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Coadsorption of samarium with oxygen on the molybdenum (2 1 1) surface

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ABSTRACT

Samarium atoms exist in two different electronic configurations, namely, divalent (Sm^{2+}) and trivalent (Sm^{3+}). Up to now, those two electronic configurations have been connected with the existence of Sm atoms in different valence states. Recent theoretical calculations performed by Yakovkin [9] show that both electronic configurations have similar LDOS around the Fermi level, and as a result, should give a similar photoelectron emission in the valence band region, which was identified earlier as the emission from the Sm^{2+} state. The Sm^{3+} signal in photoelectron emission could originate from contaminations of Sm by other elements, e.g. oxygen. To check the influence of O on the electronic structure of Sm, the XPS experiments of coadsorption of O and Sm have been performed.

1. Introduction

Samarium as a pure metal attracts a lot of scientific interest since the electronic structure investigations show that it could exist in two different electronic configurations, namely, [Xe] $4f^6(5d6s)^2$ Sm^{2+} and [Xe] $4f^5(5d6s)^3$ Sm^{3+}[1,2]. Up to now, those two electronic configurations have been connected with the existence of Sm atoms in different valence states: divalent (Sm^{2+}) and trivalent (Sm^{3+}). Sm^{3+} atoms are assumed to be present in the bulk and Sm^{2+} on the surface. The valence change is connected with a change in Sm atom diameters. An Sm^{3+} atom is similar to a Gd atom [3] with the diameter 3.61 Å, whereas an Sm^{2+} atom is bigger and similar to an Eu atom with the diameter 4.04 Å[4]. It was found experimentally that the outermost Sm atomic layer has a different lattice constant than that of layers lying beneath: (5×5) [5] and (11×11) [6] reconstructions were reported. Theoretical calculations [4,7,8] show that for bulk Sm atoms the trivalent configuration is more favorable. At some specified conditions, however, Sm atoms prefer the divalent configuration. In particular, the valence change can result from a change in the number of the nearest neighbors [4].

However, recent theoretical calculations performed by Yakovkin for Sm metal show that both Sm electronic configurations (namely, [Xe] $4f^6(5d6s)^2$ and [Xe] $4f^5(5d6s)^3$) have similar LDOS around the Fermi level, and as a result, should give a similar photoelectron emission in the valence band region [9] (identified earlier as the Sm^{2+} emission). One of the author's suppositions about the origin of Sm^{3+} signals in photoelectron emission (around 5 eV below the Fermi level) was the contamination of Sm by other elements, e.g. oxygen. During experiments concerning adsorption of Sm on the Mo (2 1 1) face no presence of oxygen was found [10], and the electron photoemission spectrum has signals both from Sm^{3+} and Sm^{2+}. During Sm adsorption on the Mo (1 1 1) face, signals from Sm^{2+} and Sm^{3+} were also detected [11] without any trace of oxygen.

Because of difficulties in preparing well-characterized Sm single crystals, thick Sm layers on a well-defined substrate are used for investigations of Sm atomic and electronic structure. Also the influence of the number of the nearest neighbors on Sm atom valency can be investigated by the adsorption of thick Sm layers on different faces of a single crystal (e.g. on the (1 1 0) [5,12,13], (1 1 1) [11], and (2 1 1) [10] faces of Mo). One should note that the theoretical calculations were performed for Sm atoms surrounded by other Sm atoms [4,7–9], while in experiments Sm atoms are surrounded with both Sm and the substrate atoms [5,10–13].

To check the influence of O on the electronic structure of Sm layers, the XPS experiments of coadsorption of O and Sm were performed. The results were compared with adsorption of Sm without oxygen on the Mo (2 1 1) face [10]. It was found that the Sm^{2+} signal is attenuated and the Sm layers contaminated with oxygen show only the emission characteristic of Sm^{3+}. In spite of applying the smallest possible oxygen exposures (around 0.03 Langmuirs), the O peak in XPS spectra was clearly visible while it was absent during pure Sm deposition.

2. Experiment

The apparatus used for the X-ray induced photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES)

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measurements was equipped with an X-ray source with an Mg anode ($K_\alpha = 1253.6$ eV) and a hemispherical electron energy analyzer. During experiments, the pressure in the apparatus was less than 5×10^{-11} Torr.

A molybdenum sample of 5N purity was cut off from a single monocrystal perpendicularly to the [2 1 1] direction with an accuracy of ±0.05°. The temperature of the sample was measured by the W5%Re–W26%Re thermocouple, attached to the back side of the sample. The sample was cleaned in a typical way by heating it at 1200 K in the oxygen atmosphere of about 10^{-7} Torr for several hours. Next, the sample was exposed for a few seconds to oxygen doses and flashed to about 2300 K to remove oxygen from the surface. The cleanliness of the sample was controlled by AES and it was believed to be clean when the carbon peak (272 eV) was 400 times lower than the molybdenum (186 eV) peak. The XPS measurements were also used to check the cleanliness of the sample and oxygen (532 eV) peak was never observed for the clean sample.

Metallic Sm of 3N purity was used for deposition. It was kept in mineral oil to prevent oxidation and hydration. Sm was evaporated from a molybdenum crucible, heated by a tungsten heating coil warped around it. The empty crucible was put into an auxiliary vacuum apparatus, where heating to about 2000 K was performed for several hours. Before inserting a piece of Sm into the crucible, it was mechanically cleaned from the oil. Next the whole Sm source was transferred in the Ar gas atmosphere and mounted again in the auxiliary vacuum apparatus where outgasing was performed. After several days of outgasing, the Sm source was transferred in the Ar gas atmosphere to the main measurement apparatus.

Oxygen of 5N purity was used in experiments and in the sample cleaning procedure. The gas cylinder with the pressure of about 10 atm was connected through the pressure reducing valve to a small volume (about several cubic centimeters). The gas pressure in this volume was about 0.1 atm. Finally, the gas was dosed to the main chamber through a precision UHV valve. This home-made gas dosing system allows us to achieve very low but stable pressure of oxygen (about 3×10^{-10} Torr) controlled by a B-A head.

The photoelectron spectra were recorded and processed using the SPECTRA software. To get the photoelectron signal intensity, XPS data recorded for every Sm layer were smoothed, and then the background substraction procedure was applied. The area under the peak was a measure of the signal intensity.

3. Results

To check the influence of oxygen on the valence of Sm atoms adsorbed on the Mo (2 1 1) surface, two experiments were performed. The first of them consisted in the adsorption of Sm in an oxygen atmosphere, and the second, in the alternate deposition of Sm and O onto the surface.

In the first experiment, the apparatus chamber was filled with oxygen (at the level $5.0 \pm 0.5 \times 10^{-10}$ Torr) and in such conditions the Sm deposition was performed. After oxygen pressure was stabilized on a required level, the Sm source was turned on and a fixed dose of Sm was evaporated onto the sample. After Sm deposition, the Sm source was turned off with simultaneous closing of the oxygen dosing valve. The measurement was started after a minute or two needed to pump out the remainig oxygen. After such a treatment, the pressure during the measurement was lower than 5×10^{-11} Torr.

Fig. 1 presents the XPS curves registered for clean Mo, a thick Sm layer and a Sm layer deposited in oxygen atmosphere in the energy range of 1060–1170 eV. There are several Sm peaks in this range. According to the literature [1,2], peaks at 1073.5 eV ($3d_{5/2}$) and 1101 eV ($3d_{3/2}$) are attributed to divalent Sm atoms, while peaks at 1082 eV ($3d_{5/2}$) and 1108 eV ($3d_{3/2}$) are attributed to trivalent Sm atoms. In general, the Sm valence could be investigated by analyzing different XPS emission peaks, namely, 4*f*, 4*d*, and 3*d*. The measurements of 4*f* peaks are difficult with the use of X-ray induced photoemission, and in this case the best results are obtained by applying ultraviolet or synchrotron radiation. The overlapping multiplet structure of 4*d* peaks in photoelectron spectra makes it difficult to analyze. The best way to determine the Sm valence with the use of the X-ray radiation is to analyze the 3*d* band, where the signal is strong, and emission lines are well separated [1,2,10,11].

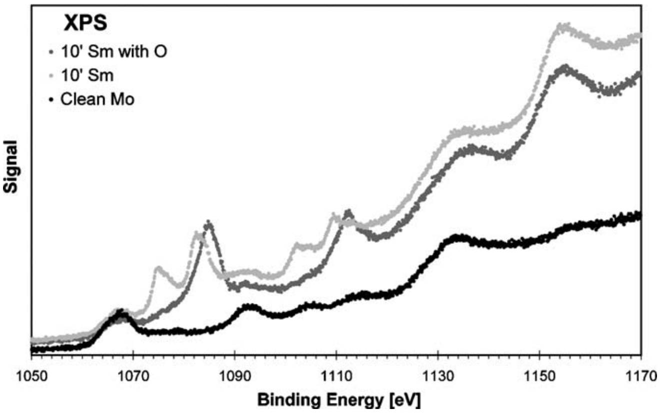

Fig. 1. XPS of clean Mo (black points) and $\theta = 3$ ML thick Sm layer deposited without (light-gray points) and with (dark-gray points) oxygen. The *y*-axis (XPS signal intensity) scale is 10^5 counts.

Changes of the intensity of the Sm^{2+} and Sm^{3+} signals at 300 K are presented in Fig. 2. To get the Sm signal intensity, recorded XPS data were processed as described in Section 2. The results presented are a sum of 1073.5 eV and 1101 eV signals for Sm^{2+}, and 1082 eV and 1108 eV signals for Sm^{3+}. For comparison, the results concerning the Sm deposition without oxygen are also

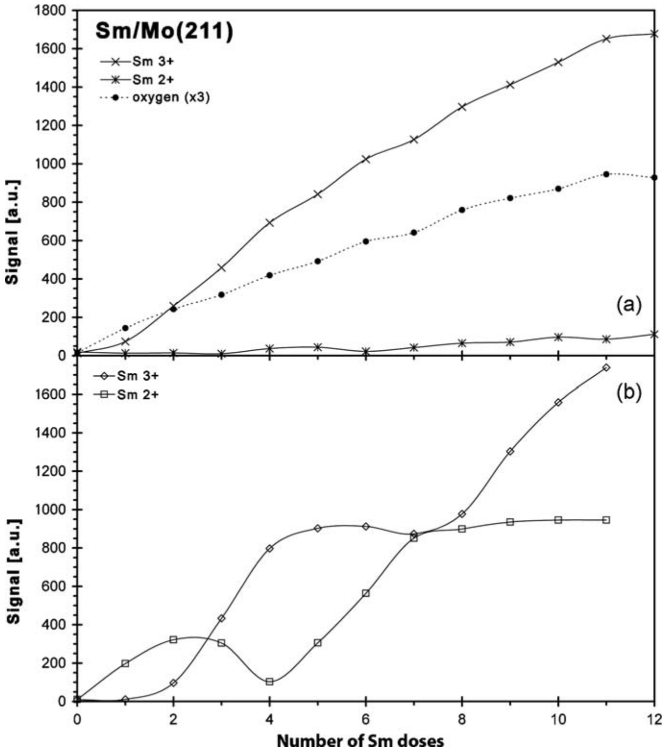

Fig. 2. XPS signals of Sm^{2+} and Sm^{3+} deposited in oxygen atmosphere (a) and in the clean vacuum (b). Black points in part (a) correspond to oxygen 532 eV signal.