VUV light induced valence degeneration in Sm over-layer on HOPG

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1. ABSTRACT
Systematic investigation of the influence of vacuum ultraviolet (VUV) irradiation on the valence degeneration in a Sm over-layer on a HOPG substrate was performed using in-situ photoemission spectroscopy (XPS, UPS, and ARPES) for the Sm coverage regime of 0.05–3.6 Å. This investigation confirmed that VUV irradiation-induced degeneration of divalent Sm exerts a more profound effect than Sm contamination during photoemission spectroscopy even under UHV. We found that the charge transfer occurs mainly from divalent Sm to the HOPG surface.

2. INTRODUCTION
Sm may be of particular interest from a fundamental point of view given that it may coexist in two different isoenergetic states: the free atomic Sm is a divalent configuration of \(4f^6(6s)^2\), whereas metallic Sm is a trivalent configuration of \(4f^5(6s5d)^3\). Generally, the formation of the trivalent state (Sm\(^{3+}\)) is roughly interpreted as being due to gain in the cohesive energy in the bulk, leading to promotion of the 4f electron to the 5d valence band. An advanced interpretation of this valence transition presented by Strange et al. using DFT calculations employing CIS affirmed that there are two types of 4f electrons; some of the 4f electrons were declared to be valent whereas the others remain localized [1]. However, Yakovkin affirmed that Sm\(^{3+}\) could not be represented as a pure ground state in the framework of the DFT calculation [2]. Evaluation of a number of systems consisting of a Sm over-layer deposited onto various substrates such as GaN, Ta, Pt, Fe, Al, Au, and amorphous C have indicated that the divalent state (Sm\(^{2+}\)) of the low-coverage Sm overlayer is strongly dependent on the substrate [3]. Due to a lack of experimental data, a means of preventing the valence fluctuation of Sm by isolation from the substrate has been not fully developed. Thus, the nature of the valence transition has not been fully understood. In order to minimize the formation of an interface alloy between Sm and the substrate, a highly oriented pyrolytic graphite (HOPG) was selected as the substrate, since the inertness of the HOPG surface may offset the sensitivity of the valence states of Sm to relatively small changes in the chemical environment [4], and the metallic properties of HOPG enable electron spectroscopy and microscopy experiments without the problem of surface charging. In general, photoemission spectroscopy (PES) serves as a useful tool for investigating the valence fluctuations by irradiating the sample with photons of various energies. However, whether the photon beam itself directly affects onto the valence transition or not, that has not been questioned. In an earlier work, we reported the coverage-dependence of the valence state of the Sm overlayer in the coverage regime of 0.3–10 Å [5]. To provide further experimental information regarding the nature of the valence transition of Sm, the current study focuses on the valence transition of a low-coverage Sm overlayer, and demonstrates the influence of vacuum ultraviolet (VUV) irradiation on the degeneration of Sm\(^{2+}\) in detail by utilizing photoemission spectroscopy (ARPES, XPS). The data suggest that the effect of the VUV irradiation on the variation of the Sm valence state must be considered for a quantitative evaluation of the valence state based on the PES. Generally, the Sm\(^{2+}\) state tends to be underestimated, while the Sm\(^{3+}\) state is overestimated.

3. EXPERIMENTAL
In-situ photoemission spectroscopy has been performed for Sm over-layer on HOPG (Sm/HOPG) in the coverage regime of 0.05-3.6 Å. The Valence band spectra of Sm were investigated in detail by utilizing UPS and ARPES for the coverage lower than 1.0 Å. The photoemitted electrons were analyzed with a hemispherical analyzer (SES2002) having a full acceptance angle of 14°. The monochromatic VUV light was employed as an excitation source from BL7 of HiSOR Hiroshima synchrotron radiation center Hiroshima University. Sm core levels of 3d and 4d were investigated separately with a surface sensitive XPS system of ESCA300 with a monochromatic x-ray (AlK\(\alpha\)) source. The Sm over-layer was performed by using an electron-beam bombardment of tantalum crucibles containing a pre-cleaned Sm ingot (99.99% purity) in a vacuum pressure of 3.4\times10^{-8}\ Pa; the rate of evaporation was determined with a quartz thickness monitor. The deposition was performed onto substrate HOPG at a room temperature. The spectra were recorded in a vacuum condition of...
1.8 × 10⁻⁸ Pa. The energy scales of the spectra were referred to the Fermi level of the Au plate. The typical resolutions of measured spectra are 0.15 eV in UPS and 0.45 eV in XPS, respectively. The HOPG was transferred immediately to the measurement system after cleaved in an atmosphere.

4. RESULTS AND DISCUSSION

4.1. Valence Band Spectra
Sm is a very active material for oxidization; generally, Sm²⁺ can be readily converted to the Sm³⁺ under residual oxygen atmosphere. This property of Sm affects the durability of the surface cleanliness of the Sm overlayer, and hence, limits the quality of the experimental data. Here, we discuss the durability of the Sm overlayer surface. An overlayer with a 0.6 Å coverage was investigated as a typical case. Figure 1(a) shows the energy distribution curves (EDC’s) taken at \( hν = 136 \) eV for Sm overlayers with 0.6 Å coverage. To simplify the comparison, all spectra used herein were subtracted from the substrate signal of HOPG; prior to this subtraction, the spectra were normalized to the incident photon intensity. The peak located around 2.4 eV is primarily due to the final 4f⁵ (4f⁵(6s⁵d)²) state resulting from the ionization of Sm²⁺ (4f⁶(6s)²) initial state, whereas the peaks between 4.5 and 12.0 eV correspond to the final 4f⁴ (4f⁴(6s⁵d)³) state resulting from the ionization of Sm³⁺ (4f⁵(6s⁵d)³) initial state. The final 4f⁵ state consists of four peaks as shown in Fig. 1(b) and explained below. The EDC in the Fig. 1(a) with the open circle plotted at the middle represents the first spectrum (1st EDC) of this sample. This spectrum was recorded at \( t = 10 \) min. after the deposition of Sm onto the HOPG substrate. The second spectrum (2nd EDC, diamond symbols) was recorded after keeping the sample under UHV condition of 1.8 × 10⁻⁸ Pa for 61 min without VUV irradiation after acquisition of the 1st EDC, thereby providing information on the time dependence of the durability of the Sm overlayer under UHV condition. The intensity of the 4f⁵ state in the 2nd EDC is observed in decrease compared to that of the 1st EDC. These two curves at the center divide the spectra into two groups depending on whether the sample position is fixed or varied (shifted). The EDC’s above the 2nd EDC belong to the first group, which are recorded by fixing the sample position (thin dotted lines). The EDC’s below the 1st EDC belong to the second group (dotted lines), which are recorded by shifting the sample position in steps of 2.0 mm to prevent overlapping of the photon beam spot at the sample surface during the measurement. The sample size is 10 × 10 mm, and the spot size of the photons is expected to have width and height dimensions smaller than 1.5 × 0.5 mm. In the first group, the intensity of the photoemission peak for the 4f⁵ state decreases rapidly with increasing duration and almost disappears 119 min after the deposition of Sm. In the case of this first group, the same position of the Sm overlayers is irradiated with VUV light for a total of 37 min. However, in the case of the second group in which each spectrum is recorded from a different position of the Sm overlayer, the intensity of the peak corresponding to the 4f⁵ state is remarkable even 236 min after the deposition process. This means that each position is irradiated with VUV light for approximately 1.5 min, given that 1.5 min is required to obtain one VB spectrum. The essential difference between the two groups of spectra here is the duration for which a particular part of the Sm overlayer is irradiated with VUV light. Furthermore, by comparing the 2nd EDC (diamond) and 7th EDC (dotted thin line), it is found that the intensity of the 4f⁵ peak of the latter (irradiated for 1.5 min) was higher than that of former (irradiated for 3.0 min) even though the 7th EDC was recorded 11 min after the 2nd EDC. This observation indicated that degeneration of the 4f⁵ structure is more...
sensitive to the irradiation time than the duration of the Sm/HOPG sample that just stays under UHV conditions without VUV irradiation. These results indicate that the VUV irradiation plays an important role in the degeneration of the Sm$^2$ species during PES. This tendency is also confirmed in the other VB spectra acquired by using different excitation energy in the range 135.0–144.0 eV. Although the mechanism underlying the photo-associated degeneration of Sm$^2$ remains unclear, the importance of the irradiation is demonstrated here. Figure 1(b) shows the intensity plot of the 0.25 Å Sm over-layer on HOPG along the Γ-K symmetry direction in the first Brillouin zone of HOPG. Non-dispersive bands are observed at the binding energies of 0.88, 1.6, 2.1, and 3.5 eV; these bands are derived from the Sm$^2$ species. In comparison with the fresh HOPG (not shown here) substrate, the π band with the maximum at 2.7 eV shifts by 0.1 eV toward higher binding energy in the Sm/HOPG specimen. This corresponds to the energy shift of the C1s core level measured by XPS shown in Fig. 2(b). No band interface between the Sm 4f level and the HOPG π band has been observed. No trace related to the oxygen signal was observed for the Sm over-layer coverage of 0.1–0.6 Å. If O$_2$ contamination is present in the Sm over-layer, it is possible to observe an O 2p band at a binding energy of ca. 6.5 eV [6,7]. The detection sensitivity for O$_2$p here is higher than that of O$_1$s in the XPS measurement, because the ionization cross-section of O$_2$p is a few times larger (at $h\nu$ =136 eV) than that of O$_1$s excited by Alkα.

4.2. Core level spectra

The XPS measurement for the Sm overlayers was performed in order to investigate the interlayer alloy between Sm and the HOPG substrate. Fig. 2(a) illustrates the coverage-dependence of the 3d core level spectra for Sm overlayers in the range of 0.1–3.6 Å. The photoelectrons were collected from the cutoff angle of 45°; the samples were excited using monochromatic X-ray (Alkα). The coverage (in angstrom unit) of the Sm overlayer is shown on the right hand side of the panel. Structures located around the 1075 eV and 1102 eV belong to the 4f$^5$ final state that ended-up with electron emitted from the Sm$^2$ species. In comparison with the fresh HOPG (not shown here) substrate, the π band with the maximum at 2.7 eV shifts by 0.1 eV toward higher binding energy in the Sm/HOPG specimen. This corresponds to the energy shift of the C1s core level measured by XPS shown in Fig. 2(b). No band interface between the Sm 4f level and the HOPG π band has been observed. No trace related to the oxygen signal was observed for the Sm over-layer coverage of 0.1–0.6 Å. If O$_2$ contamination is present in the Sm over-layer, it is possible to observe an O 2p band at a binding energy of ca. 6.5 eV [6,7]. The detection sensitivity for O$_2$p here is higher than that of O$_1$s in the XPS measurement, because the ionization cross-section of O$_2$p is a few times larger (at $h\nu$ =136 eV) than that of O$_1$s excited by Alkα.

The formation of the Sm carbide between Sm and the HOPG interlayer was also a concern. This was checked by careful evaluation of the coverage dependence of the C1s core level spectra of the Sm/HOPG. Fig. 2(b) shows the C1s core level spectrum of HOPG covered with Sm at various degrees of coverage. For the sake of simplicity, de-convolution of the C1s spectra into three components (C1, C2, and C3) was performed by a least-squares fit as indicated by a dashed line for the fresh HOPG as an example. The C1 and C2 components correspond to the bulk and surface state, respectively [8]. The C3 component is related to photoemission from a defect existing on the terrace step of HOPG [9]. The peak positions of the three components of the fresh HOPG substrate are located at 284.3, 284.7, and 285.7 eV, respectively. The positions of these peaks (C1, C2, and C3) shift to the higher binding energy with increasing Sm coverage to a maximum of 0.5 Å Sm; saturation is achieved at this coverage, and no further shift is observed for coverage greater than 0.5 Å. The extent of the respective C1, C2,
and C\textsubscript{3} shifts is ca. 0.1 eV, 0.15 eV, and 0.1 eV. These energy shifts represent the evidence of the charge transformation from Sm to the HOPG substrate. The donor in the charge-transfer process is apparently related to the atomic Sm\textsuperscript{2+} species, since the coverage-dependence of the energy shift somehow mimics the behavior of the Sm\textsuperscript{2+} species presented in the Fig. 2(a), where this species dominates the spectra at coverage below 0.5 Å and becomes minor for coverage greater than 1.8 Å. The Sm over-layer should be characterized by coalescence of a Sm cluster to form a semi-continuous film with very high surface to volume ratio, whereas the intensity of the C\textsubscript{1} peak increases monotonically with increasing coverage. The decrease in the intensity of the C\textsubscript{1} and C\textsubscript{2} components is ascribed to attenuation of the photoelectron by the Sm overlayer.

The intensity enhancement of the C\textsubscript{1} peak is anticipated to be related to the bonding of carbon to the Sm or to O\textsubscript{2} at the defect on the terrace step; nevertheless, the defect area is minor compared to the entire surface of the HOPG substrate, which was confirmed via atomic force microscopy [5]. Thus, the extent of the photoelectron signal from the defect region of HOPG would still represent a minor contribution, which should not change the nature of the spectra shown in Figs. 1(a) and 2(a).

On the other hand, we cannot ignore the possibility that the divalent Sm state degenerates because of the natural oxidization of Sm by residual oxygen species even under UHV condition. The inset in Fig. 2(b) shows the oxygen signal from the Sm/HOPG for selected coverage of Sm. The coverage is shown in the right hand side of the panel; the spectrum of unmodified (fresh) HOPG is included as a reference. No obvious trace corresponding to O\textsubscript{1s} was detected during the experiments; however, a very weak hump is observable at 530 eV with an intensity that is the same order as the background level for spectra acquired at higher coverage. We have confirmed that the intensity of the C\textsubscript{3} peak is independent of the oxygen-rich Sm over-layer, which was intentionally exposed to O\textsubscript{2} in our system. The ARPES results confirm that O\textsubscript{2} contamination on the Sm layer was negligible in the system discussed here.

Furthermore, the influence of the defect resulted in the formation of C-Sm and of C-O compounds, and Sm oxidization in the Sm over-layer during the PES process is a phenomenon common to the two groups of spectra (Fig. 1 (a)). Thus, neither the natural oxidation of Sm nor the formation of the C-Sm compound is a major cause for the difference between the degeneration behaviors of the Sm\textsuperscript{2+} states in the two groups of EDCs. This indicates that irradiation-induced degeneration of Sm\textsuperscript{2+} is a faster process than the other possibilities, and exerts a more significant effect on the Sm\textsuperscript{2+} degeneration during the present PES measurement even under the vacuum condition of 1.8 × 10\textsuperscript{-8} Pa. The present results indicate that VUV irradiation of Sm plays an important role in stimulating the degeneration of divalent multi-configuration Sm during vacuum ultraviolet photoemission spectroscopy.

5. SUMMARY
The effect of irradiating VUV photons on the degeneration of Sm\textsuperscript{2+} is more profound than compound formation and contamination of Sm during photoemission spectroscopy measurements. Sm exists in an over-layer mainly in the atomic divalent configuration at coverage below 0.6 Å; at coverage higher than 1.0 Å, the Sm is converted to the trivalent configuration and exists in the condensed state rather than as a discrete Sm cluster. A charge transfer from divalent Sm to HOPG was confirmed. No evidence of a correlation between the localized Sm 4f bands and the dispersive \pi band of HOPG has been found. For the further investigation of the valence transition phenomenon in response to VUV irradiation, a micro-spot size photon beam based photoemission spectroscopic study is recommended in an extremely high-vacuum environment.

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