

Diagnosis and Cleaning of Carbon Contamination on SiO₂ Thin Film

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A contamination on a surface is a serious problem in thickness measurement especially for thin films less than ten nanometers. Water contact angles are sensitive to the surface condition and the degree of contamination and can be a very useful criterion for a judgment of the effect in practical cleaning processes. The UV-ozone cleaning is the most effective one in removal of carbon contamination in the method we investigated.

1. Introduction

A contamination on a surface is a serious problem in thickness measurement especially for thin films less than ten nanometers. It is usually inevitable that carbon contamination occurs due to adsorption of organic compounds from the environmental atmosphere. We have been using water contact angle of surfaces to diagnose degree of contamination and to estimate cleanliness after cleaning treatments. Some information based on the contact angle is very useful for a judgment of the effect in practical cleaning processes.

In this paper we will discuss the relationship between contact angle and carbon contamination on SiO₂ thin film. We will also discuss the effects of some cleaning methods.

2. Experimental

We measured contact angles of specimens using ultraclean water with specific resistance of more than 18 MΩ cm.

We used an XPS (X-ray photoelectron spectroscopy) with monochromatic Al x-ray source to measure atomic concentration of the specimen surface. We detected nothing but Si, O, and C on the specimens.

We used a spectroscopic ellipsometer to measure thickness of SiO₂ thin film. We developed a nitrogen shower head to protect a specimen against contamination from the environmental atmosphere. It worked so well that thickness of a specimen remains the same value for over 24 hours. We used it if needed.

We tried to clean a SiO₂ surface with some organic solvents (ethanol, acetone and propa-nohl) and an nitric acid, but they did not work well. The effective cleaning methods are listed bellow.

(a) Heating in the air on a hot plate (H.P.) or in O₂ at 1 atm. in an oxidizing furnace. The H.P. was for a domestic use and heated a specimen at 200°C.

(b) Dipping in water. We dipped a specimen in ultra-clean water without any extra treatment.

(c) Dipping in ozone water: We dipped a specimen in ozone water with a few ppm to 20 ppm concentration without any extra treatment.

(d) UV-ozone cleaning (dry process of ultra-violet ray and ozone gas):

We used SiO₂ specimens thermally oxidized at 1000°C with thickness of about 9 nm.

3. Results and discussions

3.1 Contact angle and carbon contamination

Fig.1 shows changes with time in contact angles of specimens held in the atmosphere of a clean room (CR). One specimen was as -grown, other was dipped in ultraclean water for 1 min and dried with clean nitrogen gas flow. The as-grown sample (diamond in Fig.1) had a big contact angle of 51.2 deg indicating hydrophobic surface. While the contact angle kept the same value for about 100 h, the surface was contaminated with carbon of more than one monolayer as mentioned later. The as-grown SiO₂ surface had coincidentally the same contact angle as the carbon contamination surface did.

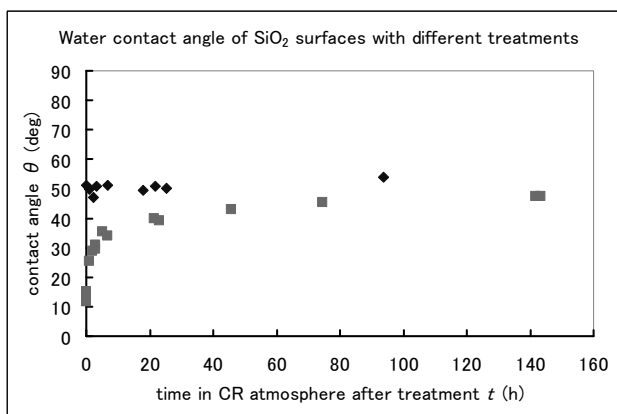


Fig. 1 Change in water contact angle of SiO₂ thin film as a function of time kept in the CR atmosphere. (1) Just after deposition (diamond), (2) after water dipping for 1 min just after deposition (square).

The contact angle showed a small value of 11.8 deg just after the water dipping indicating hydrophilic surface and increased with time of contamination-piling-up. It approached to the same value as the as-grown sample. These results indicate that contact angles were sensitive to the surface condition and the degree of contamination. The way of change in contact angles with time depends on the surface treatments. Accordingly contact angles can be a good index for surface cleanliness. A SiO₂ surface perfectly wet with water is as clean as an as-grown one. This is a very useful criterion for a judgment of the effect in practical cleaning processes.

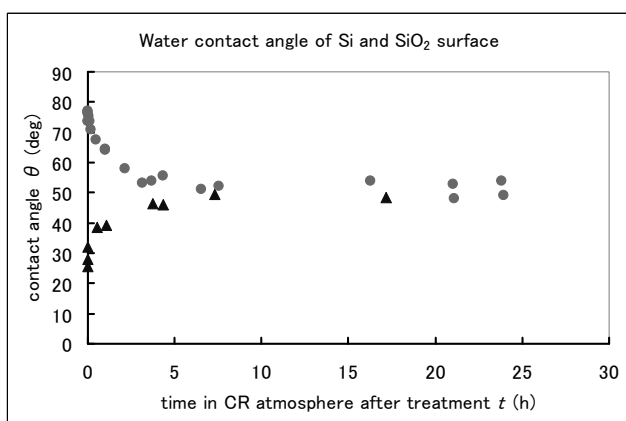


Fig. 2 A contact angle of Si and SiO₂ surfaces as a function of time in CR atmosphere. (1) SiO₂ after heating in air by H.P. (triangle), (2) hydrogen terminated Si (circle).

Fig.2 shows the results of other two samples. One was after heating in the air on the H.P. for 2 min (triangle). The other had a hydrogen-terminated surface with dilute hydrofluoric acid (HF) treatment

(circle). Contact angles reached the constant value of about 50 deg at 10 h. The amount of carbon contamination adsorbed on the surface at 10 h is estimated as 1.1 at% according to the relation between the time and the amount of carbon (Fig.3). The 1.1at% of carbon corresponds to a thickness of 0.22 nm (SiO₂ equivalent) according to the relation between the carbon amount and the carbon film thickness (Fig.4) [1]. This indicates that adsorption of carbon more than one monolayer makes a new surface independent to the underlying surfaces.

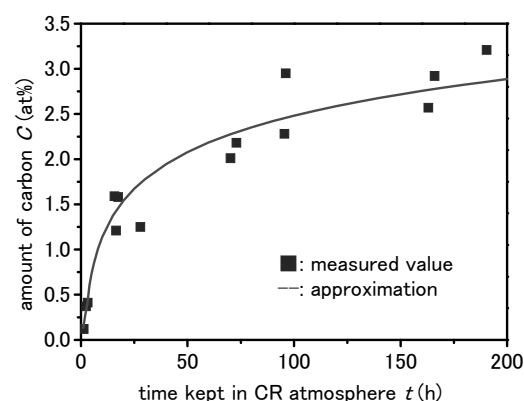


Fig. 3 Amount of carbon on SiO₂ thin film as a function of time in the CR atmosphere. The solid line represents a logarithmic approximation of data.

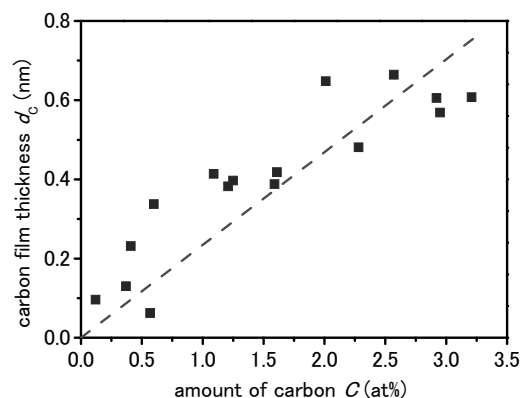


Fig. 4 Carbon film thickness as a function of amount of carbon adsorbed on the surface. The dotted line is a linear approximation of data [1].

3.2 Surface cleaning methods

3.2.1 Heating in the air or in oxygen.

Fig.5 shows changes in SiO₂ thickness of an as-grown specimen with time. We heated the specimen on the H.P. in the air three times at 200°C for 2 min. The four groups of data are on the same line. The initial thickness was 8.13 nm.

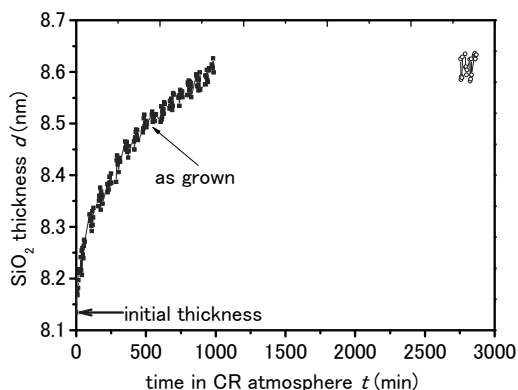


Fig. 5 Effect of heating in air by a H.P.. We repeated heating three times. Thickness came back to the as-grown value every time.

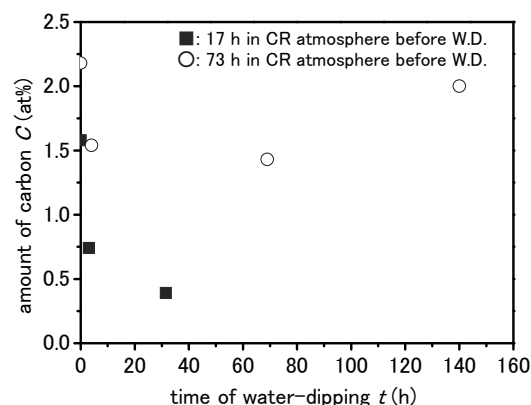


Fig. 6 Effect of dipping in ultra clean water. Contamination of 17 h can be removed with this method, but that of 73 h cannot.

SiO₂ thickness returned to the initial value after every heating. Carbon contamination adsorbed in 3000 min can be easily removed with this method. But small amount of carbon might remain on the surface because the contact angle after the heating did not return to the initial value as comparing Fig. 1 with Fig. 2. On the other hand, the amount of carbon of specimens kept in the CR for 7 months was about 3 to 5 at%. Amount of carbon contamination increases slowly for a very long time as is seen in Fig. 3.

On the other hand, Table 1 shows that a specimen kept in the CR for 7 months was not cleaned with the H.P. heating, neither with heating in oxygen at 500°C for 11 min. This indicates that the carbon contamination becomes more stable and difficult to remove with time.

The H.P. heating is useful for only contaminations of week adsorption. Heating in O₂ is more effective than the H.P. heating but not perfect.

Table 1 The effect of heating on carbon-contamination reduction.

No.	Treatment	Amount of carbon(at%)
(1)	before heating	2.9
(2)	200°C in the air	2.1
(3)	500°C in O ₂ for 11 min	1.3

(1) was a specimen kept in the CR for 7 months.

3.2.2 Dipping in ultra clean water

Fig. 6 shows change in amount of carbon contamination with time of dipping in water. One specimen was held in the CR atmosphere for 17 h before dipping in water (square). The other was held in the CR for 73 h before dipping (circle). Although the carbon amount of the 17-h sample simply decreased with time, that of the 73-h one showed almost the same value as at the start of the dipping. The carbon contamination adsorbed for a short time can be removed with this method. But the carbon contamination adsorbed for a long time cannot be removed with this method. This also indicates that the carbon contamination becomes more stable and difficult to remove with time. Dipping in water can be a good storage method for specimen.

3.2.3 Ozone-water dipping

Fig. 7 shows the effect of dipping in ozone water for 2 h. The amount of carbon of 9.7 at% before the dipping shows that some contamination occurred during the experiment. The ozone-water dipping reduced the amount of carbon down to 0.6 at%. Ozone-water dipping can remove carbon contamination adsorbed on the surface.

3.2.4 UV-ozone cleaning

This method is quite effective to remove carbon contamination on SiO₂ surface. An amount of carbon after a few minute cleaning for a sample kept in the CR for 7 months was 0.2 at% which was an inevitable contamination during the transportation and the setting for measurement. The thickness of SiO₂ did not change.

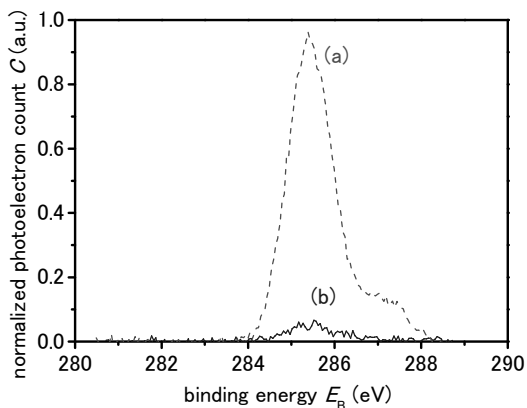


Fig. 7 Effect of dipping in ozone water.
(a) before dipping, (b) after dipping in ozone water for 2 h.

4. Conclusions

We investigated the relationship between contact angle and carbon contamination on SiO₂ thin film.

Contact angles were sensitive to the surface condition and the degree of contamination and can be a very useful criterion for a judgment of the effect in practical cleaning processes. We also examined the effects of some cleaning methods, heating in the air or in O₂, dipping in water, dipping in ozone water, and UV-ozone cleaning. The UV-ozone cleaning is the most effective one in removal of carbon contamination. The other methods worked well in some limited conditions.

5. References

- [1] Akira Kurokawa, Kenji Odaka, Hidehiko Nonaka, Ken Nakamura, Toshiyuki Fujimoto, and Shingo Ichimura; Thickness Stability of Silicon Dioxide Film with Water Immersion; ECASIA'05 abstract, p184 (2005).