Photoemission Study of Sm Overlayers Deposited on Nb

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The valence of Sm overlayers deposited on a polycrystalline Nb substrate has been studied *in-situ* by photoemission spectroscopy using synchrotron radiation. The Sm valences are determined by resonantly enhanced emissions from trivalent $(4f^5)$ and divalent $(4f^6)$ states at photon energies of 141 eV and 135 eV respectively. For coverages of less than one monolayer trivalent Sm dominates. Divalent peaks start to grow at the coverage of about one monolayer. In the mean time the relative intensity of the contribution from the divalent state increases with film thickness, indicating an influence of Sm valence by the Nb substrate near the interface region. The divalent peaks are almost completely suppressed upon exposure of 0.1 langmuir of oxygen, which suggests that the mixed valence in Sm is heterogeneous.

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I. Introduction

The interesting mixed-valency of Sm and other rare earth elements has attracted much attention since the late seventies [1, 2]. The different valence state of Sm is defined by the number of electrons in the 5d-6s band. For atomic Sm, the formal valence is 2+ with an electronic configuration of $4f^6(5d6s)^2$. In metallic Sm, the valence is a mixture of 2+ and 3+. The latter corresponds to the $4f^5(5d6s)^3$ configuration. In the recent years many studies about Sm valence have been reported based on investigations of the Sm thin films deposited on various substrates [3-5]. The valence state of Sm deposited on transition metal not only depends on the type of the substrate but also on the thickness of the Sm film [6]. In this paper we report the results of a valence band photoemission spectroscopy (PES) study of Sm deposited on a polycrystalline Nb substrate using synchrotron radiation. We choose polycrystalline Nb as a substrate because, based on the previous study [7], Nb and Sm do not inter-diffuse. Furthermore, we intend to extend the results reported in [7] with the effect of thickness on the Sm valence. Measurements were taken at beamline 08A at Synchrotron Radiation Research Center (SRRC), Taiwan, using a low-energy spherical grating monochromator (LSGM). Photoelectrons were collected via a 125-mm hemispherical electron energy analyzer with five single channel electron multipliers. The combined resolution of the spectra shown in this study is about 65 meV. The Nb substrate was cleaned by cycles of flash heating to approximately 1400±C followed by exposure to oxygen at 1000±C for several minutes in order to remove carbon. Sm was evaporated from a tungsten basket, which was initially thoroughly outgassed. The pressure during evaporation was in the range of

$10^{i\ 10}$ torr, immediately after evaporation the pressure was reduced to the base pressure of $10^{i\ 11}$ torr for *in-situ* PES measurements.

The valence of Sm is determined by resonant photoemission [3], in which photon energy is tuned between 134 and 140 eV corresponding to the maxima of resonantly enhanced $4f$ emissions from divalent $(4f^6)$ and trivalent $(4f^5)$ Sm, respectively. The off-resonant spectrum at photon energy of 126 eV was also taken for comparison. Fig. 1 plots valence-band photoemission spectra of 15 Å Sm thin film deposited on Nb. The peaks of binding energy lower than 4.5 eV are due to emissions from Sm $4f^6$ state, and the peaks of binding energy between 5 and 10 eV are due to emissions from Sm $4f^5$ state. Relative to the spectrum taken at photon energy of 126 eV, the emissions from distinctly enhanced divalent and trivalent features at photon energies of 134 and 140 eV, respectively, are observed. These enhancements are due to super-Coster-Kronig resonances [8] near the Sm $4d$ absorption threshold.

Fig. 2 plots valence-band photoemission spectra of Sm thin film of various thickness deposited on Nb at a photon energy of 150 eV. For sub-monolayer coverage trivalent features dominant. Divalent peaks start to grow at coverage of one monolayer, resulting in a mixed valent Sm. The relative intensity of divalent state increases with film thickness indicating a decrease in average valence of Sm. For the above resonant photon energy of 150 eV the photoemission

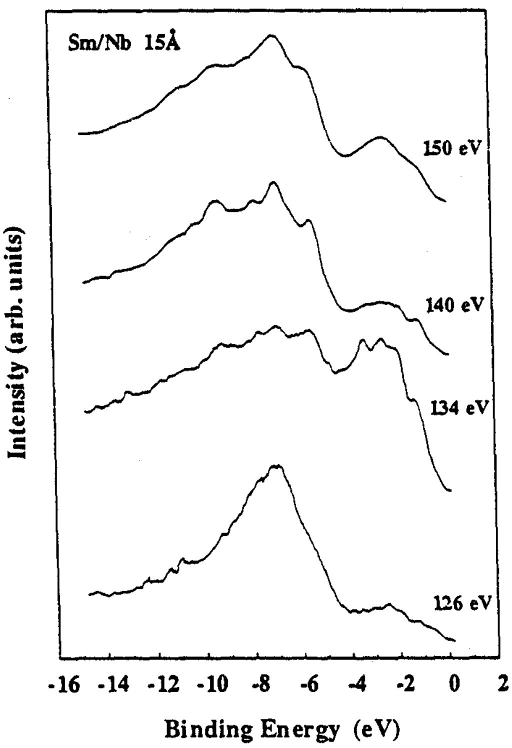

FIG. 1. Valence-band photoemission spectra of 15 Å Sm thin film deposited on Nb, hv=126, 134, 140, and 150 eV.

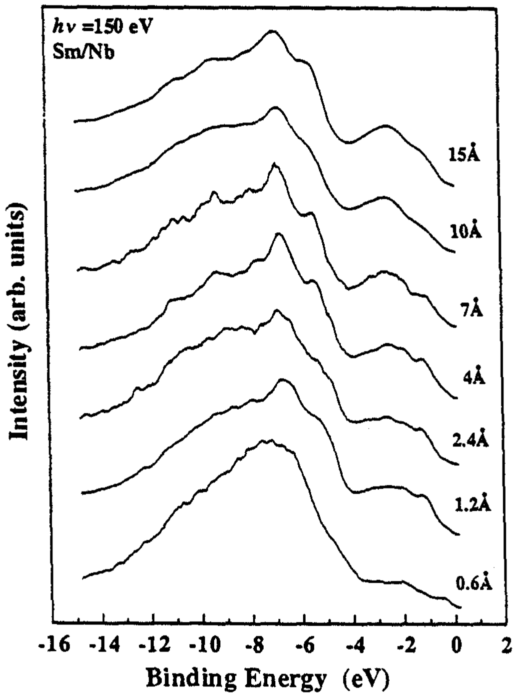

FIG. 2. Valence-band photoemission spectra of Sm thin film of various thickness deposited on Nb at a photon energy of 150 eV.

cross section for both Sm^{2+} and Sm^{3+} is approximately the same. We are able to roughly determine the average valence of Sm using the spectra taken at 150 eV photon energy. The detailed procedure for valence determination is described in Ref. 6. The results of calculated average valence as a function of film thickness is plotted in Fig. 3, in which we observed a decrease in the average Sm valence from about 2.91 to 2.78 as the thickness increases from less than 1 Å to 15 Å.

Fig. 4 shows Sm valence band photoemission spectra taken at incident photon energy of 135 eV upon exposure to the indicated dosage of oxygen. The intensites of resonantly enhanced Sm^{2+} features decrease with the amount of oxygen exposure. The divalent contributions are completely suppressed at oxygen exposure of 0.1 langmuir, which indicates that Sm^{2+} exist only in the surface area. In other words, the mixed valency of Sm is heterogeneous.

By monitoring the Nb $4p$ feature at different Sm coverage up to about 5 Å, we observed no significant change in spectral shape or binding energy indicating that there is no inter-diffusion or compound formation between Sm and Nb [9]. The Nb $4p$ feature is completely suppressed for Sm coverage of higher than 5 Å, which is about the mean free path of photoelectrons with kinetic energy around 100 eV. The observed decrease in Sm valence with increasing thickness is attributed to the charge transfer from Sm to Nb side at the interface due to the higher electronegativity of

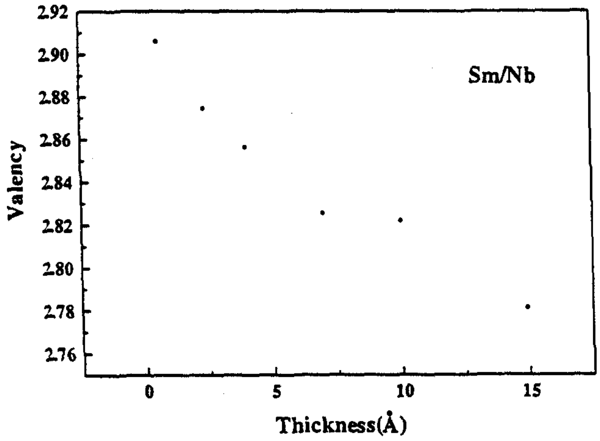

FIG. 3. The results of calculated average valence as a function of film thickness.

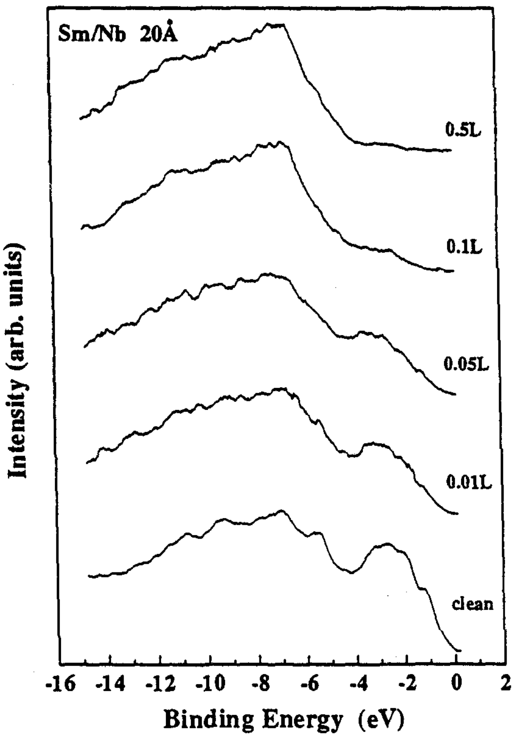

FIG. 4. Sm valence band photoemission spectra taken at an incident photon energy of 135 eV upon exposure to the indicated dosage of oxygen (0.01, 0.05, 0.1, and 0.5 langmuir).

Nb. At lower coverage the Sm layers are very close to the Sm-Nb interface, where Sm valence is nearly 3+ due to charge transfer. As the Sm thickness increases, the Sm^{3+} contribution from the interface decreases. Whereas, the Sm^{2+} contribution from surface becomes more prominent resulting in a decrease in the average valence of Sm. It is also observed, from Fig. 3, that the average valence tends to saturate as the Sm film thickness increases, and the interface effect becomes less significant.

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[9] In agreement with that predicted from Sm-Nb phase diagram, see *Handbook of Binary Phase Diagram*, ed. W. G. Moffet (General Electric Co., Schenectady, NY, 1976).