Comparison of XPS Spectra of Inorganic Materials with Various Kinds of Pre-treatment Methods

N. Fukumoto, B. Q. Li, and I. Kojima

*National Institute of Materials and Chemical Research
Higashi 1-1, Tsukuba, Ibaraki 305-8565, JAPAN*

Comparison of fine structures of X-ray photoelectron spectroscopy (XPS) spectra obtained by several different pre-treatment methods was carried out. Even though argon ion sputtering is quite effective in removing contamination elements, it generally causes increase of peaks widths. Fracture of the specimen in vacuum chamber also was tested, but sometimes the atomic composition at fractured surface is different from that of bulk body presumably due to elemental segregation. Scratching sample in vacuum chamber showed good result for a specific case. From the results of various kinds of samples, the necessity of choosing appropriate method for each material was demonstrated.

1.   Introduction

In order to create a comprehensive database of physical parameters concerning generation of photoelectron or Auger electron by X-ray or electron beam, electron spectra of various materials in ideal condition (without contamination and other disturbances) have to be obtained. Contaminants on top of the sample surface have to be removed without disturbing the elemental composition and chemical state of the sample to obtain high quality electron spectra, which meet this requirement. It also is important to avoid contamination of pre-treated surface before or during the acquisition of the spectra. In this paper, the authors compared X-ray photoelectron spectroscopy (XPS) spectra of several inorganic compounds with various kinds of pre-treatment techniques.

2.   Experimental

The XPS measurement was carried out by an ESCALAB 220iXL (VG Scientific) type spectrometer and the monochromatic X-ray source (Al Kα) was used. The spectrometer is equipped with the R2P3 type pre-treatment chamber, which has several extra ports to connect additional chambers. A pre-treatment chamber with a diamond file and a tool for breaking samples in ultra high vacuum (UHV) environment was developed and used for this study. The entire system was kept in UHV in the order of 10^{-7}-10^{-8} Pa and the treated specimen can be carried to the analysis chamber without taking out of UHV. The schematic diagram of the spectrometer and the pre-treatment chamber is shown in Fig. 1.

Firstly, the influence of argon ion sputtering to XPS spectra was examined. Even though this technique is quite effective in removing surface contaminants and widely used for surface cleaning, it has been reported that there are several problems [1-2] such as selective sputtering and increase of peak widths, which means change of chemical states of the elements. These effects are often of significant problem in obtaining high quality XPS spectra of compounds. XPS spectra for several kinds of inorganic compounds before and after ion sputtering were observed and changes in FWHM's were examined.

Secondly, creating a fresh surface by fracturing the sample was attempted. As a fracturing tool operable in UHV was not ready at that time, the sample was fractured in a globe box filled with pure-nitrogen gas and enclosed in a vacuum tight transfer vessel. The transfer vessel was connected to the R2P3 chamber of the spectrometer and evacuated to UHV. Then the gate valve was opened and the sample was introduced into the analysis chamber without exposing to the atmosphere. Even though exposure to the atmosphere was avoided, the nitrogen gas was not clean enough to avoid carbon contamination at the fractured surface and this result showed the necessity of fracturing tool operable in the UHV chamber.

Scribing the surface of the sample is another option to create fresh surface of bulk solid sample. A diamond file was attached on top of a manipulation bar operable from outside the vacuum chamber. The scribed surface of ZnO was found to be very clean (virtually no carbon was detected for this case) and no significant change in Zn/O ratio was found. On the other hand, in case of Si₃N₄, the Si/N ratio for scribed surface was somewhat different from that of sputtered surface.

Detailed discussion of these results is shown in the next section.

5. Results and Discussion

The comparison of FWHM's of XPS peak for sevaral inorganic compounds such as SiO_2 and SiC, before and after ion sputtering is shown in Table 1. In both cases, the FWHM's of both elements showed slight increase. It is generally recognized the increase of FWHM's like thismeans creation of compounds of different chemical states mainly due to
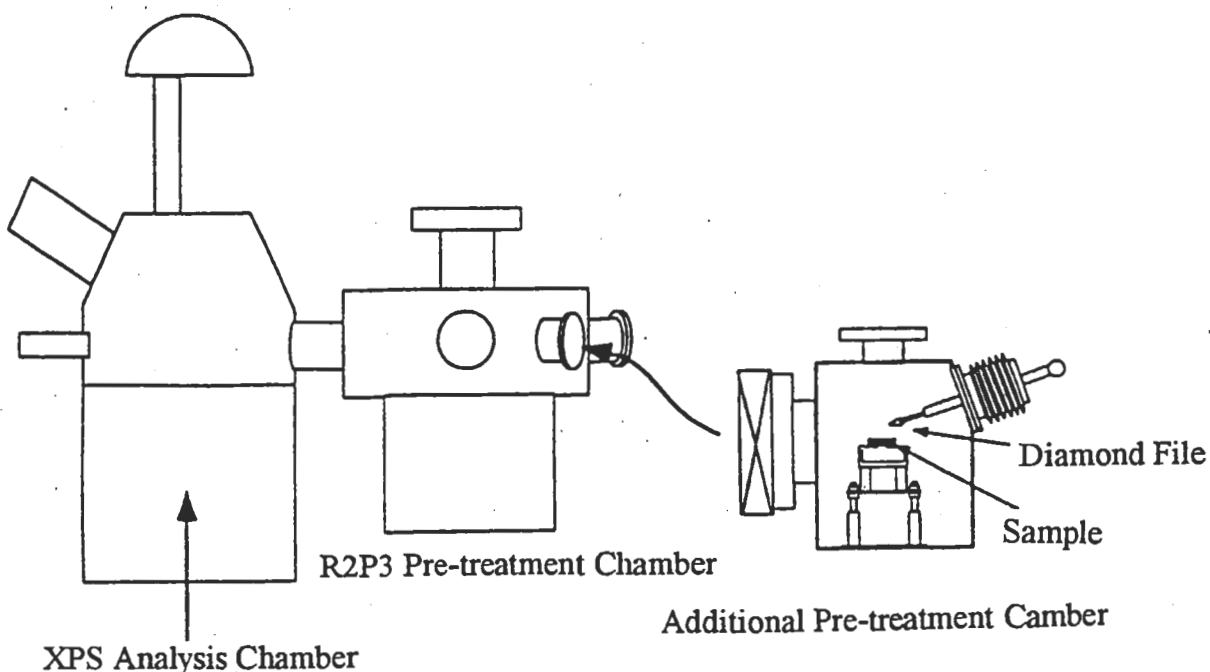
Fig. 1 A schematic diagram of the XPS spectrometer and the sample pre-treatment attachment.

Table 1 The comparison of FWHM's of XPS peak for several inorganic materials before and after ion sputtering.

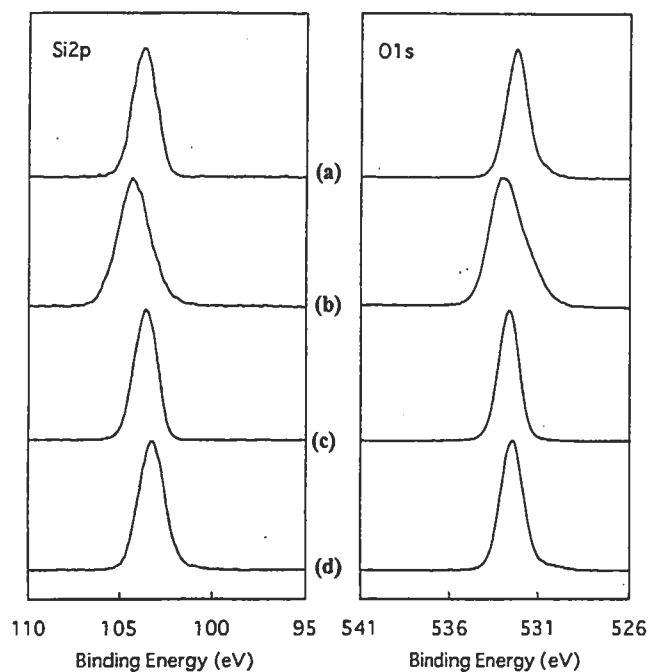| Compounds	SiC	SiO2	ZnO	CdO	Si3N4
XPS Transition	Si2p	Si2p	Zn2p	Cd3d	Si2p
FWHM Before Sputtering / eV	1.10	1.35	1.56	1.12	0.50
FWHM After Sputtering / eV	1.50	1.87	1.67	1.30	0.71

Fig. 2 The comparison of Si2p and O1s XPS spectra of SiO₂ with various pre-treatment methods. **(a)**:untreated, **(b)**:sputtered, **(c)**:fractured in the air, **(d)**: fractured in a nitrogen-filled globe box.
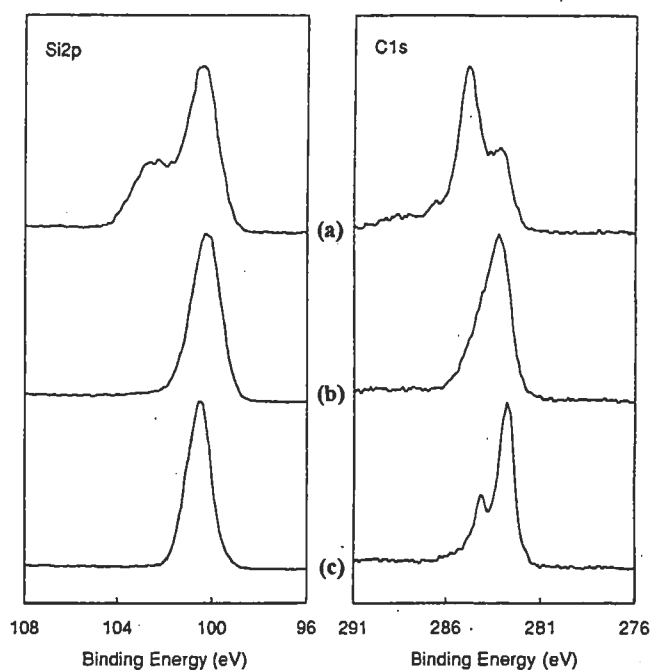

Fig. 3 The comparison of Si2p and C1s XPS spectra of SiC with various pre-treatment methods. **(a)**:untreated, **(b)**: sputtered, **(c)**: scribed in UHV.

Table 2 The value of Si/O ratio calculated from the peak areas and amount of carbon in each sample shown in **Fig. 2**.

	Si/O	C
Untreated	2.33	30%
Sputtered	2.07	7%
Fractured(in the air)	2.17	4%
Fractured(in nitrogen)	2.24	5%

Table 3 The value of Si/C ratio calculated from the peak areas and amount of oxgen in each sample shown in **Fig. 3**.

	Si/C	O
Untreated	0.41	25%
Sputtered	0.76	3%
Scribed in UHV	0.75	1%

partial oxidization or reduction. As argon ion acts as reductant, non-stoichiometric ststes such as SiO_{2-x} or SiC_{1-x} could be created.

The XPS spectra of SiO_2 fractured in N_2 filled box and transferred to the spectrometer showed the existence of carbon. The amount of carbon on top of the sample was estimated to be approximately 5% in atomic concentration. In case of the XPS spectra of the sample fractured in UHV, this kind of carbon contamination was not found.

From the result of samples scribed in UHV environment, both the carbon concentration in ZnO and oxygen concentration in SiC was found to be approximately 1%. On the other hand, in case of Si_3N_4 scribed in the UHV chamber, the atomic ratio of Si/N did not match the value of sputtered or fractured sample. Even though the reason of is discrepancy is not clear yet, the change of chemical composition at the scribed surface due to plastic flow is one possible explanation.

The comparison of Si2p and O1s XPS spectra of SiO_2 with various pre-treatment methods (a: untreated, b: sputtered, c: fractured in air, d: fractured in nitrogen) are shown in Fig.2. The value of Si/O ratio calculated from the peak areas and amount of carbon in each sample are shown in Table 2. The widths of both Si2p and O1s peak for sputtered sample was considerably greater than those of fractured ones.

The comparison of Si2p and C1s XPS spectra of SiC with various pre-treatment methods (a: untreated, b: sputtered, c: scribed in UHV) are shown in Fig. 3. The values of Si/C ratio calculated from the peak oreas and amount of oxygen in each sample are shown in Table 3. In the C1s spectra of the scribed sample, there seems to be two various spices of carbon, one larger peak with lower binding energy for carbon from SiC and the other smaller peak with higher binding energy presumably due to contamination. As the two peaks are separated far enough, this second component could be removed by peak separation procedure. After numerically removing this contaminant component, the Si/C ratio of 1.0 was obtained.

4. Concluding remarks

From the results of this study, the following conclusions were obtained.

1) Argon ion sputtering is quite effective in removing contaminants. However it quite often causes increase in peak widths and is not appropriate as a pre-treatment method for precise spectrum observation.

2) Fracturing or scribing the sample are effective methods to obtain clean surface without disturbing the chemical states of the elements in various kinds of inorganic materials. In applying these techniques, attention should be paid to examine if changes in elemental composition are occurring.

3) Numerical peak separation also is useful to remove the influence of residual contaminants in some cases.

References
[1] A. Kurokawa J. Surf. Anal. 3, 653 (1997)
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