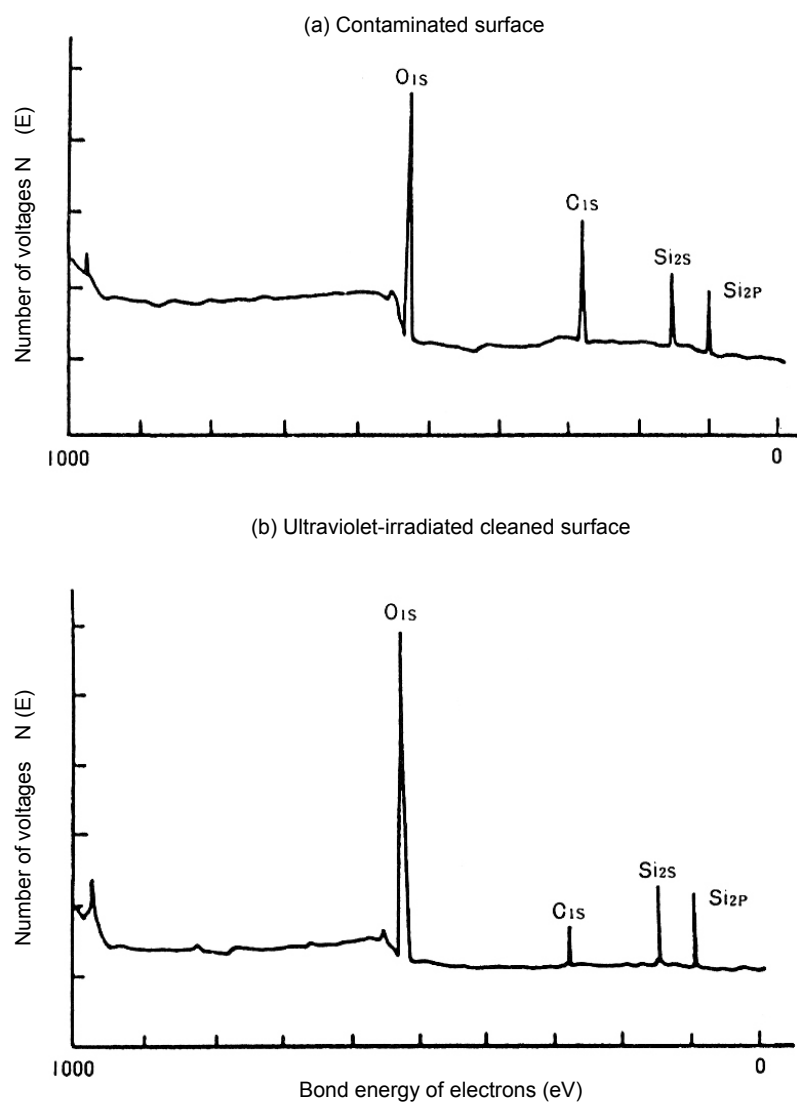


Fig. 1



(a) Composition of the contaminated surface

O-14%, Si-8%, C-78%

(b) Composition of the cleaned surface

O-65%, Si-33%, C-2%

Fig. 2. ESCA analysis results of the quartz surface before and after ultraviolet irradiation³⁾

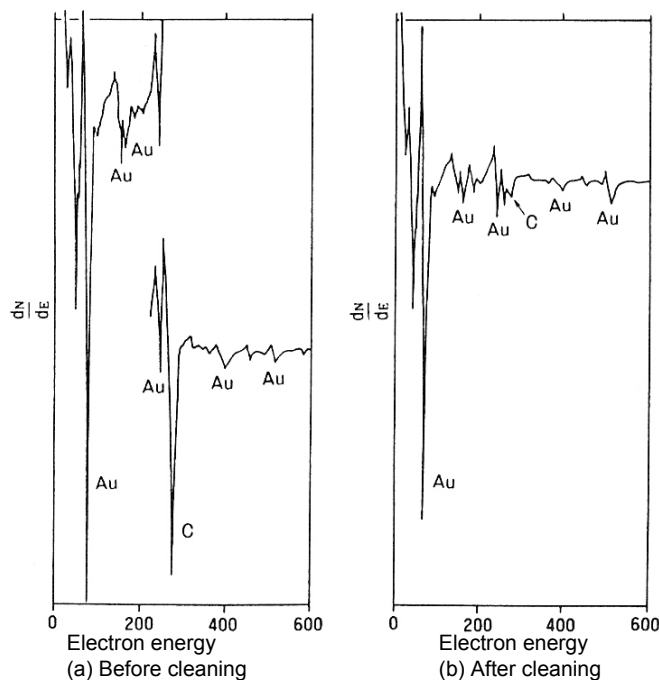


Fig. 3. AES analysis results of the gold surface before and after ultraviolet-rays/ozone cleaning⁴⁾

4. Importance of preliminary cleaning

UV-O₃ cleaning is effective in removing organic compounds, but is not effective in removing dust and inorganic salts. In addition, if contaminants of organic compounds form a thick film, many polymers in the surface area may be decomposed by ultraviolet irradiation. However, the polymers on the inside containing no oxygen crosslink with each other and do not cause photolysis.

For this reason, effective UV-O₃ cleaning requires preliminary cleaning of the surface. The preliminary cleaning is conducted primarily to remove contaminants such as dust and salts that cannot be converted into volatile products by the oxidation action of UV-O₃ cleaning, and secondarily to remove a thick coating of the contaminants, the majority of which is likely to be converted into a UV-resistant coating by the crosslinking action of ultraviolet rays immersing from the surface.

5. Ultraviolet-ozone cleaning lamp

Practically usable ultraviolet-ozone cleaning lamps must effectively radiate lights with wavelengths of 184.9 nm and 253.7 nm. Ultraviolet

rays with a wavelength of 184.9 nm are absorbed by oxygen to form ozone. On the other hand, ultraviolet rays with a wavelength of 253.7 nm are absorbed by ozone to decompose the ozone, or is absorbed by most hydrocarbon substances to decompose them.

Thus, the coexistence of wavelengths of 184.9 nm and 253.7 nm causes the continuous formation and/or decomposition of ozone. In particular, atomic oxygen formed during the formation and decomposition of ozone acts as a strong oxidizer.

Light sources include low-pressure mercury lamps, medium-pressure mercury lamps, and high-pressure mercury lamps. The light of a low-pressure mercury lamp consists of 90% of 253.7 nm and several % of 184.9 Å. Fig. 4 shows the radiation spectral distribution of a low-pressure mercury lamp, and Fig. 5 shows the absorption properties of ozone. When ozone exists between a light source and a sample, the absorption changes the illuminance on the sample according to the distance and concentration of the ozone. Ozone has a broad absorption band in the vicinity of 260 nm, and an absorption coefficient of 120 cm⁻¹atm⁻¹ for 253.7 nm. Fig. 6 shows the absorption coefficient according to the wavelength of ozone.

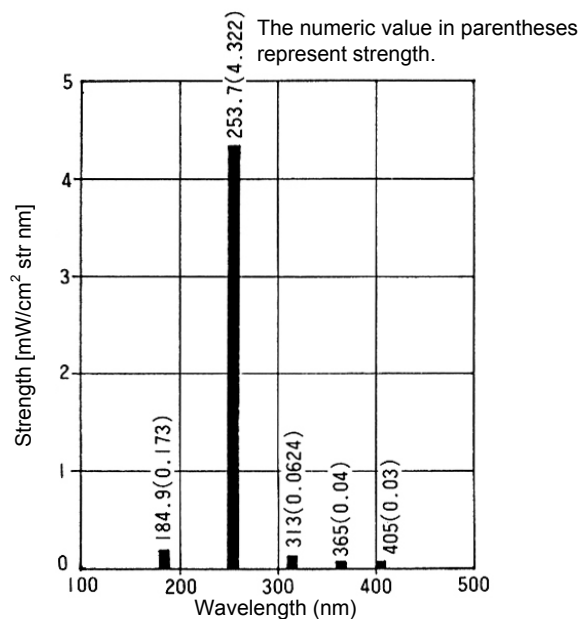


Fig. 4

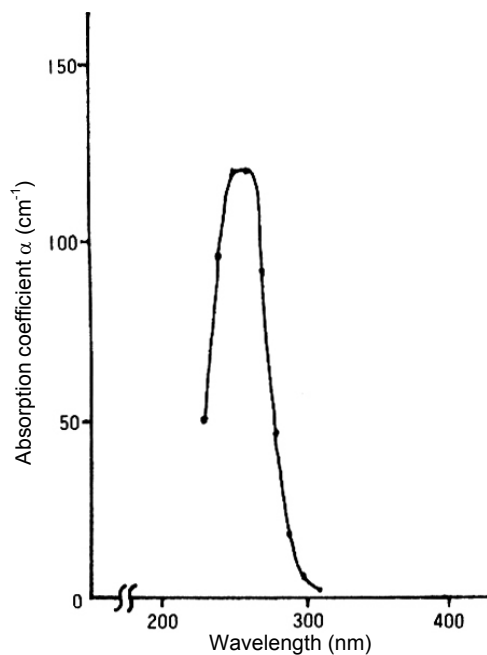


Fig. 5⁵⁾

When the wavelength falls within the range, the following equation holds:

$$I = I_0 e^{-120Pd}$$

Where P is the mean pressure of ozone between the light source and the sample, and d (cm) is the distance between the light source and the sample.

When the distance between the light source and the sample was 5 mm and 13 cm, the cleaning time was 20 seconds and 20 to 30 minutes, respectively.

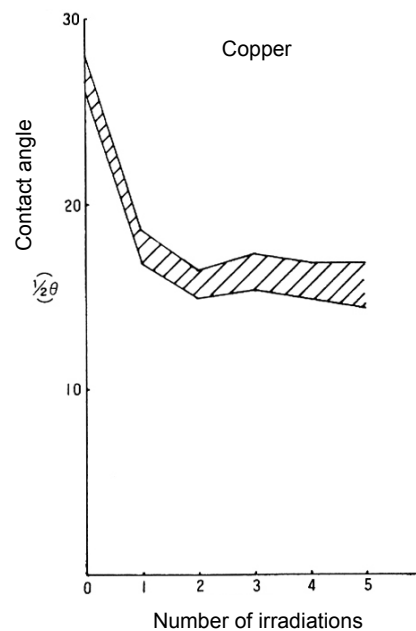


Fig. 6

6. Structure of the ultraviolet-ozone cleaning apparatus

The structure of ultraviolet-ozone cleaning apparatuses must ensure protection from ozone and shortwave ultraviolet rays. Exposure to strong shortwave ultraviolet rays will cause disorders of the skin and eyes in a short time. Therefore, the apparatus must not leak ultraviolet rays, and must have a door switch or the like to automatically shut off the lamp when the door is open. If the leakage of ultraviolet rays cannot be completely prevented by any applications (e.g., a doorway of the conveyor type), minimize the leakage and be sure to wear adequate clothing and eye protection in order to prevent skin burns and eye disorders.

Another deleterious material is ozone, which is toxic. When the apparatus is installed, exposure to ozone concentration must not exceed 0.1 p.p.m. to human exposure, which is the recommended value of the Japan Society for Occupational Health.

Organic substances decomposed by ozone or ultraviolet rays, such as plastic insulating materials, cannot be used in a radiation room that is exposed to ozone and ultraviolet rays from the apparatus. In addition, clean air or oxygen containing no potential contaminants such as dust, moisture, fats, or oils must be always supplied to the interior of the radiation room.

7. Results of UV-O₃ cleaning experiments

Cleaning experiments were conducted on various materials, and the following results were obtained.

Cleanliness can be evaluated in various methods, such as the steam method, contact-angle method, AES method, and ESCA method, but in this experiment it was evaluated by the contact angle using water droplets.

The materials were pretreated by:

1. I. P. A. immersion cleaning
2. Flon immersion cleaning
3. Flon steam cleaning

The following eight types of materials were used as the samples:

- | | |
|------------------------------|---------|
| (1) Oxygen-free copper plate | Fig. 6 |
| (2) SUS 304 plate | Fig. 7 |
| (3) Aluminum plate (99.99%) | Fig. 8 |
| (4) Acryl plate | Fig. 9 |
| (5) Chrome mask | Fig. 10 |
| (6) Nesa film | Fig. 11 |
| (7) Si wafer | Fig. 12 |
| (8) White plate glass | Fig. 13 |

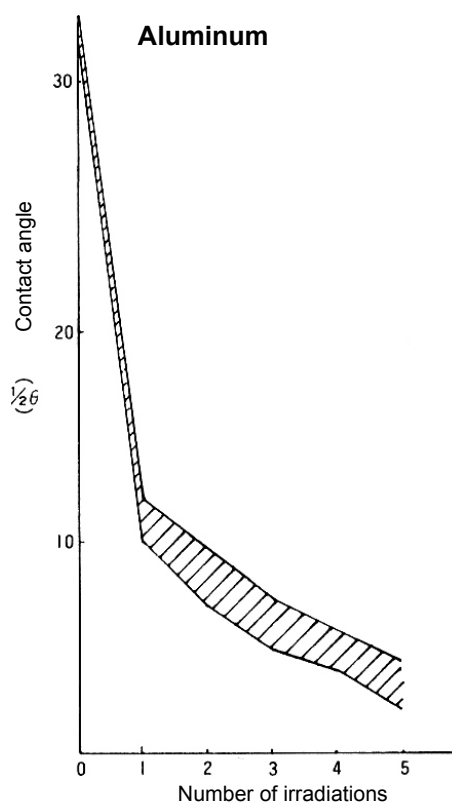


Fig. 8

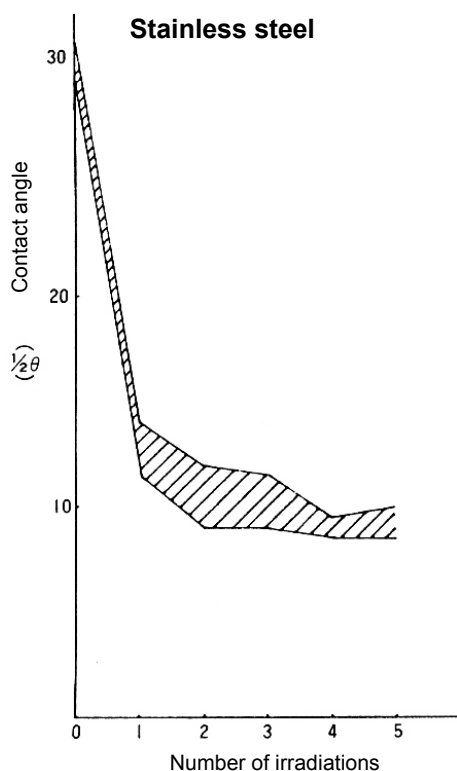


Fig. 7

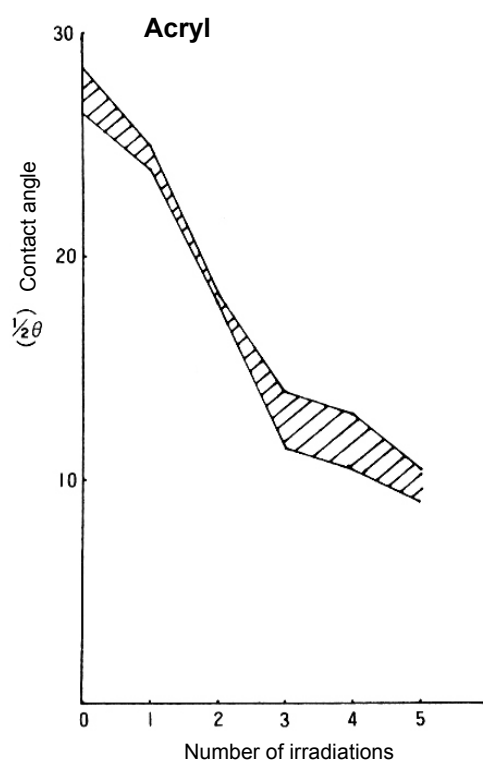


Fig. 9

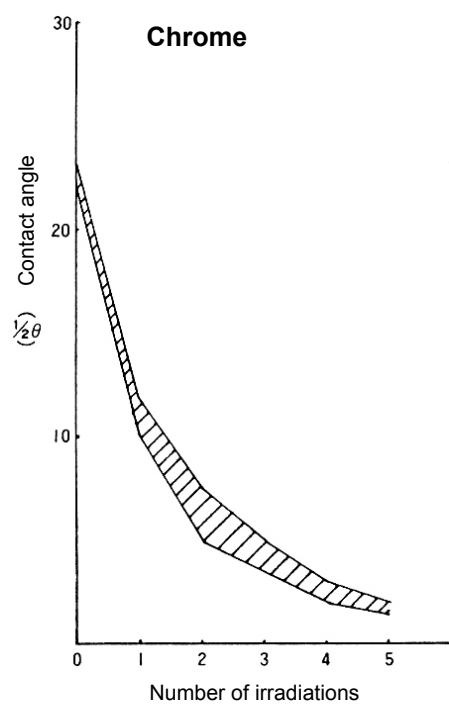


Fig. 10

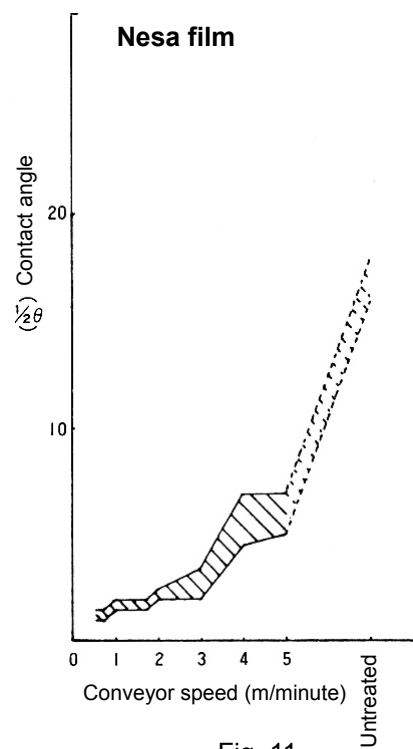


Fig. 11

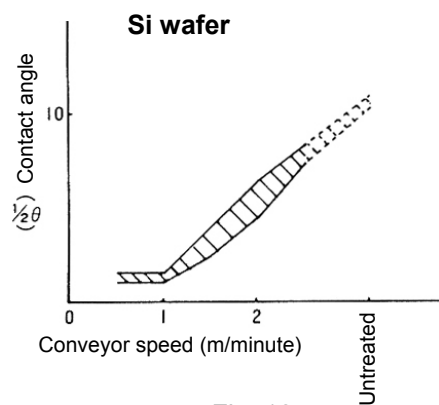


Fig. 12

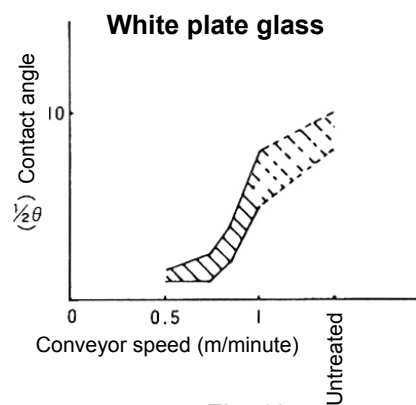
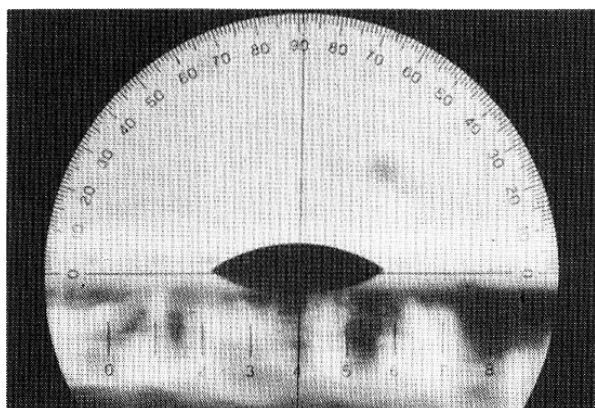


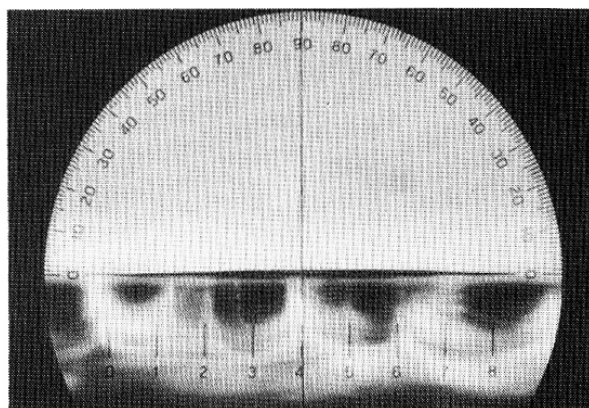
Fig. 13



Fig. 14



Before cleaning Contact angle ($\frac{1}{2}\theta$): Approx. 17°



After cleaning Contact angle ($\frac{1}{2}\theta$): Approx. 3°

Fig. 15

The experiments were conducted using a conveyor-type apparatus in which six U-shaped 110-W lamps were arranged in a direction at right angles to the direction of travel.

Distance between the sample and lamp 10 mm

The horizontal axis of the experimental data represents the following:

The conveyor speed (m/minute) in Figs. 11, 12, and 13

The number of radiations at a conveyor speed of 0.5 m/minute in Figs. 6, 7, 8, 9, and 10

The diagonally shaded areas represent the variation range at five points measured for each sample.

The contact angle of oxygen-free copper, SUS 304, acryl, and Mylar did not decrease significantly, but water wettability was improved by UV- O_3 cleaning of the entire surface of the samples, in comparison with the very poor water wettability prior to UV- O_3 cleaning.

Fig. 14 shows the progress of contamination of the surface of the white plate glass over time in a class-100 atmosphere as measured by the contact angle.

The photographs in Fig. 15 show the cleanliness of the Nesa film before and after UV- O_3 cleaning as measure by the contact angle.

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