

Chemical States of Trace-level Strontium Adsorbed on Layered Oxide by XPS and XANES under Total Reflection Condition

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1 Introduction

The behavior of hazardous radionuclides released into the environment as a result of accident of a nuclear power plant or a nuclear weapon test is of considerable worldwide concern. Among these nuclides, ⁹⁰Sr which emits β -rays with a half-life of 28.8 years is one of the most hazardous radionuclides, because it has a property to be strongly retained in living organisms, mainly in the bones [1]. It has been elucidated that clay minerals present a high sorption capability for strontium [2]. In order to clarify the behavior of Sr in environment, the adsorption states of strontium in clay minerals is of great importance. The chemical states of Sr in clay minerals have been investigated by EXAFS [3] and X-ray absorption spectroscopy [4]. However, it should be noted that the number of atoms in radioactive ⁹⁰Sr is extremely small compared with that in non-radioactive strontium. The chemical property of such trace-level element is in many cases different from that of macro quantity. In this report, chemical states of Sr adsorbed on a layered oxide (mica), which is the main trapping site of Sr in clay, have been investigated by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) spectroscopy. In order to observe trace-level Sr, XPS and XANES were measured under total reflection condition of incident X-rays.

2 Experimental

The mica used was a single crystal of artificially synthesized phlogopite. The chemical composition of the mica was $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$. Sr was adsorbed on mica by immersing it in $20 \text{ mmol} \cdot \text{dm}^{-3}$ strontium nitrate solution. In order to simulate the decontamination procedure, Sr-adsorbed mica was washed by various procedures such as splashing water and immersing in water.

The XPS and XANES were measured at the BL-27A station. For normal XPS, the X-rays were irradiated at 35° from the surface and the take-off direction of the photoelectrons was surface normal. In the TR-XPS mode, the incident X-rays were irradiated at 0.2° from the surface which is smaller than the critical angle of the total reflection at 3 keV photons (0.65°). The take-off direction of photoelectrons in TR-XPS was surface normal. In the TR-XANES measurements, the angle of the incident X-rays was 0.2° from the surface. TR-XANES spectra were measured by plotting a sample drain current as a function of the photon energy (total-electron-yield mode).

3 Results and Discussion

Fig. 1 shows the XPS wide-scan spectra of Sr-adsorbed mica for two incident X-ray angles. The background in the TR-XPS around 2000 eV where Sr $2p$ peak is located is reduced to less than one-tenth of that in normal XPS. This is because the inelastically scattered electrons from the bulk due to the Si $1s$ photoelectron emission disappear in TR mode. Owing to the background reduction and the

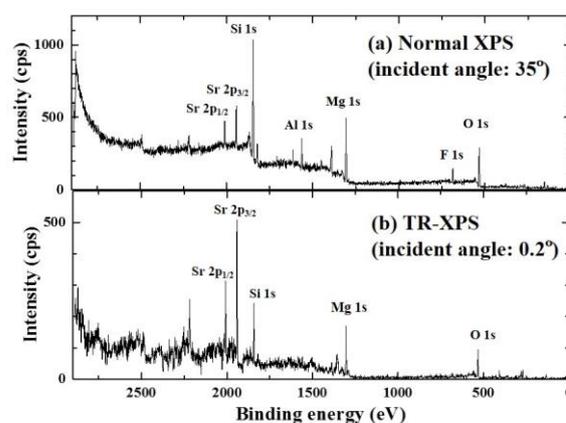


Fig. 1: XPS wide scan spectra of Sr-adsorbed mica for two X-ray incidence angles. Photon energy was 3000 eV.

enhancement of the Sr $2p_{3/2}$ peak in TR-XPS, we could observe ultra-thin layer down to 0.004 nm. This thickness corresponds to $150 \text{ pg} \cdot \text{cm}^{-2}$ ($1.03 \times 10^{12} \text{ atoms} \cdot \text{cm}^{-2}$). If all of the Sr is composed of ⁹⁰Sr, this weight corresponds to about 300 Bq of ⁹⁰Sr.

Fig. 2 shows the TR-XPS narrow scans in Sr $2p_{3/2}$ region for Sr-adsorbed mica with various thickness. From the intensity of the Sr $2p_{3/2}$ and Si $1s$ peaks, we can estimate the averaged thickness of adsorbed layer which is shown in each spectrum. On the right of Fig. 2 displays the Sr $2p_{3/2}$ peak energy as a function of the thickness. When the logarithmic scale is set on the thickness, the Sr $2p_{3/2}$ peak energy decreases almost in proportion to the decrease in the thickness.

On the left of Fig. 3 shows TR-XANES spectra at the Sr L_3 -edge for Sr-adsorbed mica with various thickness. The thickness of the strontium layer is indicated in each spectrum. In all spectra, sharp resonance peaks are observed around 1943 eV. Based on the probabilities of dipole allowed transitions, the main peaks can be identified as the resonance excitations from the Sr $2p_{3/2}$ ground states to the valence unoccupied $4d^*$ states [5]. On the right of Fig. 3, the resonance peak energy is plotted as a function

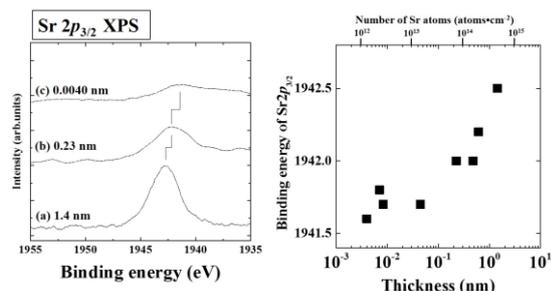


Fig. 2: Left figure shows the TR-XPS narrow scan spectra in Sr $2p_{3/2}$ region for Sr-adsorbed mica. Thickness of the strontium layer is indicated in each spectrum. Right figure displays the relation between the layer thickness and the binding energy of Sr $2p_{3/2}$ line.

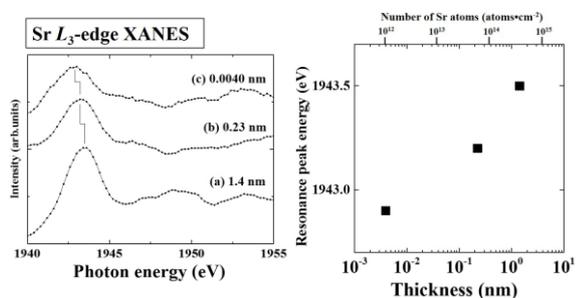


Fig. 3: Left figure shows the Sr L_3 -edge TR-XANES spectra for Sr-adsorbed mica. Thickness of the strontium layer is indicated in each spectrum. Right figure displays the relation between the layer thickness and the resonance peak energy.

of the thickness. Similar to the Sr $2p_{3/2}$ peak in XPS, the resonance peak energy decreases almost in proportion to the decrease in the thickness.

For XPS, a chemical shift of core-level binding energy is caused by various factors such as charge transfer within a simple point-charge, the long-range electrostatic interactions (Madelung potential), and final-state contributions due to extra-atomic relaxation of the core-hole (screening effect). But the contributions of the latter two factors are negligible in the present experiments because thin films less than monolayer were measured (Madelung potential can be ignored) and the insulating substrates were used (screening effect is negligible). Thus, we will qualitatively discuss the origin of the observed binding-energy shifts on the basis of the charge transfer within a simple point-charge.

When we consider a compound M-X (M: metal, X: anion), the higher the polarization of an M-X bond is, the higher the core-level energy of M becomes. In other words, when the δ value in $M^{\delta+}-X^{\delta-}$ bond becomes large, the core-level of M shifts to higher energy side. This tendency is generally observed in most of the metals. However, this general tendency does not hold for some of alkali metals and alkali-earth metals. Strontium compounds show the

reverse tendency to the most of the other metal compounds. Vasquez has measured Sr $3d_{5/2}$ -XPS spectra for various strontium compounds, and has shown that the higher the polarization of a Sr-X bond is, the lower the Sr $3d_{5/2}$ energy becomes [6]. For example, the energy of Sr $3d_{5/2}$ core-level is in the order of $SrI_2 > SrBr_2, SrCl_2 > SrF_2$ [6]. Also it was reported that energy of Sr $3d_{5/2}$ core-level energy decreases on going from Sr-O to Sr-F [7]. Considering the difference in the tendency of the energy shifts between general metals and strontium as discussed above, it is deduced that the chemical bond between trace level strontium and mica is more polarized than that for thick layer. This means that the ultra-trace amount of strontium adsorbed on mica is more ionically bonded with the substrate compared with the thicker layer.

These speculations are supported by the peak energy shift in the XANES spectra (Fig. 3). The main peak assigned as Sr $2p_{3/2} \rightarrow 4d^*$ resonance shifts to lower energy side with the decrease in the thickness, which is similar to the Sr $3d_{5/2}$ core-level shift in XPS. But it should be noted that the energy shift of resonance peak in XANES spectra is caused by those of both Sr $2p_{3/2}$ (initial) and $4d^*$ (final) states. As to this point, we consider the resonance energy shift in the XANES spectra is mainly caused by the Sr $2p_{3/2}$ energy shift, in comparison with the 3d transition-metal compounds where the direction and absolute value of the $2p_{3/2} \rightarrow 3d^*$ resonance energy shift in XANES is similar to that of $2p_{3/2}$ in XPS [8]. Also it was reported that the Ti $2p$ level in titanium oxides is more sensitive to the chemical environment than Ti $3d^*$ levels [9]. On the basis of these speculations, the energy shift in Fig. 3 similar to that in XPS supports that the chemical bond between trace level strontium and mica is more polarized than that for thick layer.

Although more detailed analysis of the chemical bonding states is needed from both experimental and theoretical viewpoints, it is suggested that the ionically bonded state of ultra-trace amount of strontium with mica is one of the reasons that the radioactive strontium is hard to be released from clay minerals.

References

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