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Growth of Sn on Mo(110) studied by AES and STM

A. Krupski *

Institute of Experimental Physics, University of Wrocław, pl. Maxa Borna 9, PL 50-204 Wrocław, Poland

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ABSTRACT

Scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES) have been used to investigate the growth behavior of ultra-thin Sn films on a Mo(110) surface at room temperature. An analysis of STM and AES measurements indicates that layer-by-layer growth (Frank-van der Merwe mode) for the first two layers of Sn is observed. For submonolayer coverage, tin prefers to nucleate randomly and creates one atom high islands on Mo terraces. In the completed first and second layer, no ordered regions were observed. As the sample is post-annealed to 800 K, the rearrangement of an existing film suggests a Sn–Mo surface alloy formation.

1. Introduction

A large number of studies on epitaxy have been carried out for many years. Ultra-thin epitaxial film systems exhibit a variety of interesting properties owing to the strong correlation between the electronic structure of the film and its morphology, strain, and defect structure [1,2]. Structural studies of fcc/bcc systems provide a great deal of information on the connection between the geometrical properties of the adsorbed atomic layers and the atomic arrangements of the substrates. Various fields are concerned with epitaxial growth; these range from basic research on the growth mechanism of thin films to advanced research on the development of devices. In this case of the deposition of face-centered cubic (fcc) or body-centered tetragonal (bct) metals on body-centered cubic (bcc) metals, there have been many excellent investigations of surface structures and growth modes.

Up to now, the surface structures and growth modes of various adsorbate metals on a Mo(110) substrate have been investigated by a variety of experimental and theoretical methods in a number of works (e.g. Sn [3,4], Pb [4–7], Au [8–12], Ag [13–19], Cu [20], Co [21], Fe [22], Ni [23], Mg [24], Ba [25], K [26], S [27], Al [28], Pd [29], Ir [30], Te [31], Yb [32], etc.). Recently, the oxide formation on transition metal (TM) surfaces has also received considerable attention [33–36], including Mo(110) surface [37,38]. The adsorption, initial film growth, alloying and desorption of Sn on the Mo(110) surface has been investigated by reflection high-energy electron diffraction (RHEED) [3] and Auger electron spectroscopy, low energy electron diffraction, work function change measurements, and thermal desorption spectroscopy [4]. The first monolayer of tin grows two-dimensionally on top of Mo(110), displaying lattice structures that are different from the lattice of the Mo substrate or the (111) surface of bulk tin.

In the present work, we show the results of investigations of the morphology of ultrathin Sn layers deposited on a Mo(110) surface in ultrahigh vacuum at room temperature. These results were obtained for the first time by scanning tunneling microscopy.

2. Experiment

The measurements were carried out in a stainless steel ultra-high vacuum chamber with base pressure of 2×10^{-10} mbar. The chamber was equipped with reverse-view LEED optics, which were used for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, and also with an Omicron variable-temperature scanning tunneling microscopy (STM) stage. The Mo (110) crystal was mounted on a home-built transferable sample holder with an integrated electron beam heater. The sample could be heated to 2400 K. The crystal temperature was measured with a W5% Re-W26%Re thermocouple. The Mo(110) crystal was cleaned by repetitive flashing (30×5 min) to 1200 K in a $p = 3 \times 10^{-7}$ mbar oxygen atmosphere to remove residual carbon contamination. The oxygen was removed by heating the sample at 2400 K for 15 s. The flashing to 2400 K was repeated before each experiment. This procedure was repeated until the carbon peak became invisible in the AES spectrum and the LEED pattern of a clean Mo(110) surface with sharp spots and low background was obtained. Tin (99.999%) was

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* Fax: +48 71 328 73 65.
E-mail address: akrupski@ifd.uni.wroc.pl.

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evaporated onto the crystal surface from a quartz crucible surrounded by a tungsten resistive heater in a vacuum of 5.0×10^{-10} mbar or better. Owing to the geometry of the system it was possible, during the deposition of tin on the sample surface, to record the Auger peak heights for the molybdenum MNN transition at 186 eV and the tin MNN transition at 430 eV under computer control. The time dependence of h_{Mo} (186 eV) and h_{Sn} (430 eV), where the h_{Mo} and h_{Sn} are Auger peak heights for Mo and Sn, respectively, were recorded in the dN/dE mode. In addition, in our measurements the adsorbate deposition is not interrupted for the recording of Auger peaks. Thus, our AES kinetics concern a continuous growth of the deposited layer. All STM measurements were performed at room temperature with W tips, in constant current mode. STM data were processed by freeware image-processing software [39].

3. Results and discussion

A plot of the AES peak heights of the substrate and of the adsorbate as a function of deposition time (AES(t) plots) enables the determination of the monolayer formation as well as the growth mechanism [40–43]. In case of our adsorption system, for room temperature, two linear parts of the AES(t) plot for 186 eV molybdenum can be distinguished, see Fig. 1. The scatter of experimental points for the tin signal is large because this signal taken with the use of the retarding field analyzer (RFA) is low, and the ratio of noise to signal is large. It seems from this part of the AES(t) plot that two-dimensional growth of the first and second layer is observed. If $\alpha^{A}_{S}=h_{S1}/h_{S0}$ define the coefficient of attenuation of the substrate Auger peak due to the presence of a monolayer of adsorbate, then the expected height of the substrate Auger peak for the layer by layer growth after completion of the *n =2nd, 3rd, 4th, …* layer is given by the equation $h_{Sn}=h_{S0}\,(\alpha^{A}_{S})^{n}$ [40–43]. Curve (1) in Fig. 1 is calculated for the Frank-van der Merwe (FM) growth with the formula described above, under the supposition that at the (h_{S1}; t_1) point the first tin layer is completed. It seems from comparison of our calculated and experimental AES(t) plot that also two-dimensional growth of the second and third tin layer is observed. However, one cannot recognize any distinct breaking point after deposition time t_3 on the experimentally found AES(t) plot. Such kind of shape of the AES(t) plot suggests Stranski–Krastanov growth mode (3D) after formation of the second layer. Further we will suppose, that the first linear part of the curve corresponds to the formation of the first layer (θ = 1 ML) of tin, where a 1 ML of Sn(111) film corresponds to an atomic packing density of 5.48×10^{14} atoms/cm^2. In Fig. 1, arrows denoted as "STM," mark the coverages, where the STM measurements described below have been performed.

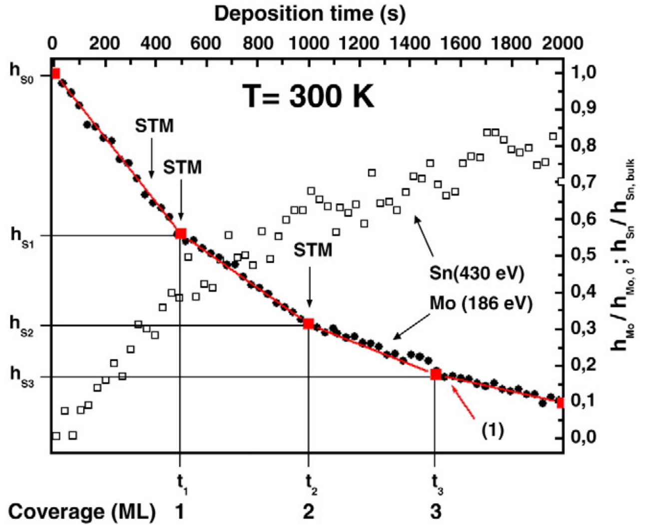

Fig. 1. AES(*t*) plot of Mo MNN and Sn MNN peak heights for silver deposition on Mo (110) face at T = 300 K. (1) AES(*t*) plot calculated for the Frank-van der Merwe growth.

Fig. 2 displays an STM image taken on a low-index Mo(110) substrate with terraces between 30 and 200 nm wide separated by monatomic steps aligned along the $\left[1\bar{1}1\right]$ direction. The height of the steps on the Mo(110) surface was measured by STM to be 2.3 Å. Fig. 2(b)–(e) shows STM images of the Mo(110) surface with different Sn coverages below two monolayers in order to illustrate the morphology of the Sn layers deposited on Mo at room temperature. The inset in Fig. 2(b) presents differentiated STM images with enhanced contrast. Fig. 2(b) shows a typical STM image corresponding to a submonolayer coverage of θ ≈ 0.7 ML. The bright features represent tin islands. A height profile (A) taken across the Sn islands (Fig. 2(c)) shows that these are one monolayer high islands. Such behavior of tin at the initial stage of growth on the Mo(110) surface confirm experimental results obtained during our AES measurements and previous studies [4]. The observed conical shape of tin islands on the substrate is a consequence of tip convolution and the finite island size [44,45]. At this point, an analysis of the STM measurements indicates that, for coverage less than 1 ML, the distribution of the tin islands is random on the Mo terraces. Namely, in Fig. 2(b) it seems that the tin islands do not prefer to grow along defined directions. Fig. 2(d) shows an STM image corresponding to a complete monolayer, i.e. θ ≈ 1.0 ML, as deduced from our AES experiment. The first tin two-dimensional layer is disordered. In addition, it is not possible to identify further positions of the tin islands in the first layer anymore because of the observed coalescence effect [44–51] from 0.55 to 0.65 ML. For a coverage θ ≈ 2 ML, see Fig. 2(e), a second complete but disordered tin layer is visible, as was expected from literature [4] and our AES studies. Generally, the growth modes are determined by the surface free energy γ of the film and the substrate. Namely, a thermodynamic description of growth is based on the specific surface free energy γ of a particular crystal facet, defined as the reversible work per unit area required to create the surface [52]. Different growth modes may be distinguished according to the balance between the surface free energy of the substrate (γ_S) and film (γ_A) and the interface energy (γ_I). Namely, layer-by-layer or Frank-van der Merwe (FM) growth is expected if $\gamma_S\geq\gamma_A+\gamma_I$. In heteroepitaxial systems, the total free energy increases with the number of film layers (n) so that the FM condition will no longer be valid at a critical film thickness (n^*) and three-dimensional (3D) crystals form (Stranski–Krastanov (SK) mode). The Volumer–Weber (VW) mode, where 3D growth begins immediately, corresponds to $n^*=1$. Table 1 contains sets of structural parameters and surface energies (γ) of Mo, Sn and also Pb, Ag, Au with respect to Miller plane orientation reproduced from [53–62]. The theoretically determined surface free energy of Mo(110) is $\gamma_{Mo}=3.0\ \mathrm{J\cdot m^{-2}}$ and that of Sn is $\gamma_{Sn(001)}=0.387\ \mathrm{J\cdot m^{-2}}$, $\gamma_{Sn(110)}\,0.509\ \mathrm{J\cdot m^{-2}}$, $\gamma_{Sn(100)}=0.716\ \mathrm{J\cdot m^{-2}}$. The higher surface energy of the Mo substrate (and the similar atomic size of Sn, see Table 1) allows the Sn film to grow in pseudomorphic registry with the substrate. When the sample is post-annealed to 800 K, the morphology of the surface changes, as shown in Fig. 3(a), (c), and (e). At this temperature the rearrangement of an existing tin film is observed. These STM results show similarity to previous studies concerning the possibility of a 2D growth mode [4] between 790 and 1020 K. However, one should remember that post annealing to the certain temperature (in our case 800 K) and growth at the same certain temperature 800 K could not be compared straightly because of different kinetic path ways. This rearrangement between the monolayer and bilayer regime gives rise to a non-regular well separated Sn island network, see Fig. 3(a), (c) and (e) for 0.7, 1.0 and 2.0 ML, respectively. The 0.7, 1.0 and 2.0 ML discussed here are the *initial* coverages before the post annealing procedure. The