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Coadsorption of lanthanum with boron and gadolinium with boron on Mo(1 1 0)

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ABSTRACT

Submonolayer to multilayer coadsorption of lanthanum (La) with boron (B) and gadolinium (Gd) with boron on the surface of Mo(1 1 0) has been studied by means of Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and work function (ϕ) measurements. The equilibrium state of double adsorbate systems achieved either by adsorption of rare-earth metal (REM) on boron precovered Mo(1 1 0) surface held at room temperature or after moderate annealing of the system with opposite order of adsorption (B on REM films) is the layer which is the inhomogeneous mixture of boron and REM atoms with preferential concentration of boron in the surface area of the mixed film. The work function of such films even at REM to boron concentration ratio much higher than 1/6 are very close to the values of corresponding bulk LaB_6 and GdB_6, favoring assumption of surface rearrangement as the dominant reason of high electron emission efficiency of hexaborides. Almost total similarity of the results for La–B and Gd–B systems can be viewed as the consequence of weak participation of Gd f-electrons in determining the thermionic properties of corresponding double layers.

1. Introduction

Rare-earth metal hexaborides are materials of long standing technological relevance mainly as low temperature thermionic emitters [1,2]. Among all the hexaborides LaB_6 is one which is most widely used for emitter fabrication due to unique combination of low work function (2.7 eV in average) and stability [3,4]. Unique emission properties of LaB_6 are seen from comparison of its emission current density (65 A/cm^2 at T = 1873 K) with that of tungsten (1.75 A/cm^2 at T = 2700 K) [4]. More recently LaB_6 receives additional interest because of potential application in electron emitting tip devices, nanoscopy and nanolithography [5–7]. Application importance motivated an extensive research of LaB_6, as well as other hexaborides, which has been done for last several decades. Most of the studies were focused on elucidation of the origin of low work function. So far such an extensive study yields however no clear evidence whether the low work function is an intrinsic property of the material or is due to REM^+–B^- dipole layer which forms on the surface [8–13]. Almost all studies of LaB_6 and other hexaborides focus on bulk material. At the same time in order to distinguish between the two ongoing viewpoints on low work function of LaB_6, as well as other hexaborides, it would be informative to study some model systems which emphasize the role of "pure" REM–B dipole layer. In relation to this the aim of the present work is to investigate the properties of double submonolayer to multilayer films which are obtained by controlled growth of La–B and Gd–B films on metallic substrate (Mo(1 1 0)). Apart from the application importance such investigation is also interesting from fundamental standpoint. These model systems are prototypes of the systems obtained by coadsorption of electronegative (B) and electropositive (La,Gd) atoms, and thus allow gaining additional information on chemisorption process in such complex systems. Motivation of the choice of La and Gd with electronic configurations La [Xe]5d^{1}6s^2 and Gd [Xe]4f^{7}5d^{1}6s^2 is to determine the effect of f-electrons on the properties of the systems under consideration. Adsorption of some rare-earth metals on a number of substrates has been quite extensively studied previously [14–20], whereas almost no data are reported on their coadsorption with boron. Also extremely lacking are the works studying adsorption of boron alone on metal substrates [21,22].

2. Experimental

Measurements have been carried out in ultra-high vacuum system (base pressure: 2×10^{-10} Torr) consisting of stainless steel chamber equipped with retarding four-greed hemispherical electron analyzer with coaxial electron gun for Auger electron spectroscopy and electron energy loss spectroscopy, low-energy electron gun, operating at energies lower than 10 eV for work function measurements (Anderson method), sample holder allowing heating to temperatures as high as 2800 K, quartz microbalance

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and adsorbate sources. The chamber was also equipped with the leak valve for controlled oxygen dose and residual gas mass-spectrometer. Energy resolution of the electron spectrometer derived from elastic peak width was lower than 1%. Sensitivity of AES measured via controlled dose of oxygen was 0.03 monolayers (ML). This was estimated by gradual exposure of Mo(1 1 0) held at room temperature to molecular oxygen until O KLL Auger signal can be detected at an exposure of 0.04 L (1 L = 10^{-6} Torr s). The latter according to structural analysis of O–Mo(1 1 0) system corresponds to 0.03 ML of oxygen atoms [23]. The Auger spectra were measured in dN/dE whereas EELS in $N(E)$ form with constant $\Delta E/E$ and 7 V modulation. The EELS in the configuration used was mainly sensitive to collective and interband transitions. The Mo(1 1 0) sample of a rectangular shape ($10 \times 5 \times 0.3$ mm^3) was mounted on the sample holder with the WRe 0.3 mm diameter wires spot-welded at the four corners of the back of the sample. Direct current through these wires allowed heating the sample to about 1400 K. Higher temperatures were achieved by electron bombardment of the sample by the tungsten filament placed in a tantalum screen behind the sample. The temperature was measured by W–WRe thermocouple spot-welded to the back upper side of the sample.

Lanthanum and gadolinium were deposited on Mo(1 1 0) by thermal evaporation through direct heating of the 0.2 mm thick and 1 mm wide M-shape tantalum foil to which the corresponding bulk materials (ca. 0.5 mm^3) of 99.97% (La) and 99.98% (Gd) purity were spot-welded in ethanol environment. The latter was necessary to avoid oxidation by the ambient oxygen during welding. The foils with welded La and Gd were placed in tantalum screens with a nozzle on an upper side. Constructed in this way sources of rare-earth metals had high stability of the produced flux. Boron evaporation needs higher temperature which was achieved by electron bombardment. This was done from the 0.2 mm diameter grounded tungsten spiral wrapped around the peace of bulk boron fixed in a positively biased (+2 kV) tantalum rod and placed in tantalum screen. All Ta foils and W filaments used for construction of the sources were preliminary outgased in a separate chamber at a pressure of ca. 10^{-8} Torr. After placing into UHV chamber the sources were carefully outgased for prolonged time until no contaminations were detected by AES. Deposition flux of the adsorbates was measured by quartz microbalance and verified by AES via monitoring the Mo signal attenuation and the growth mode. For correct determination of the flux, and hence the adsorbate coverage, the similarity of deposition geometries for sample and the quartz was achieved by their strictly coaxial and coplanar placement on a manipulator. Combination of quartz microbalancing (assuming unity sticking probabilities on sample and the quartz) and AES allowed measurement of surface concentration with the accuracy of ca. 0.15 of 1 ML coverage. The latter relates to accuracy of measurement of deposited adsorbate flux which is different from the above mentioned meaning of AES apparatus sensitivity to adsorbed oxygen, which is 0.03 ML. It was assumed that the values of surface concentrations (n) of 1.1×10^{15} cm^{-2} for La, 1.3×10^{15} cm^{-2} for Gd and 2.7×10^{15} cm^{-2} for B correspond to unity coverage ($\theta = 1$).

The Mo(1 1 0) crystal was cleaned by the usual procedure of heating at 1300 K in an oxygen ambient (10^{-6} Torr) to remove carbon and sulfur contaminations and subsequent high-temperature (2700 K) flashing cycles in UHV. The surface was considered clean if no contaminations can be monitored by AES at the most sensitive scale. After each set of adsorbate deposition and measurement the surface was cleaned by cycles of high-temperature flashing and the cleanliness was checked by AES. Sometimes, after a certain set of measurements, even after high-temperature flashing the carbon C (KLL) signal could be detected by AES. In this case annealing of the sample in oxygen ambient to remove carbon contamination was applied.

3. Results

Coadsorption of La and Gd with boron was studied for different orders of adsorption of the corresponding components. This order was found to be a crucial point determining the properties of the systems formed at the substrate held at room temperature. Even small amount of preadsorbed boron dramatically changes the work function versus coverage plots for subsequent adsorption of both La and Gd compared to that on bare Mo(1 1 0). The corresponding dependences for different initial boron coverage combined in one plot are shown in Fig. 1. The curves marked by asterisk correspond to La and Gd adsorption on Mo(1 1 0) not precovered by boron. Generally they are similar to those reported previously [14,16]. There are several points differentiating the work function versus coverage plot from that of both La and Gd on bare Mo(1 1 0): Minima region of $\phi(\theta)$ curve is no longer available at all initial boron concentrations studied; the saturation work function is considerably lower; more La and Gd adsorbate concentrations are needed to stabilize the work function; initial slopes of La and Gd work function plots determining the initial dipole moments are notably higher and increase with the preadsorbed boron concentration. It is noteworthy that the stabilization work function is close to the values of bulk lanthanum and gadolinium hexaborides: 2.7 and 2.9 eV, respectively.

The AES results may help to account for the above differences in the work function plots for La(Gd)–B–Mo(1 1 0) and La(Gd)–Mo(1 1 0). An important point in studying the adsorbate system is to evaluate the morphology of the layer. AES can help to distinguish between two- or three-dimensional growth mode of the film, by plotting the Auger uptake curves of both adsorbate and substrate. Plotting of such curves for La, Gd and B may not be informa-

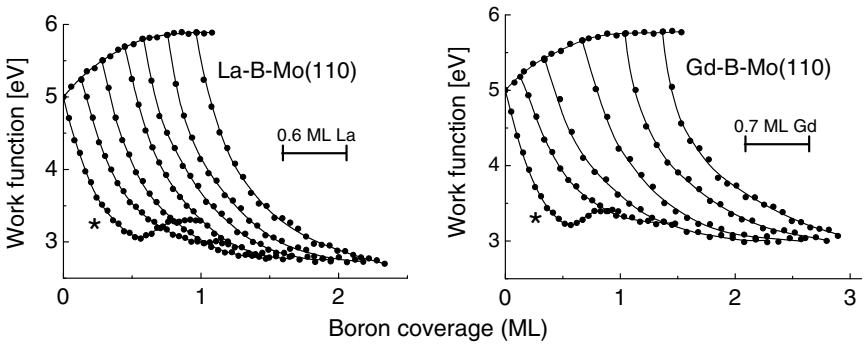

Fig. 1. Work function versus coverage dependences for adsorption of La and Gd on Mo(1 1 0) precovered by different amounts of boron. For convenience all measured curves are combined in one plot. The corresponding bars define the La and Gd coverage scale. Curves marked by asterisk correspond to La and Gd on bare Mo(1 1 0).