

REMOVAL OF ORGANIC IMPURITIES FROM THE SILICON SURFACE BY OXYGEN AND UV CLEANING

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Abstract – We have studied the effect of oxygen and water vapor on the removal of organic impurities from the porous silicon surface under UV irradiation. Infrared spectrum observations of the treated surface suggest that decomposition of oxygen to produce ozone, atomic oxygen, and hydroxyl radical is a rate determination step for the overall cleaning process.

Key words: Porous Silicon, UV Cleaning, Ozone, Atomic Oxygen, Hydroxyl Radical

INTRODUCTION

Performance of semiconductor devices is affected by the contaminants incorporated during the device fabrication processes. As in the case of native oxide, organic impurities which are of hydrocarbon type cause many problems such as generation of interface traps, promotion of native oxide growth, and modifying the oxidation kinetics [Ruzyllo et al., 1987; Okada et al., 1993].

Since Bolon and Kunz [1972] demonstrated that ultraviolet (UV) light depolymerized photoresist polymers to produce an extremely clean surface, many efforts have been made to remove organic impurities from silicon surfaces by UV cleaning [Tabe, 1984; Baunack and Zehe, 1989]. Recently, Bedge et al. [1992] have investigated the effect of humidity and O₂ partial pressure on the removal of organic impurities and have suggested a simplified reaction network for the UV cleaning process. This result and those from other similar studies suggest that UV cleaning is a potential alternative method to replace the conventional liquid-based RCA cleaning [Kern and Poutein, 1970].

In this paper, we have observed the role of oxygen and water vapor in UV cleaning characterizing the surface with Fourier transform infrared spectroscopy (FTIR). We also have proposed a rate determination step in the UV-cleaning process.

EXPERIMENTAL

Experiments were conducted with 0.5×12×13 mm³ p-type Si(100) whose surface had been anodized into a porous layer following the procedure of Bomchil et al. [1983]. The surface area of the sample after the anodization was about 2 m²/cm² of the sample cross section, which was high enough to allow IR observation of the surface species.

The porous sample retains the crystallinity of the original sil-

icon wafer as confirmed by many previous studies with FTIR, electron energy loss spectroscopy (EELS), and double-crystal x-ray diffraction (XRD) [Chabal and Raghavachari, 1985; Chabal and Raghavachari, 1984; Chabal, 1985]. According to our study, the porous sample exhibited sharp and pronounced IR peaks assigned unambiguously to mono- and dihydrides on the silicon surface. The location and the relative intensity of the peaks were identical to those for Si(100) 2×1, supporting the notion that the surface crystallinity was preserved after the anodization.

The porous silicon sample was contaminated intentionally with vacuum oil (Moresco MR-200) as follows. Oil diluted in n-hexane solution was spread on the sample surface, then the sample was placed in an oven for 20 hours for evaporation of n-hexane from the surface.

A low-pressure mercury lamp (Kumkang Co.) was used as a light source for emission between 100 nm and 400 nm. The oil-contaminated sample was placed in a reactor attached with a synthetic quartz (Suprasil) window transparent to 185 nm and 254 nm lines. High purity oxygen passing through deionized (DI) water was injected into the reactor. DI water and UV-irradiation time were fixed at 70°C and 1 hour respectively, and the oxygen flow rates were varied. The sample surface was characterized with FTIR (Midac).

RESULTS AND DISCUSSION

Fig. 1 is an IR spectrum of the oil-contaminated silicon sample. Yonekawa et al. [1994] assigned peaks from 3020 cm⁻¹ to 2820 cm⁻¹ to stretching modes of the hydrocarbons on the silicon surface. Accordingly, we can estimate the amount of the organic impurities on the silicon surface by monitoring the peak intensity.

Fig. 2 shows changes in the IR spectrum of the UV-cleaned Si(100) treated under various conditions. Because the IR spectrum before the UV cleaning was used as a reference, negative peaks in Fig. 2 represent decrease of the organic impurities on the surface.

The extent of the impurity removal is given by the following equation.

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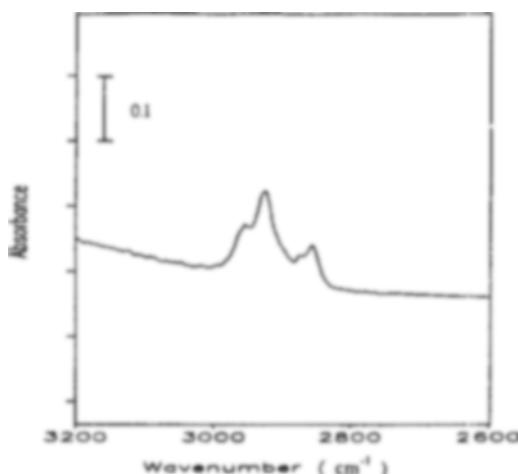


Fig. 1. IR spectrum of Si(100) contaminated with vacuum oil.

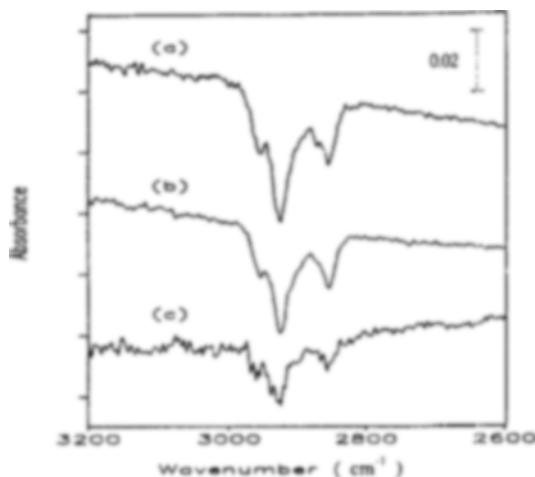


Fig. 2. Changes in the IR spectrum of the UV-cleaned Si(100) with cleaning conditions: (a) UV irradiation with O₂ and H₂O, (b) UV irradiation with O₂, (c) UV irradiation with H₂O.

$$\text{Cleaning Efficiency}(\%) = \frac{\text{amount of impurities removed by cleaning}}{\text{initial amount of impurities before cleaning}} \times 100 \quad (1)$$

Although we have used an identical condition to contaminate the silicon surface with vacuum oil, the amounts of contaminants seem to vary with samples. Accordingly, we have compared the amounts of the organic impurities before and after the cleaning for each sample.

Table 1 shows the cleaning efficiency after each UV treatment. The efficiency is the highest when oxygen and water vapor are injected together into the reactor under UV irradiation. This result is explained as follows based on the reaction mechanism proposed by previous workers [Bedge et al., 1992; Wood et al., 1993].

Molecular oxygen strongly absorbs UV light at wavelengths below 200 nm. Irradiation at a wavelength of 185 nm results in dissociation of O₂ into triplet atomic oxygen, O(³P), and this species can react with molecular oxygen to form ozone, O₃. Irradiation at a wavelength of 254 nm results in dissociation of O₃ into singlet molecular oxygen, O₂(¹Δg), and singlet atomic oxygen, O(¹D). O(¹D) is a source of hydroxyl free radicals, OH·,

Table 1. Cleaning efficiency of various UV treatments¹⁾

| Treatment conditions before cleaning ²⁾ | IR peak area of hydrocarbons (A ₀) | IR peak area of hydrocarbons due to cleaning ²⁾ (ΔA) | Cleaning efficiency (%) | Relative cleaning efficiency (%) |
|--|--|---|-------------------------|----------------------------------|
| UV+O ₂ +H ₂ O | 1.000 | 0.2449 | 24.49 | 100 |
| UV+O ₂ | 0.8691 | 0.1860 | 21.40 | 87.46 |
| UV+H ₂ O | 0.7144 | 0.1076 | 15.06 | 61.52 |

1) UV-irradiation time = 1hr, reactor volume = 52 cm³

2) The peak areas have been normalized with respect to the case of UV, O₂ and H₂O.

produced by reaction with water vapor. Also, UV light at the above wavelengths is capable of dissociating directly the C-C and the C-H bonds in the adsorbed organic molecules producing fragments that are more readily oxidized than the parent compounds.

Fig. 3 shows a simplified reaction mechanism for the UV-O₂ cleaning [Bedge et al., 1992]. Because ozone, atomic oxygen, and hydroxyl radicals are directly associated with removal of organic impurities, the cleaning efficiency is the best when oxygen and water vapor are injected together under UV irradiation.

The reaction mechanism shown in Fig. 3 is classified into three steps. One (step I) is a set of reaction steps to produce species such as ozone, atomic oxygen, and hydroxyl radical which play a role in removing the organic impurities. The other (step II) is the surface reaction of these species with organic impurities on the silicon surface, and the third (step III) is the desorption of the oxidized organic impurities from the silicon surface. We performed the UV-O₂ cleaning by varying the oxygen flow rates in order to determine the rate-determining step (RDS).

Fig. 4 shows dependence of the cleaning efficiency on the oxygen flow rate under UV irradiation. The efficiency decreases initially with the oxygen flow rate, then remains unchanged at high oxygen flow rates. If desorption of the oxidized organic impurities from the silicon surface (step III) were the rate determination step, the cleaning efficiency should increase with the oxygen flow rate. This is contrary to the results of Fig. 4, and therefore step III is not the rate determination step.

We made two additional experiments to determine the RDS. First, oxygen was flowed into the reactor, and then the UV light was irradiated into the oxygen-filled reactor. Changes in the cleaning efficiency with the UV-irradiation time are shown in Fig. 5. The cleaning efficiency increases slowly with the irradiation time, which suggests that either decomposition of oxygen to produce the reactive oxygen species (step I) or their reaction with the surface hydrocarbons (step II) proceeds slowly and is assisted by the UV irradiation. To determine which of the above two steps was slower, we measured the temperature change of the silicon surface during UV irradiation.

Fig. 6 shows that the silicon-surface temperature increases during the initial about 30 minutes. If oxidation of the surface hydrocarbon (step II) was the RDS for the overall rate, the temperature should rise over the entire period of UV irradiation, i.

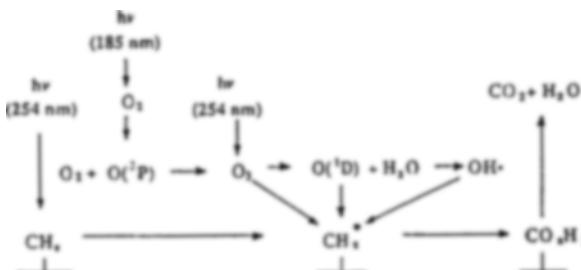


Fig. 3. Reaction network for UV-O₂ cleaning [Bedge et al., 1992].

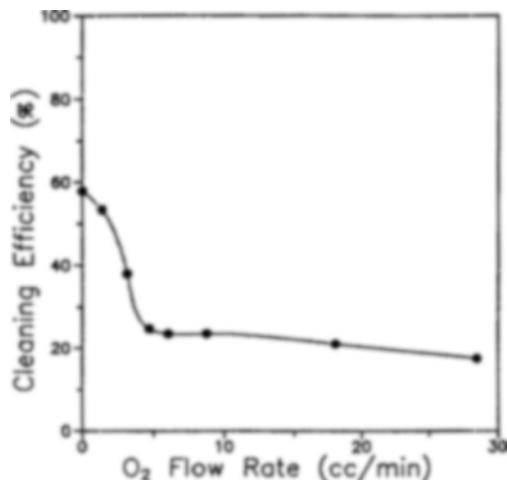


Fig. 4. Dependence of the cleaning efficiency on the O₂ flow rate under UV irradiation (UV-irradiation period was 1 hour).

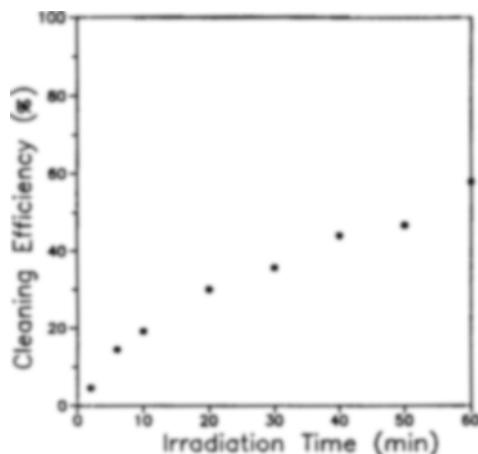


Fig. 5. Dependence of the cleaning efficiency on the UV-irradiation time (Oxygen remained in the reactor during UV irradiation).

e., 1 hour as in the case of Fig. 5. However, since the temperature rise is observed during only the initial period, i.e., 30 minutes in Fig. 6, we may conclude that step II is not the RDS for the overall rate. Instead, step I determines the overall rate.

In summary, we have shown by experiments that ozone, atomic oxygen, and hydroxyl radical play a key role in removing the organic impurities from the porous silicon surface and a step to produce the oxygen-containing species determines the overall rate of the cleaning process.

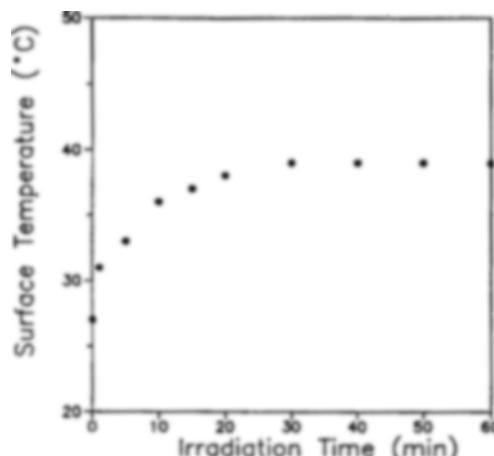


Fig. 6. Dependence of the silicon-surface temperature on the UV-irradiation time (Oxygen remained in the reactor during UV irradiation).

REFERENCES

- Baunack, S. and Zehe, A., "A Study on UV/Ozone Cleaning Procedure for Silicon Surfaces", *Phys. Stat. Sol. (a)* **115**, 223 (1989).
- Bedge, S., McFadyen, J. and Lamb, H. H., "Kinetics of UV/O₂ Cleaning and Surface Passivation: Experiments and Modeling", *Materials Research Society Symposium Proceedings*, **259**, 207 (1992).
- Bolon, D. A. and Kunz, C. O., "Ultraviolet Depolymerization of Photoresist Polymers", *Polymer Engineering and Science*, **12**, 109 (1972).
- Bomchil, G., Herino, R., Barla, K. and Pfister, J. C., "Pore Size Distribution in Porous Silicon Studied by Adsorption Isotherms", *J. Electrochem. Soc.*, **130**, 1611 (1983).
- Chabal, Y. J., "Infrared Study of the Chemisorption of Hydrogen and Water on Vicinal Si(100) 2×1 Surfaces", *J. Vac. Sci. Technol.*, **A3**, 1448 (1985).
- Chabal, Y. J. and Raghavachari, K., "Surface Infrared Study of Si(100)-(2×1)H", *Phys. Rev. Lett.*, **53**, 282 (1984).
- Chabal, Y. J. and Raghavachari, K., "New Ordered Structure for the H-Saturated Si(100) Surface: The (3×1) Phase", *Phys. Rev. Lett.*, **54**, 1055 (1985).
- Kern, W. and Poutein, D. A., "Cleaning Solutions Based on Hydrogen Peroxide for Use in Silicon Semiconductor Technology", *RCA Rev.*, **31**, 187 (1970).
- Okada, C., Kobayashi, H., Takahashi, I., Ryuta, J. and Shingyuuji, T., "Growth of Native Oxide and Accumulation of Organic Matter on Bare Si Wafer in Air", *Jpn. J. Appl. Phys.*, **32**(8A), L1031 (1993).
- Ruzyllo, J., Duranko, G. T. and Hoff, A. M., "Preoxidation UV Treatments of Silicon Wafers", *J. Electrochem. Soc.*, **134**(8), 2052 (1987).
- Wood, P. C., Wydeven, T. and Tsuji, O., "Critical Process Variables for UV-Ozone Etching of Photoresist", *Materials Research Society Symposium Proceedings*, **315**, 237 (1993).
- Yonekawa, N., Yasui, S. and Ohmi, T., "Cleaning Technology and Analysis Technology for Hydrocarbon Contamination on Si Wafer Surface", *Extend Abstracts of the 1994 International Conference on Solid State Device and Materials*, **428** (1994).