A Practical Procedure for Surface Protection of a Bulk Specimen in the Air

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We propose the Same Surface Contact Method (SSCM) that is useful to protect the surface of a specimen against contamination and oxidation in the air. The contamination and the oxidization of the surfaces of Fe-Si-Al films were investigated by X-ray photoelectron spectroscopy (XPS). Surface oxidation gradually proceeded in the air, while the increase in surface contamination was restrained for a long time in the air by SSCM. It was also found that the surfaces could be protected against oxidization in the nitrogen atmosphere.

1. Introduction

A specimen surface is contaminated and oxidized by exposing it to the air. In order to obtain information for a clean surface, it is necessary to allow specimen insertion into a spectrometer without atmospheric contact or with a short time exposure to the air [1].

However, in some cases, the measurement location and the specimen preparation location are remote from each other. Furthermore, it is not always possible to measure surface properties immediately after a specimen preparation. Therefore, a practical method for the surface protection from contamination and oxidation is strongly required [2].

In general, aluminum foil, wrapping paper, a plastic case or a dry box has been used for the surface protection. But when surfaces of aluminum foil and wrapping paper are already contaminated, contaminants are transferred to specimen surfaces. As for the packing method with aluminum foil or wrapping paper, it is difficult with these methods to protect the surface from contamination. Contaminants increase and surface oxidation is induced during long-term storage. The storage with a plastic case gives rise to secondary contamination due to a chemical admixture or gas from materials. Above methods are not enough for preventing the specimen surface from contamination and oxidation.

Consequently, we propose the Same Surface Contact Method (SSCM) that is useful to conserve the surface condition and prevent oxidation in the air.

In this paper, at first, we report the changes of surface conditions on Ta films as a function of the exposed time to the air by contact angle measurement. The SSCM effects for specimen surface protection are reported based on the changes of surface conditions of Fe-Si-Al films exposed long-term in the ambient atmosphere by X-ray photoelectron spectroscopy (XPS).

2. Experimental

Two kinds of specimens of RF sputtered Ta and Fe-Si-Al films on a glass substrate were used. The contact angle of water was measured with model FACE CA-D (Kyowa Kaimen Kagaku, Japan). XPS spectra were recorded at 2×10^{-8} Pa base pressure with Axis-HSX (Simadzu-Kratos) using Mg Kα (1253 eV) X-ray radiation, with the instrument resolution of 0.98 eV as the full width at half maximum of Ag $3d_{5/2}$ spectrum.

The scheme of SSCM is shown in Fig.1. We prepared two specimens whose surface conditions were the same. The specimen surfaces were contacted with each other and the edges of the contacted specimens, shown in Fig.1, were sealed by non-adhesive polytetrafluoroethylene (PTFE) sealing tape.

This tape is sold commercially for pipe sealing. It has excellent properties for sealing, cleanness and flexibility.

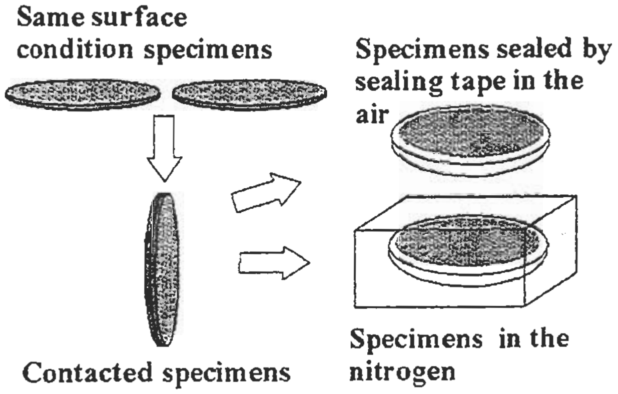

Figure 1. The schematic procedure of the Same Surface Contact Method (SSCM).

3. Results

Generally, contact angle between liquid droplet and solid phases is sensitive to the changes of surface condition, and angle reflects the surface free energy.

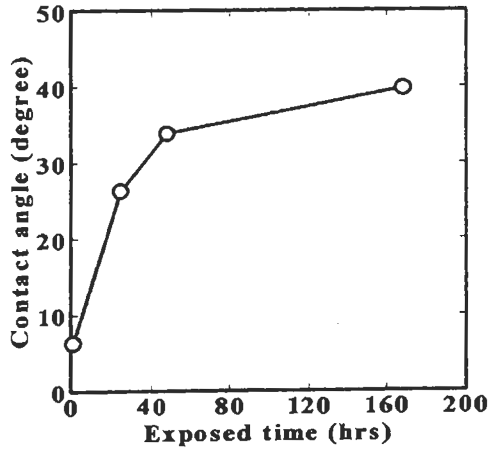

Figure 2. The dependence of contact angle of water on Ta thin film surfaces to the exposed time in the air.

Fig.2 shows the dependence of contact angles of water on the Ta thin film surfaces to the exposed time in the air. The contact angle of water increases with increasing exposed time in the air. The result indicates increasing adsorbate such as contamination to the specimen surfaces.

It showed a sharp change of contact angle of water within 24 hours. Hence, for getting true surface information, it is necessary to protect the specimen surface immediately against contamination.

Table 1. Specimen information.

	SSCM	atmosphere	time
A	Use	Air	1 day
B	Use	Nitrogen	30 days
C	Use	Air	30 days
D	Non-use	Nitrogen	30 days
E	Non-use	Air	30 days

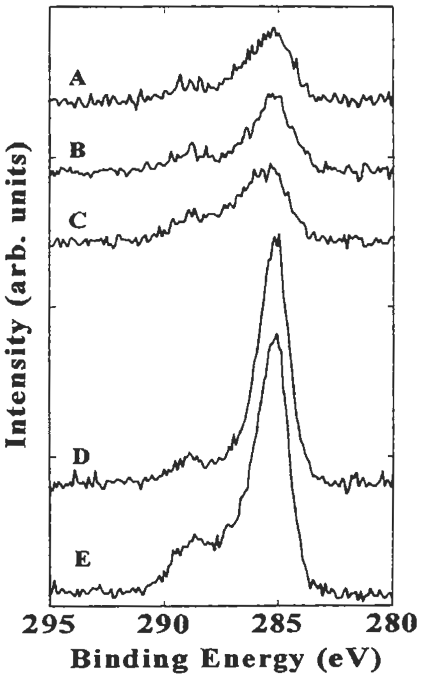

Figure 3. C 1s spectra of each specimen. A is as-deposited Fe-Si-Al thin film. B and C are the specimens maintained with SSCM for 30 days in the nitrogen and the air, respectively. D and E are the specimens maintained without SSCM for 30 days in the nitrogen and the air, respectively.

The specimens used are summarized in Table 1. In this experiment, as SSCM was carried out in the air, all specimen initial surfaces were given rise to increase contamination and oxidation. The XPS spectra for the specimens listed in Table 1 are presented in Fig. 3 (C 1s region), Fig. 5 (Fe 2p region), Fig. 6 (Si 2p region) and Fig. 7 (Al 2p region).

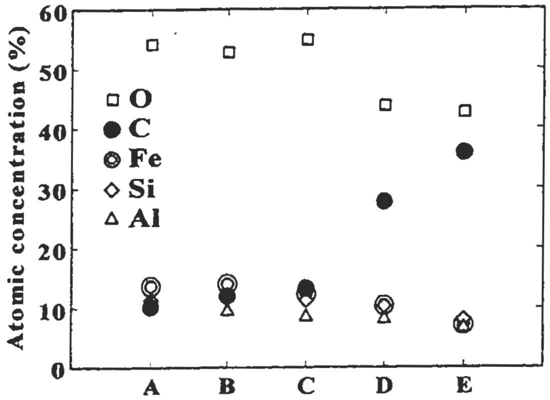

Figure 4. Surface composition of each specimen. A is as-deposited Fe-Si-Al thin film. B and C are the specimens maintained with SSCM for 30 days in the nitrogen and the air, respectively. D and E are the specimens maintained without SSCM for 30 days in the nitrogen and the air, respectively.

Figure 4 shows the surface composition of the specimens listed in Table1. Mean surface compositions were calculated by dividing the recorded C 1s, O 1s, Fe 2p, Si 2p, and Al 2p signal intensities by the appropriate spectrometer sensitivity factors. It can be seen that the as-deposited specimen (specimen A), which was maintained with SSCM for one day in the air, has the lowest carbon (●) concentration. Even after 30 days, a distinguished change in the surface composition was not detected (specimen C). The carbon concentration in the nitrogen (specimen B) and the air (specimen C) were similar. It was found that SSCM was able to protect the specimen surface from increasing carbon contamination. After 30 days without SSCM, carbon concentration increased in the nitrogen (specimen D) and the air (specimen E). The change of carbon concentration for specimen E is larger than that of specimen D. The increasing main carbon peak could be assigned to hydrocarbon.

The oxygen concentration of specimen D and specimen E decreased due to the covering hydrocarbon. Therefore, we were not able to evaluate the change of surface oxidization from surface composition of each specimen. Thus, the change of surface oxidization has been investigated by means of a peak shift on Fe, Si and Al spectra.

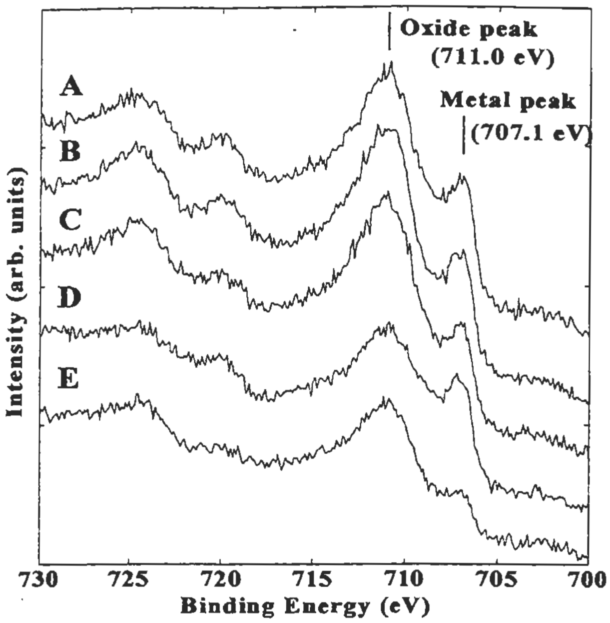

Figure 5. Fe 2p spectra of each specimen. A is as-deposited Fe-Si-Al thin film. B and D are the specimens maintained with and without SSCM for 30 days in the nitrogen, respectively. C and E are the specimens maintained with and without SSCM for 30 days in the air, respectively.

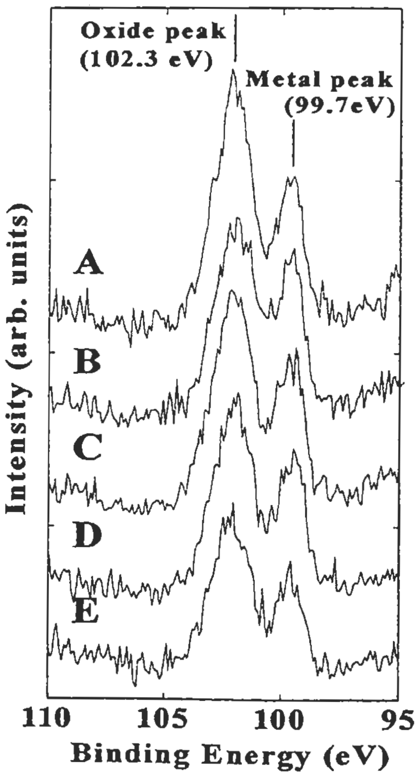

Figure 6. Si 2p spectra of each specimen. A is as-deposited Fe-Si-Al thin film. B and D are the specimens maintained with and without SSCM for 30 days in the nitrogen, respectively. C and E are the specimens maintained with and without SSCM for 30 days in the air, respectively.

Figure 5 shows the Fe 2p spectra of each specimen. The oxide peak and the metal peak are positioned at approximately 711 and 707 eV, respectively. Similarly, in the Si 2p and Al 2p spectra one could observe a chemical shift at a higher energy position from the metal peak, clearly indicating that more than surface oxidization is present on the specimen surface.

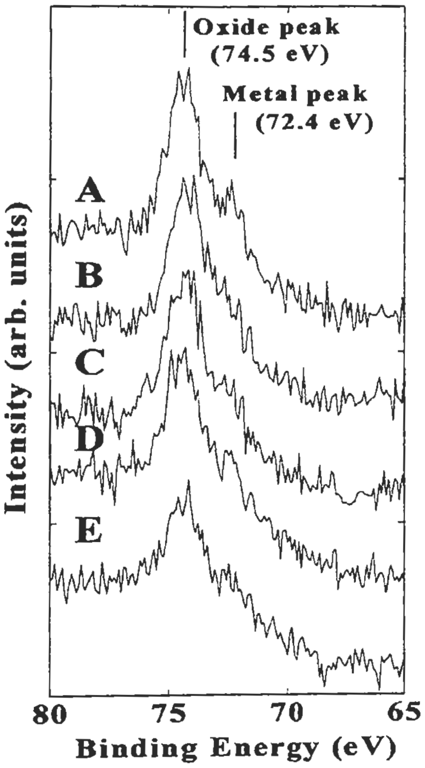

Figure 7. Al 2p spectra of each specimen. A is as-deposited Fe-Si-Al thin film. B and D are the specimens maintained with and without SSCM for 30 days in the nitrogen, respectively. C and E are the specimens maintained with and without SSCM for 30 days in the air, respectively.

Intensity ratios of oxide and metal peaks for Fe 2p, Si 2p and Al 2p spectra, respectively, are shown in figure 8. The increasing oxidization of iron was remarkable. The surfaces of the specimens protected in the nitrogen were less oxidized, independent of using SSCM (see specimen B and D). The intensity ratio for specimen C was smaller than specimen E. By using SSCM, it was indicated that the oxidization in the air had been delayed.

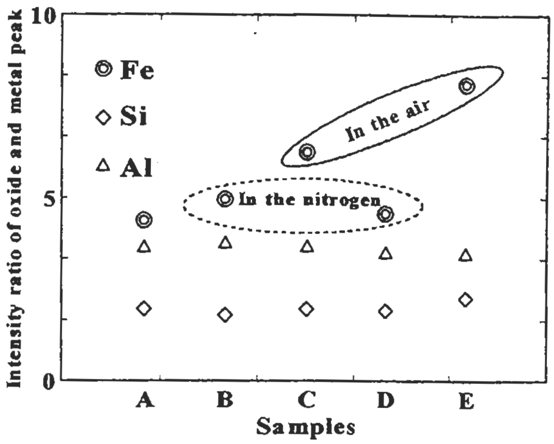

Figure 8. Intensity ratios of oxide and metal peak For Fe 2p, Si 2p and Al 2p spectra, respectively.

4. Conclusions

SSCM is practical, convenient, easy and useful procedure. We confirmed that increasing surface contamination in the air was prevented for at least 30 days by means of SSCM. A surface oxidization could not be prevented for long-term storage in the air. However, we have indicated that surface contamination and oxidization could be minimized by means of SSCM and storage in the nitrogen.

Furthermore, SSCM and vacuum packaging would have potentially possibilities for long-term storage.

5. References

[1] J. C. Riviere, in Practical Surface Analysis, second edition, Vol.1, ed. by D. Briggs and M. P. Seah, Chapt.2, pp.36 - 40, John Wiley & Sons, Chichester (1990).

[2] K. Doumae, X-ray photoelectron spectroscopy, ed. by the Surface Science Society of Japan, Chapt.4, pp.51 - 54, Maruzen (1998). (in Japanese)