

Growth, structural evolution and electronic properties of ultrathin films of Sn on W(110)



Suvankar Chakraborty^{*,a,b}, Krishnakumar S.R. Menon^b

^a Department of Applied Sciences, Haldia Institute of Technology, Haldia Purba Medinipur, 721657, West Bengal, India

^b Surface Physics and Material Science Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India

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ABSTRACT

Growth and structure of Sn on W(110) from submonolayer to thick film (up to 8 monolayers) coverages at room temperature (RT) and as-well-as for higher temperatures (HT) (up to 673 K) have been studied using low energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES) techniques. Surface structural evolution was studied where (3×1) , (1×3) and (1×4) LEED patterns were observed for RT whereas (3×1) and (1×4) LEED patterns were observed for growth at 673 K due to the energetically available adsorption sites for Sn atoms on W(110) surface. The absence of alloy formation between Sn and W was confirmed by the XPS data where surface core level shift of Sn $3d$ was observed whereas no shift was observed for W $4f$ levels. Detailed electronic structures were studied along $\bar{\Gamma} - \bar{H}$ and $\bar{\Gamma} - \bar{N}$ directions for Sn deposited on W(110) with the help of ARPES. ARPES data for RT and HT case is mostly similar. A pair of splitted bands was observed due to the deposition of Sn near the surface projected band gap.

1. Introduction

Study of Sn thin films is on the rise after the discovery of stanene [1,2] and also since it was shown that they could host topologically protected electronic surface states when Sn is deposited on a surface with a square lattice, InSb(001), and stabilizes in the -phase [3,4]. InSb(001) is one the few substrate where epitaxial thin films were reported [3–5]. On the other hand, Sn is reported to form alloy with noble metal surfaces viz., platinum, copper and gold on both (001) and (111) surfaces [6–16]. Our previous studies of Sn growth on Ag(001) [17,18] and Ag(111) [19] showed that Sn forms surface as-well-as bulk alloy where the growth was of body-centered tetragonal (bct) metal on a face-centered cubic (fcc) metal both at RT as well as moderate HT (473 K). So, in order to complete the Sn growth studies, it would be appropriate to study a case where there would be no alloying effect. In contrast to noble metals the problem of intermixing is greatly reduced in the case of refractory metals, such as tungsten. The high melting point, absence of intermixing with the overlayer and the possible growth at high temperatures, make tungsten a good candidate for this study. Moreover, tungsten has a large spin-orbit coupling, which may be used to modify the electronic properties of the overlayer. In this case of the deposition of bct metals on body-centered cubic (bcc) metals, there have been many excellent investigations of surface structures and growth modes [20–25]. Unlike tin and silver, tin and tungsten are very different

metals physically. Tungsten has the highest melting point of all the metals (3683 K), while Sn already melts at 505 K. Tungsten is hard and brittle, particularly in presence of impurities like oxygen and carbon whereas, tin is soft. Due to this reason, one expects Sn to grow on W(110) in a pseudomorphic layer as intermixing of these two metals is not possible.

Even though there is no detailed growth study available in the literature for Sn on W(110), there are few old papers available concerning Sn and tungsten [26–28] where the surface structure and stability of tin covered tungsten tip in a field-ion microscope were mainly studied. A close-packed structure was reported for Sn on tungsten at about 1000 K [27] which occasionally transformed into an ordered Sn-W alloy having cubic structure [28]. However, a more detailed surface structural study of Sn on similar surface, Mo(110) is reported [20,21,29,30]. Layer-by-layer growth was reported for Sn on Mo(110) for the first two layers then three-dimensional islands form. No alloy or intermetallic compound was observed for the Sn-Mo system at room temperature (RT), although upon annealing beyond 1073 K, Sn-Mo alloy was formed [20]. We will check whether similar energetics and growth mode can be observed for Sn growth on W(110).

In this paper, we have undertaken detailed growth study of Sn on W(110) both at RT and HT from sub-monolayer to thick coverages using Low Energy Electron Diffraction (LEED), X-ray Photoemission Spectroscopy (XPS) and Angle-resolved Photoemission Spectroscopy

* Corresponding author at: Department of Applied Sciences, Haldia Institute of Technology, Haldia 721657, Purba Medinipur, West Bengal, India.
E-mail address: suvophy11@gmail.com (S. Chakraborty).

(ARPES) techniques. For lower coverage, the evolution of surface structure is evidenced by LEED. The evolution of LEED pattern is explained with the help of an atomic model. The formation of Sn thin film on W(110) is also confirmed by XPS studies. Electronic structures have been studied after suitable growth optimization processes where band splitting was noticed. Our studies are important in understanding the growth mechanism of Sn films on W(110) and may shed some light on the electronic structure study particularly band-splitting.

2. Experimental details

Densely packed (110) surface of tungsten is the most used substrate for thin film growth. A number of recipes have been proposed to clean the surface of W(110) from its main impurity carbon (C) [31,32]. It is usually observed that annealing of a W crystal leads to the segregation of carbon from the bulk onto the surface. The presence of carbon can be confirmed by LEED as well as XPS. So, to remove the surface carbon impurities, the tungsten crystal is annealed in oxygen environment followed by a short time high temperature flashes. However, in this process the tungsten surface gets oxidised (forming WO_3) which can only be removed at HT ($T \geq 2300$ K). From the literature it is seen that, oxygen annealing temperature T_{ox} , oxygen partial pressure p_{ox} , flash temperature T_f and the flash duration vary among different cleaning procedures and may strongly influence the final outcome [33]. In laboratory, following the usual cleaning recipes it was found that sometimes impurity can be found other than the integer order spots (extra superstructural spots) on the surface as can be seen in Fig. 1(a) which can only be observed with a very sensitive CCD camera. In our case, the W(110) was cleaned by the process as suggested by Bode et al. [33] where oxygen anneal was done at five different pressure p_{ox} starting from 1×10^{-6} mbar to 2×10^{-8} mbar in the final step. At each step, annealing was done for 30 min. Flashing was done for very short time (~ 5 -10 s) at temperature > 2373 K. The final clean W(110) surface LEED pattern can be seen in Fig. 1(b).

The W(110) single crystal, (MaTeC GmbH, Germany) was mounted on PTS 2000 EB/C-C sample holder (PREVAC sp. z o.o., Poland) which could be heated up to 2300 K using electron beam heating. After cleaning the sample surface Sn was evaporated onto the W(110) using a well-degassed home-made Sn-evaporator. The rate was calibrated using a water-cooled quartz microbalance at the growth position and always kept ~ 0.1 ML/min. LEED measurements were performed at RT using a four-grid LEED apparatus (OCI Vacuum Microengineering) coupled with a highly-sensitive 12-bit CCD camera, to determine the crystalline quality of the deposited film, as well as the crystallographic symmetry directions. XPS and ARPES measurements were performed in the analysis chamber with base pressure better than 8×10^{-11} mbar and attached to the preparation chamber. ARPES measurements were performed using a combination of VG SCIENTA-R4000WAL electron energy analyzer with a 2D-CCD detector and a high flux GAMMADATA VUV He lamp attached with a VUV monochromator, which has been described in detail elsewhere [34]. We used He I_α (21.218 eV) resonance line to excite the photoelectrons from the sample surface for

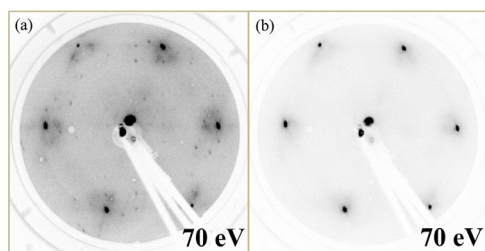


Fig. 1. LEED pattern of W(110) cleaned by (a) conventional high temperature oxygen annealing and flashing (b) method suggested by Bode et al. [33]. Some faint spots due to impurity on the surfaces can be seen in (a).

the ARPES measurements while Al K_α monochromatic X-ray source (1486.6 eV) from VG Scienta is used for XPS measurements. The binding energy (BE) of each peak was calculated by fitting the curve using CasaXPS software. All ARPES and XPS measurements were performed at RT with total experimental energy resolutions better than 0.1 eV and 0.6 eV, respectively.

3. Result and discussion

Sn was grown on W(110) both at RT as-well-as at HT (673 K) on to the tungsten face after cleaning the surface. The cleanliness of W(110) surface was confirmed by XPS where no carbon and oxygen contaminations were observed and also by LEED pattern where sharp p (1×1) spots were observed. In Fig. 2(a), we show the Sn 3d core-level spectra measured for different Sn coverages on W(110), grown at RT. Sn 3d spectra show a doublet corresponding to Sn $3d_{5/2}$ and Sn $3d_{3/2}$ with a spin-orbit splitting of about 8.3 eV. The Sn 3d peak position is shifted towards higher binding energy with increase in coverage [see Fig. 2(c)] before finally reaching the bulk value of Sn by 2 ML, similar to what was noticed in the growth of Sn on Ag(001) and Ag(111) [17–19]. The W 4f core level spectra with spin-orbit splitting of about 2.2 eV corresponding to W $4f_{7/2}$ and W $4f_{5/2}$ is shown in Fig. 2(b), where almost no binding energy (BE) shift can be observed with increasing Sn coverage as shown in Fig. 2(c). This is unlike the case of Sn growth on Ag where both Sn 3d and substrate Ag 3d peaks shift in the higher binding energy direction due to alloying [17,18]. This indicates that there is no alloy formation between Sn and W(110) at RT for any coverage. In order to study the growth of Sn on W(110), we plot the area under the Sn $3d_{5/2}$ and W $4f_{7/2}$ XPS peaks which was calculated using CasaXPS after Shirley background subtraction, as a function of the Sn coverage by taking into account the relative sensitivity factor in Fig. 2(d). The Sn (W) signal intensity increases (decreases) as the Sn coverage increases almost linearly up to 4 ML coverage. It is clear from the data that the substrate intensity does not get suppressed substantially despite the deposition of many ML coverages of Sn. It is difficult to conclude whether it is a Stranski–Krastanov growth or 3D island growth from the current set of data. It should be noted, in this regard that Stranski–Krastanov growth mode was also reported for Sn growth on Mo(110) [20]. However, beyond 4 ML Sn coverage the intensity of Sn (W) decreases slightly. The change in intensity is about 9% for Sn. So, beyond 4 ML it actually moves towards a constant value. This kind of local fluctuation in intensity was also reported for In/W(110) data [23] which is due to the change in sticking coefficient. Lattice misfit [$f = (a_s - a_f)/a_f$], where a_s and a_f are the lattice constant of the substrate and film respectively, plays a crucial role in determining the surface structure of grown film as elastic energy is proportional to f^2 [20,35], whereas dislocation energy is proportional to f . The strain energy due to the misfit also contributes to the surface energy of the deposited layer. Now, if the strain energy becomes large then it is favourable for the film to grow in three dimensional islands on top of the initially grown layer films. For Sn and W(110), there exists a misfit of $f = -0.6\%$ in the [001] direction taking lattice dimensions 3.16 and 3.18 and $f = -45.7\%$ in the [110] direction taking lattice dimensions 4.47 and 8.24 [20,36] which leads to a high strain energy in [110] direction between Sn layer and W substrate. Surface energy also plays a crucial role in determining the surface structure and growth mode of the grown films. Theoretically determined surface energy for W(110) is $\gamma_{W(110)} = 4.005$ Jm $^{-2}$ whereas surface energy for Sn(110) is $\gamma_{Sn(110)} = 0.620$ Jm $^{-2}$, which differ by a factor of ~ 7 [37]. As the free energy of Sn is lower than W, it is expected that Sn will wet the surface of W(110), from the free-energy considerations. Moreover, alloying is energetically not viable for this system because metal systems, in which a low surface energy metal is adsorbed on a high surface energy substrate, the first monolayer does not mix with the substrate [20] and neither bulk alloys nor stable intermetallic compounds are known for this system. Although from energy consideration it seems Stranski–Krastanov growth

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