BL-27A/2014G553

Chemical-state Analysis of Ultra-trace Amount of Cesium Adsorbed on Oxide Surface by Total Reflection X-ray Photoelectron Spectroscopy

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1 Introduction

Radioactive cesium (^{137}Cs or ^{134}Cs), once trapped in minerals such as clay and soil, is hard to be released. Recent spectroscopic measurements have shown that cesium at a specific site in minerals is strongly bound [1]. It should be noted that the number of cesium atoms in radioactive cesium is extremely small compared with that observed by spectroscopic methods. Since the chemical behavior of such ultra-trace amount of elements is sometimes quite different from that of macro-quantity, it is important to clarify the chemical states of ultra-trace amount of cesium adsorbed on mineral surfaces in order to know why radioactive cesium is hard to be released. In this report, we demonstrate that chemical states of ultra-trace amount of cesium on oxides can be measured by total reflection X-ray photoelectron spectroscopy (TR-XPS) [2].

2 Experiment

The oxide samples used were silicon dioxide, which was made by oxidizing Si(001) single crystal at 1000ºC for 2 hours. The SiO_2 substrate was immersed in 10 mM cesium chloride solution for two days, and dried in atmosphere. Measurements were performed at the BL-27A. For normal XPS measurements, the X-rays were irradiated at 35º from the surface. For TR-XPS, the incident X-rays were irradiated at 0.2º that is lower than the critical angle of total reflection.

3 Results and Discussion

Figure 1 shows wide-scan XP spectra for clean surface of SiO_2 irradiated by two incident angles. For 0.2º incidence (TR-mode), the background around 720 eV, where Cs 3*d* peak is located, reduced less than 1/10 compared with that for 35º incidence. This is because the incident X-rays were totally reflected, so the amount of inelastically scattered electrons produced by O 1*s* photoelectron emission fairly decreased.

Spectrum (a) of Fig. 2 shows the narrow-scan TR-XPS in Cs 3*d* region for Cs-adsorbed SiO_2. Next, the Cs-adsorbed sample was rinsed by ultrasonic cleaning in water for 15 min. The spectrum for the sample after rinsing is shown (b). Before rinsing, the energy of the Cs $3d_{5/2}$ peak is located at 725.5 eV, which is close to the reported value for cesium oxide [3]. The $3d_{5/2}$ peak energy was almost constant irrespective of the adsorption condition. After rinsing, the intensity of Cs $3d_{5/2}$ fairly decreased but a small peak is still seen. Thickness of this sample estimated from XPS peak intensities was about 4.4 pm, which corresponds to 2.2×10^{-3} layers. The amount of cesium in this layer is only about 205 pg·cm^{-2}. This weight corresponds to about 400 Bq ^{137}Cs. Thus it is demonstrated that ultra-trace amount of cesium comparative to radioactive ^{137}Cs level can be detected by TR-XPS.

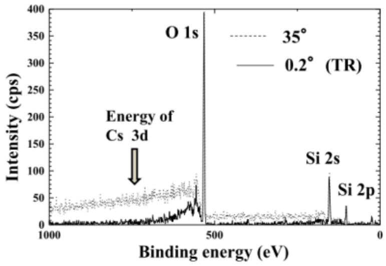

Fig. 1: Wide-scan XP spectra for clean surface of SiO_2 irradiated by two incident angles (35º and 0.2º).

As to the chemical states, the Cs $3d_{5/2}$ peak of spectrum (b) shifted by 0.7 eV to higher binding energy compared to that of spectrum (a). It was reported that in contrast to most of metals, the higher the polarization of Cs-X (X: anion) bond is, the lower the Cs binding energy becomes [4]. Thus the Cs-O bonds remaining after rinsing is less polarized than those before rinsing. This suggests that the ultra-trace amount of cesium is covalently bonded with oxygen rather than ionically bonded.

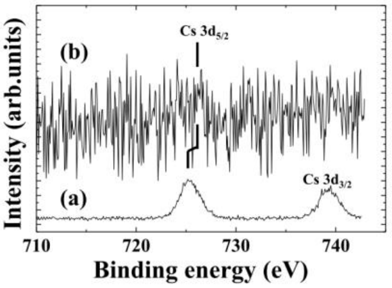

Fig. 2: Narrow-scan TR-XP spectra for SiO_2 in Cs 3d region. (a) Cs was adsorbed by solution method. (b) Cs-adsorbed sample was rinsed by ultrasonic cleaning.

References

[1] C. Benjamin *et al.* Environ. Sci. Technol. **36**, 2670 (2002).
[2] J. Kawai, J. Electron. Spectrosc. Relat. Phenom. **178-179**, 268 (2010).
[3] M. Ayyoob, M.S. Hegde, Surf. Sci. **133**, 516 (1983).
[4] E.A. Podgornov *et al.* J. Mol. Catal. A: Chemical **158**, 337 (2000).

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