CHAPTER 3

Growth and electronic structure of Sn on Ag(001)

3.1 Introduction

Tin (Sn) and its alloys have been at people’s service since 3000 BC when bronze (alloy of tin and copper) was produced in large scale. They have unique properties and find applications in various engineering fields. Correspondingly, there is abundant information waiting to be clarified surrounding these Sn-related materials. As the key element used for solder alloys, the properties of Sn alloys have been of great interest to the electronic packaging community. At the same time, the intriguing phenomenon of spontaneous Sn whisker growth from Sn/Sn-alloy thin films have bothered, yet also inspired materials scientists for over sixty years. Studies of two-dimensionally (2D) ordered thin films are of immense importance because of different properties.

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they display compared to their bulk counterparts due to the confinement in a thin layer. Monolayer of many layered materials such as graphite, molybdenum disulfide (MoS$_2$) etc. show interesting properties with potential applications to new types of devices have led the research in this direction lately [138–143]. Recently, it has been theoretically predicted that one monolayer (ML) tin, called 'stanene' is a topological insulator and may display dissipationless currents at its edges near room temperature [11]. Soon after, topological behavior for Sn based thin films were found experimentally [25, 48] on InSb(001) surfaces. Very recently, it is also predicted theoretically that graphene like sheet of Sn is possible on Au(111) surfaces [13]. Hence, it is important to study the detailed growth mechanism of Sn thin films on suitable noble metal substrates. Generally, the P-block metals like Pb, Bi, Sb form alloys with noble metals with high negative enthalpy of formation [15, 144] and are extensively used in fields of heterogenous catalysis [15, 16]. These surface alloys give rise to wealth of surface phenomena at atomic scale like formation of 2D phases, long-range undulation due to lattice mismatch, sandwich surface layers etc. which cannot be observed in bulk systems. Despite this, it should be pointed out that there are relatively a few studies of Sn growth on noble metal surfaces. Moreover to my knowledge, growth of Sn on Ag(001) substrate is not reported in the literature so far. This acted as a motivation to explore the growth and structure of ultrathin Sn films on Ag(001) substrate for different Sn coverages at both room temperature (RT) as well as high temperature (HT).

### 3.2 Types of tin

It is well known that Sn has two stable phases: $\alpha$-Sn with diamond structure ($a = 6.49$ Å) [145], a semiconductor with zero band gap and stable at temperatures below 286 K, while $\beta$-Sn, metal with tetragonal structure ($a = 5.81$ Å) [see Fig. 3.1] and stable above 286 K [146–148]. Sn is known to form a bulk alloy with Ag above
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Figure 3.1: Structure of tin. (a) white or beta tin (b) grey or alpha tin. Image generated by the VESTA (Visualisation for Electronic and STructual Analysis) software.

494 K with a stable structure of Ag₃Sn [149]. Below this temperature, $\beta$-Sn phase is expected while $\alpha$-Sn is known to be stable below 286.2 K, as per the Sn-Ag phase diagram [149]. As we are interested in the formation of epitaxial monolayer of Sn on Ag(001), the growth of Sn was performed at room temperature (RT) to stabilize the $\beta$-Sn phase and to avoid the formation of the bulk alloy phases and $\alpha$-Sn. In order to form a flat monolayer of Sn on Ag(001), lattice matching between Sn and Ag(001) are necessary. This appears to be difficult as Ag is face-centered-cubic with a lattice parameter of 4.09 Å while the normal cubic Sn ($\alpha$-Sn) as well as tetragonal Sn ($\beta$-Sn) are poorly lattice-matched with Ag(001). However, a second tetragonal phase of Sn [Sn(II)] is known to be formed at a higher pressure of 39 kbar [150], whose interatomic distances along the $a$- and $c$-axes are 3.81 Å and 3.48 Å, respectively. The lattice matching of this Sn(II) phase along the $ab$-plane with the Ag(001) is about 7 %, which could be sufficient to form a pseudomorphic layer of Sn on Ag(001) substrate. This Sn(II) phase could be stabilized by the Ag-Sn bonding at the surface during the kinetic-driven growth process at suitable conditions.
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3.3.1 Growth

A well-ordered Ag(001) single crystal substrate was prepared by repeated cycles of Ar$^+$ ion sputtering (600eV, 1µA) for 15 min, followed by annealing to 823 K for 30 min, until a sharp $p(1\times1)$ LEED pattern was observed. Cleanliness of the substrate was also confirmed with XPS measurements where no impurity peaks were detected. Additionally, the presence of sharp and intense Tamm-like surface state (SS) of Ag(001) at $\overline{M}$ symmetry point observed in the ARPES measurements also confirmed a clean well-ordered Ag(001) surface [151]. High purity Sn (99.999% from Alfa Aesar) was evaporated in the preparation chamber from a homemade resistive-type evaporator. The rate of deposition was maintained at 0.2 Å/min, calibrated using a water-cooled quartz crystal thickness monitor mounted on a linear drive which was moved to the sample position for rate measurements prior to deposition. Chamber pressure was maintained below $2 \times 10^{-10}$ mbar during Sn evaporation. Cleanliness and purity (like oxidation, contamination etc.) of the grown films were checked by XPS after every deposition. A ML is defined as an atomic density of $1.21 \times 10^{19}$ atoms/m$^2$, corresponding to that of the Ag(001) surface. Sn films of different coverages were grown on clean Ag(001) surface at RT [152].

3.3.2 Experimental results

3.3.2.1 LEED study

Sn was deposited on clean and well-ordered Ag(001) substrate kept at RT for coverages varying from submonolayer to 20 ML thick film. After every Sn deposition, the surface structure was monitored by LEED while the core and valence levels were measured by XPS and ARPES, respectively. The LEED patterns obtained for some of the Sn coverages studied here are shown in Fig. 3.2. An evolution of the LEED...
Figure 3.2: LEED patterns for different coverages of Sn grown on Ag(001) at RT. (a) clean Ag(001) with surface Brillouin zone and symmetry points. (b) 0.25 ML Sn showing \( p(2\times2) \) pattern. (c) 0.5 ML Sn having twin domain \((1\times10)\) pattern. (d) 0.75 ML Sn showing complex \((1\times6)\) twin domain pattern. (e) 1 ML Sn showing \( p(1\times1) \) pattern. (f) 1.5 ML Sn having faint \( c(2\times2) \) superimposed on \( p(1\times1) \) pattern. (g) 5 ML Sn with same pattern as (f). (h) 20 ML Sn with same pattern as (f) and (g). Two clear spots are visible within the marked circle at 50 eV electron beam energy in (h) as splitting of the spots is not clearly observed at 55 eV while it is apparent at the electron energy of 50 eV. See text for details.

Pattern till 1.5 ML Sn coverage is observed, while for higher Sn coverages no further evolution is observed and the pattern remains the same as that of 1.5 ML coverage. The \( p(1\times1) \) LEED pattern for clean Ag(001) substrate at a primary electron beam energy \( (E_p) \) of 55 eV is shown in Fig. 3.2(a). The sharp first-order \((1,0)\) LEED spots are distinctly visible here with the corresponding first surface Brillouin zone \( (SBZ) \) depicted over the LEED pattern indicating the symmetry points. For very small coverages \((0.1\text{ ML})\), no visible change in the LEED pattern (not shown) was observed as the amount of Sn is likely too small to form an ordered layer. For a coverage of 0.25 ML, a sharp and well-ordered \( p(2\times2) \) pattern was observed as shown in Fig. 3.2(b). Even though this \( p(2\times2) \) pattern was observed up to 0.33 ML (not
shown), the intensity of the spots was diminished indicating gradual weakening of this phase. The \( p(2\times2) \) pattern was lost completely beyond 0.4 ML and at 0.5 ML we observed a well-ordered pattern [see Fig. 3.2(c)] which could be indexed as a \((1\times10)\) twin domain LEED pattern. Due to the four-fold symmetry of the surface, the twin domains appear in LEED at right angles to each other. Interestingly, by 0.75 ML Sn coverage, the LEED pattern gets further modified to a more complex \((1\times6)\) twin domain pattern with split fractional order diffraction spots [see Fig. 3.2(d)]. The LEED pattern can be characterized as a single spot at \((0,2/6)\) and \((0,4/6)\) positions, doublet at \((0,1/6)\) and \((0,5/6)\) positions, with \((0,3/6)\) being split into a quartet, along with their analogues of an orthogonal domain. Up on completion of a Sn monolayer coverage, this complex LEED pattern disappears and a simple \( p(1\times1) \) pattern [see Fig. 3.2(e)] emerges. Up on further Sn deposition to 1.5 ML, a faint \( c(2\times2) \) pattern is observed in addition to the \( p(1\times1) \) LEED pattern [see Fig. 3.2(f)]. This LEED pattern was found to be stable up to 20 ML as can be seen in Fig. 3.2(g)-(h).

The LEED patterns provide some insight into the surface structure of Sn on the Ag(001) substrate. The well-ordered \( p(2\times2) \) pattern seen at 0.25 ML indicates that Sn atoms are arranged on the surface with double the lattice spacing as that of the substrate. From the Ag-Sn bulk phase diagram [149], no bulk alloy occurs at RT as the solid solubility of Ag in \( \beta \)-Sn is very small [149]. Because of the large differences in the melting points of Sn and Ag as well as the larger metallic radii of Sn atoms (1.62 Å) [43] compared to metallic radii of Ag atoms (1.44 Å), diffusion of Sn into the underlying Ag lattice to form solid solution should also be negligible at RT. Thus, the Sn atoms can form different high symmetry overlayer structures or an ordered surface structure which can yield the \( p(2\times2) \) pattern observed. The Sn atoms on the Ag(001) surface can occupy either four-fold hollow sites, bridge sites, top sites or substitute every alternate Ag atoms of the surface as can be seen in Fig. 3.3. In case of Sn/Ni(001), it was shown that the substitutional site is energetically most preferable for the Sn atom to occupy [36,37]. Moreover, growth of p-block elements
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Figure 3.3: Atomic model of arrangement of Sn on Ag(001) $p(2 \times 2)$ pattern. Sn atoms on the Ag(001) surface may be able to occupy (a) four-fold hollow sites, (b) bridge sites, (c) top sites or substitute site.

like Pb, Bi, Sb and Sn on Ag(111) surfaces are well known to produce a 1/3 ML ordered surface by substituting every third Ag atom of the surface layer, forming a $(\sqrt{3} \times \sqrt{3})$R30° reconstruction [33, 40, 41, 153, 154]. Similar energetics should also be followed in the case of Sn/Ag(001) and form an ordered surface structure. Thus, during initial stages of growth, Sn atoms are likely incorporated into the topmost layer of the substrate by substituting every alternate Ag atoms. As the surface energy of Sn(001) (0.39 Jm$^{-2}$) [155] is much smaller than the Ag(001) substrate (1.20 Jm$^{-2}$), Sn is expected to form an overlayer on top of the Ag(001) substrate. However, it is known that clean metal surfaces are always under tensile stress due to broken bonds [156]. As pointed out by Tersoff [157], incorporation of large atoms onto the surface is an efficient way to relieve this tensile stress even though they are immiscible in the bulk. Ag(001) surface is known to have a tensile stress [158]
of about 0.6 eV Å\(^{-2}\). So, incorporation of larger Sn atoms into Ag surface lattice would relieve the tensile stress and reduce the energy of the system rather than forming an overlayer. However, this ordered surface is rumpled due to the atomic size mismatch, with atoms of the constituent elements having different layer spacing than the underlying substrate layer spacing [36].

At 0.5 ML coverage of Sn, the surface structure displays a (1×10) reconstructed LEED pattern, which is unique among the submonolayer growth of a metal on metal. Similar reconstructed patterns are observed in case of clean metals (for e.g. V(100) [159] and Ir(100) [160], alloy surfaces (for e.g. Pt\(_{25}\)Co\(_{75}\)(100) [161]) and multilayers (for e.g. Au/Pt(100) [162]). In case of Sn on Cu(001), it is known that Sn atoms displace Cu atoms from their regular lattice cites [35], similar to the case of Sn/Ni(001) [36,37]. Hence, it is likely that the Sn atoms are substitutionally incorporated into the lattice replacing the Ag atoms, with lattice periodicity along one direction while providing a 10-fold periodicity along the perpendicular direction. However, the nature of surface ordering and the exact geometry of the surface coincidence cell need to be further investigated. The (1×6) LEED pattern obtained at 0.75 ML Sn coverage is further complicated by the fractional spot splitting and appears to originate from a moiré-like structure. This LEED pattern appears to have some similarity to the case of clean Pt(100) and Au(100) surfaces where the LEED patterns have been explained within the framework of a hexagonally closed packed surface layer resting on top of an atomic layer with a square lattice which is biaxially contracted with a large coincidence lattice [163]. Moreover, the relative position of the spots in Fig. 3.2(d) does not change with electron beam energy, ruling out any possible faceting. In order to understand the exact atomic surface structure of this phase, LEED IV calculations are required with plausible structure models, which is not attempted and is beyond the scope of the present study.

For the case of 1 ML Sn coverage, primarily a \(p(1\times1)\) pattern is visible along with broad and weak intensity streaks joining the (1,0) and (0,0) spots [see Fig. 3.2(e)].
The presence of $p(1\times1)$ LEED pattern, with the same in-plane lattice parameters as that of clean Ag(001) substrate, suggests that the Sn overlayer is either completely disordered so that one sees the underlying Ag(001) substrate pattern or the overlayer is well-ordered, pseudomorphically with the Ag(001) substrate. The high intensity observed for the $p(1\times1)$ spots indicates that this LEED pattern originates from the top layer of the surface and rules out the presence of disordered surface layer. Moreover, presence of well-ordered LEED patterns above the ML coverages (up to 20 MLs) necessitates the formation of an ordered surface layer for 1 ML coverage. Thus, it can be concluded that for 1 ML coverage, a pseudomorphic Sn layer is formed on Ag(001) surface. The presence of weak intensity streaks are likely due to the increased mosaicity of the surface, attributed to the rippling of the Sn film on the Ag(001) surface due to the atomic size mismatch between Sn and Ag atoms. In case of Sn on Cu(001), channeling experiments by Abel et al. [35] showed that an equal number of Cu atoms are displaced to accommodate the deposited Sn atoms and does not show any evidence of Cu-Sn bulk alloy formation up to about 1 ML coverage. This also suggest that in case of Sn on Ag(001) surface, the top layer Ag atoms are progressively replaced by Sn atoms till the formation of a monolayer Sn coverage without any Ag-Sn bulk alloy formation at RT.

Observation of similar LEED pattern for Sn coverages above 1.5 ML (see Figs. 3.2(f)-(h)) suggests that the surface structure does not evolve any further and indicates the growth of bulk Ag-Sn alloy film. This LEED pattern is clearly a superposition of two different LEED patterns; a weak $c(2\times2)$ pattern superimposed on an intense $p(1\times1)$ pattern. Here, two spots are clearly visible near each integral order spot position, as marked by the encircled dotted lines [see Fig. 3.2(g)]. The splitting of the $(1x1)$ LEED spots can be observed for all Sn coverage above 1 ML. However at 55 eV electron energy, the intensity of the $(1x1)$ spots corresponding to Ag(001) is maximum and the other (inner) split spot of the $c(2\times2)$ pattern cannot be observed clearly. For this reason, the LEED pattern for 20 ML at 50 eV electron...
energy [see Fig. 3.2(h)] has been shown where the split spots can be observed very clearly. The outer sharp $p(1\times1)$ spots are with the same in-plane lattice parameters as that of clean Ag(001) substrate, while the faint inner spot corresponds to the $c(2\times2)$ pattern. The separation between these two spots is also found to be constant ($\sim 6\%$ of the in-plane Ag lattice parameter), irrespective of the Sn coverage in the 1.5-20 ML range. The $p(1\times1)$ pattern appears to be originating from Ag(001) surface, though it is unlikely to be from the underlying Ag(001) substrate as the pattern remains unchanged up to the 20 ML Sn coverage. So, it suggests that above 1 ML Sn coverage, Ag segregates to the top surface, forming platelets of Ag and yielding an intense $p(1\times1)$ pattern. Further, our ARPES measurements suggest the formation of Ag platelets on the top surface (see discussion of Fig. 3.6). Even though LEED pattern of Ag$_3$Sn bulk alloy surface is not available in the literature, LEED pattern for a closely matched system, Pt$_3$Sn(001) shows a similar $c(2\times2)$ pattern [164]. Thus, the observed weak $c(2\times2)$ pattern is most likely to arise from the Ag-Sn (Ag$_3$Sn) bulk alloy film formed beneath the Ag overlayer platelets. Moreover, the lattice parameter estimated from the $c(2\times2)$ LEED pattern is found to be 6.16 Å which is close to the lattice parameters of bulk Ag$_3$Sn [165]. So, the observed LEED pattern is a mixture of $p(1\times1)$ and $c(2\times2)$ spots, originating from the Ag platelets and Ag-Sn bulk alloy phase, respectively.

### 3.3.2.2 XPS study

In Fig. 3.4(a), the Sn 3$d$ core-level spectra measured for different Sn coverages on Ag(001) for RT growth are shown. Sn 3$d$ spectra shows a doublet corresponding to Sn 3$d_{5/2}$ and Sn 3$d_{3/2}$ with a spin-orbit splitting of about 8.3 eV. In order to study the growth mode, the area under the Ag 3$d_{5/2}$ and Sn 3$d_{5/2}$ XPS peaks is plotted as a function of the Sn coverage in Fig. 3.4(b). As Sn coverage increases, the intensity of the Sn 3$d$ peaks increases while the intensity of the substrate Ag 3$d$ peaks decreases,
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Figure 3.4: (a) XPS of Sn 3d core-level for different Sn coverages. A gradual shift of the peaks towards higher binding energy can be seen. (b) Area under the curve for Ag 3d$_{5/2}$ and Sn 3d$_{5/2}$ for different Sn coverages. Area of Sn 3d$_{5/2}$ (Ag 3d$_{5/2}$) initially increases (decreases) before reaching a constant value for coverage more than 1.5 ML. Shift in binding energy with coverage for Sn 3d$_{5/2}$ peak position in (c) and for Ag 3d$_{5/2}$ peak position in (d).

as expected. However for both Ag and Sn signals, we can clearly observe an abrupt change of slope of the curves at 1.5 ML coverage, as marked in the figure by dotted line. Up to 1.5 ML, there is a linear decrease of the Ag signal and a linear increase of the Sn signal. Above 1.5 ML Sn coverage, the Ag and Sn signal intensities do not change much and saturate to a fixed value, up to the highest thickness (20 ML) studied. This abrupt change of slope clearly indicates a dramatic change in the growth mode of the Sn on Ag(001) surface. The linear increase (decrease) of the Sn (Ag) signal for sub-monolayer Sn coverages indicates the growth of a pure Sn layer, without bulk alloying or island formation and completing a flat monolayer by 1 ML Sn coverage. This is in agreement with the LEED results [see Fig. 3.2], indicating that the completed Sn monolayer is ordered epitaxially with Ag(001) substrate. However in Fig. 3.4(b), the change of slope occurs at 1.5 ML instead of
1 ML Sn coverage, due to the sensitivity of XPS to deeper layers. The constant Ag and Sn signal for higher Sn coverages indicates the formation of a Ag-Sn bulk alloy film with a near constant stoichiometry, as also indicated by the similar LEED pattern up to 20 ML film. Surface stoichiometry obtained from the XPS analysis indicates an Ag rich phase, in agreement with the presence of Ag overlayer on the bulk alloy film. However, our measurements are in qualitative agreement with the formation of bulk $\text{Ag}_3\text{Sn}$ alloy film. This also confirms that Ag atoms diffuse through the Sn layer to the surface forming the Ag-Sn alloy, though such an alloy formation appears to be suppressed until the completion of the Sn monolayer. As the size of the Sn atoms is larger than Ag atoms, the diffusion of Sn atoms into the Ag lattice is highly unlikely. As the size of the Sn atoms are larger than Ag atoms, the diffusion of Sn atoms into the Ag lattice is highly unlikely. In fact, the diffusion constant of Sn into Ag is known be $1.9 \times 10^{-23} m^2/s$ at 473 K [166]. However, the Ag atoms can diffuse into the Sn layers much faster as it occurs via an interstitial mechanism with a small activation energy [167]. This helps the migration of Ag atoms to Sn layer and facilitate the formation of Ag-Sn alloy.

In Fig. 3.4(c), the binding energy (BE) shifts of Sn $3d_{5/2}$ core-level peak position with Sn coverage is shown. Up to about 1.5 ML coverage of Sn, the BE position of Sn $3d_{5/2}$ increases almost linearly while for higher coverages, the BE position gets saturated. BE position of the bulk Sn $3d_{5/2}$ peak is 485.0 eV [168], which is marked in Fig. 3.4(c) as a dotted line. For very low coverages of Sn, the Sn atoms are isolated impurities on Ag(001) substrate and show lower BE position due to the reduced coordination at the surface. As the Sn coverage increases, the effective coordination of Sn atoms also increases resulting in shift of the their BE to higher values in a near-linear manner. By 1 ML coverage, the Sn monolayer is completed and the BE position reaches close to the bulk value [see Fig. 3.4(c)]. This also confirms that Sn is grown as a progressive flat layer up to 1 ML, as otherwise, clustering of Sn atoms would occur increasing the coordination and BE position to near-bulk value.
for the submonolayer coverages of Sn. For higher Sn coverages, the coordination number and BE position of Sn get saturated. However, the saturated BE position for Sn $3d_{5/2}$ peak appears to be higher than the bulk value, possibly due to the the formation of Ag$_3$Sn alloy phase for higher Sn coverages. It is also interesting to note the behaviour of Ag $3d_{5/2}$ BE position [see Fig. 3.2(d)] with Sn coverage; it varies in a similar manner as Sn $3d_{5/2}$. When Sn atoms are in contact with Ag substrate, from the simple electronegativity considerations it may appear that there is an electron transfer from Sn to Ag, as Ag has a higher Pauling electronegativity than Sn (1.9 compared to 1.8). Then, we would expect the Ag $3d$ peaks to shift to lower BE values. However, both Ag $3d$ and Sn $3d$ peaks shift in the same direction, to the higher BE position with increasing Sn coverage. This is similar to the situation observed in case of Au-Sn alloys [169]. It is shown that BE position can shift in either direction depending on the change in the valence configuration in metals during alloying [170,171]. Thus, the shift of the Ag $3d$ to the higher BE is likely due to the $4d\rightarrow5s$ intra-atomic charge transfer [169], which counters the shifts to lower BE due to the charge transfer from Sn to Ag.

3.3.2.3 ARPES study

The electronic structure of Sn films grown on Ag (001) substrate at RT is also studied using ARPES technique. In Fig. 3.5, the ARPES spectra collected at $\overline{M}$ position of the surface Brillouin zone using He I$_\alpha$ photons at RT are shown. The spectrum of clean Ag(001) substrate shows a featureless region up to about 3.7 eV due to the Ag $5sp$ derived bands. At 3.8 eV, a sharp and narrow feature corresponding to the emission from a Tamm-like surface state (SS), characteristic of the (1×1) symmetry of Ag(001), is observed [see Fig. 3.5]. This state is known to be derived from the Ag $4d_{xy}$ orbitals split-off from the bulk $d$ band by surface potential [172]. This SS entirely vanishes with the deposition of even 0.25 ML of Sn at RT, suggesting the complete
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Figure 3.5: ARPES spectra at $\overline{\mathbf{M}}$ point of Ag(001) for different coverage of Sn grown on Ag(001) using He I$_\alpha$ photons. Dashed lines are guide to the eye.

destruction of the (1$\times$1) translational symmetry of the Ag(001) surface, as also observed by the LEED pattern [see Fig. 3.2]. This further confirms our LEED and XPS results that the Sn does not form clusters at RT, but is uniformly distributed, forming a $p(2\times2)$ Ag-Sn surface ordered alloy. A weak structure seen near the SS position in Fig. 3.5, is attributed to the bulk band [marked ‘B’ in Fig. 3.6(a)] of silver [151]. In case of 1 ML Sn deposited on Ag (001), a sharp feature at 4.1 eV BE with similar width and dispersion as that of the Tamm SS on Ag(001) is seen. However, for higher coverages of Sn, this feature at 4.1 eV disappears and a new intense peak at 4.5 eV shows up. In case of 0.25 ML, two peaks at 5.7 eV and 6.3 eV are observed which are absent for clean Ag(001), indicating their surface origin. The peak at 5.7 eV is prominent for 0.25 ML while its intensity decreases for higher Sn coverages indicating the origin of this feature from the $p(2\times2)$ Ag-Sn ordered surface alloy. It is known from previous studies [173–176] that peak at 6.3 eV is a clear signature of the segregated Ag atoms on top of the surface. As the Sn atoms displace the Ag atoms from the surface, it is likely that these displaced Ag atoms segregate
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on the surface yielding this peak at 6.3 eV in the 0.25 ML case. This 6.3 eV peak is present till 1 ML Sn coverage, however, is absent for higher coverages of Sn. This also indicates that for higher Sn coverages, the surface Ag layer (on top of the Ag-Sn alloy) is well-ordered (as shown by LEED patterns in Fig. 3.2) and does not yield the segregated (clustered) Ag signal at 6.3 eV.

![Figure 3.6: Band dispersion near $\overline{M}$ point of (a) clean Ag(001) with Tamm surface state (marked SS and denoted by black dashed line) and bulk band (marked B and denoted by yellow dashed line). (b) 1 ML Sn coverage. (c) 5 ML Sn coverage. (d) 20 ML Sn coverage. Dashed lines in (b)-(d) shows the position of modified surface state. Dashed lines are guide to the eye. The data were taken with He I$\alpha$ photons. See the text for details.](image)

The ARPES band dispersion images close to $\overline{M}$ position obtained using He I$\alpha$ photons at RT is shown in Fig. 3.6 for clean Ag(001), 1, 5 and 20 ML Sn coverages. Fig. 3.5 displays the ARPES spectra extracted from Fig. 3.6 at the $\overline{M}$ position. For clean Ag(001) [see Fig. 3.6(a)], the high intensity Tamm SS can be observed (marked as black dotted line) at 3.8 eV BE at the $\overline{M}$ position. Along with this, the bulk band of Ag (marked as ‘B’ and represented by yellow dashed lines) can be observed
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at 3.9 eV. The intensity around 4.1 eV and 4.5 eV are due to further bulk bands of Ag(001) [151]. The ‘B’ band almost overlaps with the Tamm SS while the other bulk bands are weaker compared to the SS and are barely visible in Fig. 3.6(a). As discussed in the earlier paragraph, for 1 ML Sn coverage, we observe a sharp feature at 4.1 eV BE position (see Fig. 3.5). In Fig. 3.6(b), this feature (marked as black dotted line) at the \( \overline{M} \) position with similar dispersion as that of the Tamm SS can be seen, but shifted to higher BE position by 0.3 eV. This modified Tamm SS is unlikely to be originated from the Sn monolayer, but is a characteristic feature of the Ag(001) surface. One possibility is that the Sn monolayer is not covering the Ag(001) substrate completely and we observe the Tamm SS from the uncovered Ag(001) surface regions. However, this would have resulted in the observation of Tamm SS at 3.8 eV and not at 4.1 eV. The presence of shifted Tamm SS suggests that it is originating from the Ag platelets segregated on top of the Sn monolayer. The shift of the Tamm SS can be understood to be due to the different surface potential experienced by these Ag atoms sitting on top of the Sn layer. The sharp peak at 4.5 eV observed in Fig. 3.5 for higher Sn coverages can also be observed in Fig. 3.6(c) and (d) (marked as black dotted line) with similar dispersion as that of SS. We associate this feature also with the surface state (resonance) originating from the Ag(001) platelets on top of the Ag-Sn alloy. However, in this case, it is further energy shifted due to yet different surface potential the Ag atoms experiencing on top of the Ag-Sn alloy. These shifting of the modified surface state (or surface resonance) BE positions can occur only when the top layer Ag atoms of the Ag platelets (which are responsible for producing the SS) are sitting on top of the Sn or Ag-Sn layer. These modified surface resonances (for higher Sn coverages) are broader compared to the SS (at 3.8 eV) due to the hybridization with the bulk Ag 4\( d \) states [151] as well as with the Sn 4\( d \) states, however, are much narrower than the bulk Ag 4\( d \) states (see Fig. 3.5). Similar shifts of the SS have also been observed in other systems [174,175,177] as well as on the Sn growth on Ag(001) at 473 K [173], due to
the changes of the surface potential, leaving the surface coated with a layer of Ag atoms. Further, the presence of Ag bulk states along with the modified SS for higher Sn coverages up to 20 ML (see Fig 3.6) confirms the presence of Ag platelets on the film surface as these states could not have come from the substrate Ag (001). These findings are also in good agreement with the growth model obtained from the LEED and XPS measurements.

The band structure of Ag(001) has been reported in literature in great detail [178,179]. So, band structure of Ag(001) will not be covered in detail in this thesis. The main interest here is the electronic structure of the Sn/Ag(001) alloy. The electronic valence bands of Sn alloy films grown on Ag(001) at RT have been shown in Fig. 3.7. The grown film surfaces have been probed by He I $\alpha$ ($\hbar \omega = 21.2$ eV) along $\Gamma - X$ direction of Ag(001). The valence bands shown in the figure are plotted as 'binding energy ($E_B$) vs parallel component of momentum ($k_\parallel$)'. The Ag 4$d$ bands appear within the 4-7 eV binding energy window. Due to this reason the ARPES image is plotted upto 4 eV binding energy below the Fermi energy ($E_F$) to avoid the 4$d$ Ag(001) bands. Only Ag $sp$ band is visible in the shown energy range in Fig. 3.7(a) at $X$ points which meets another $sp$ bands form the next Brillouin zone around the Fermi level. With deposition of 0.1 ML Sn, the crossing at $X$ moves downward in binding energy to -0.6 eV and crosses Fermi level at $k_\parallel = 1.1$ and 1.25 Å$^{-1}$ respectively as can be seen in Fig. 3.7(b). For 0.25 ML coverage, the crossing moves to -1.45 eV binding energy at $X$ point (see Fig. 3.7(c)). Bands, similar to the ones at the $X$ point but very faint in nature is appeared at $\Gamma$ point. The exact meeting point can not be located due to the masking by another parabolic bands which starts from -0.8 eV BE at $k_\parallel = 0.58$ Å$^{-1}$ dispersing in higher BE energy side reaches a minimum at -2 eV BE at $\Gamma$ point. Another parabolic band is observed at higher binding energy compared to the other one. The second parabolic band has a minimum at around -1.2 eV at $\Gamma$ disperse to cross the Fermi level at $k_\parallel = 0.35$ and -0.35 Å$^{-1}$. The crossing at $X$ further shifted to -1.7 eV BE for 0.33 ML coverage.

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Figure 3.7: ARPES data probing the valence bands along $\Gamma - X$ direction for (a) bare Ag(001) (b) 0.1 ML (c) 0.25 ML (d) 0.33 ML (e) 0.5 ML (f) 0.75 ML (g) 1 ML (h) 2 ML (i) 10 ML coverage of Sn.

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0.5 ML coverage, it is shifted to -2.2 eV with the appearance of another two bands split off from the already existing bands at $\overline{X}$ (see Fig. 3.7(e)). Though the new bands disperse in the same way, they do not cross each other as they hybridised with the other bands to open a gap between them. The scenario changes for 0.75 ML coverage. From Fig. 3.7(e), it is clear that the crossing shifted to further higher BE side around -3 eV. But the point is not clear due to the presence of other bands. The split off bands are still present around the $\overline{X}$ points. The straight split off band, in-between $\overline{\Gamma} - \overline{X}$ direction, crosses the Fermi level at -1.22 Å$^{-1}$. Two comparatively thick metallic bands start to appear around $\overline{X}$ starting from the crossing around -3 eV BE dispersed linearly in the upward direction and finally crosses the Fermi level at -0.91 Å$^{-1}$ and -1.45 Å$^{-1}$. These two bands look like a mirror image of Ag sp bands making a ’V’ shape at $\overline{X}$ point. The crossing moves to -3.2 eV for 1 ML coverage. The ’V’ shaped band becomes prominent with a separation of 0.6 Å$^{-1}$ (two ends at -1.45 Å$^{-1}$ and 0.85 Å$^{-1}$). Beyond this coverage the band structure remains mostly stable and no further changes is observed for higher coverage than 2 ML. The crossing can not be observed as it is moved beyond the BE range covered during scanning with photon. From Figs. 3.7(h)-(i), it is clear that there is no difference in band structure for 2 ML and 10 ML coverage. Beyond 2 ML, the band dispersions remain same for all coverage (not shown here) upto the highest coverage studied. The shifting of the crossing at $\overline{X}$ to the higher binding energy with increase in coverage may be due to the fact that with more and more Sn the band loses the Ag property and Sn bands becomes prominent and it hybridised and finally reaches a stable electronic structure. We have also performed the band structure along the $\overline{\Gamma} - \overline{M}$ direction, but not shown here. As it is clear, the evolution of the electronic band structure is rather complex as it goes through many phases as can be observed in the LEED pattern in Fig 3.2. The complete understanding of the evolution of the surface electronic structure of the system requires the help and support of detailed
3.4. High temperature study

We have undertaken a detailed growth study of Sn on Ag(001) substrate at an elevated temperature of 473 K for different Sn coverages to understand if there is any difference in growth mechanism between RT growth and HT growth. Sn films of different coverages were grown on Ag(001) at 473 K while all the measurements were performed at room temperature (RT) [173]. The films were grown by same process as discussed in previous section for RT case.

3.4.1 LEED study

In Fig. 3.8, the LEED pattern obtained for a range of Sn coverages on Ag(001) for electron energies corresponding to the maximum intensity of the LEED spots are shown. In Fig. 3.8(a), the clean Ag(001) LEED pattern along with the corresponding first SBZ indicating the symmetry points can be seen. In case of 0.1 ML Sn coverage, a weak c(2×2) pattern (see Fig. 3.8(b)) is observed which changes to a p(2×2) pattern at a coverage of 0.25 ML as seen in Fig. 3.8(c). The well-ordered p(2×2) diffraction pattern indicates that the Sn atoms are arranged in such a way that their lattice parameter is twice that of Ag. This p(2×2) structure is formed by the same procedure followed in the case of RT growth by substituting every alternate Ag surface atom with Sn atoms and is likely to form substitutionally ordered surface alloy. By 0.5 ML Sn coverage, this p(2×2) pattern disappears with the emergence of a p(1×1) pattern with the same in-plane lattice parameters as that of clean Ag(001). This p(1×1) pattern can be observed up to 3 ML Sn coverage, which is the highest coverage studied here. However, we expect similar p(1×1) pattern to exist for even
3.4. High temperature study

Figure 3.8: LEED pattern for different Sn coverages grown on Ag(001) at 473 K. (a) Clean Ag(001) with surface Brillouin zone and symmetry points. (b) 0.1 ML Sn showing weak c(2×2) pattern. (c) 0.25 ML Sn showing p(2×2) pattern. (d) 0.5 ML Sn, (e) 1 ML Sn, (f) 3 ML Sn, all showing p(1×1) LEED pattern. Electron primary beam energy is mentioned on the figure for each case.

higher Sn coverages. So, this p(1×1) surface structure is stable with Sn beyond 0.5 ML coverage.

During initial stages of growth, the Sn atoms are incorporated into the topmost layer of the silver substrate by substituting every alternate Ag atoms. Though from surface energy consideration it may appear that Sn should form an overlayer on top of Ag as the surface energy of Sn(001) (0.39 Jm$^{-2}$) [155] is much smaller than the Ag(001) substrate (1.20 Jm$^{-2}$), this is not the situation here. It is known that clean metal surfaces are always under tensile stress due to broken bonds [156]. Incorporation of large atoms onto the surface is an efficient way to relive the stress as proposed by Tersoff [157], even for systems that are immiscible in the bulk. Now,
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Ag(001) has a surface tensile stress \([158]\) of about 0.6 eV Å\(^{-2}\), which can be relieved by incorporation of large size Sn atoms into the Ag surface lattice. However, due to the atomic size mismatch, these surface alloys show a rumpled surface, with atoms of the constituent elements having different layer spacing than the underlying substrate layer spacing \([36]\). Observation of \(c(2\times2)\) substitutionally ordered surface has been reported in case of Sn/Ni(001) \([36]\) and Au/Cu(001) \([157]\) although in the present case, \(c(2\times2)\) ordering is seen only for very small coverages (0.1 ML) of Sn. By 0.25 ML Sn coverage, it gives way to a \(p(2\times2)\) surface ordering. Apart from the presence of \(c(2\times2)\) and \(p(2\times2)\) spots, we also observe two perpendicular streaks joining the (1,0) and (0,0) spots (see Figs. 3.8(d)-(e)). The origin of these streaks are due to the increased mosaicity of the grown surface \([180]\), due to the surface rumpling induced by the atomic size mismatch between Sn and Ag atoms.

The origin of \(p(1\times1)\) pattern in addition to a diffuse background, with the same in-plane lattice parameters as that of clean Ag(001) for Sn coverages above 0.5 ML is rather intriguing. The streaking of the spots is attributed to the rippling of the film as mentioned earlier, while the diffused background intensity is due to the presence of surface defects. Unlike in case of RT, we do not observe the double spots for the integral spots. So the situation is different from the RT case and we do not have the weak \(c(2\times2)\) pattern. The appearance of \(p(1\times1)\) pattern suggests that either the Sn overlayer is completely disordered that we see the underlying Ag(001) substrate pattern or the overlayer is well-ordered, with the Ag(001) substrate. Even for the highest coverage studied, clear \(p(1\times1)\) spots relative to the diffused background can be observed. For 3 ML Sn coverage, the expected thickness of the film is about 10 Å in case of layer-by-layer growth (1 ML Sn is 3.23 Å thick) and even thicker in case of alloy formation. As the inelastic mean free path of electrons at these energies through Sn is only about 6 Å \([181]\), it is clear that the \(p(1\times1)\) LEED pattern originates from the top layers and not from the underlying Ag(001) substrate. Although, formation of 3D clusters of Sn on Ag(001) substrate can explain these results, our XPS and
3.4. High temperature study

ARPES results completely rule out this possibility (see below). Diffusion of Sn into the bulk Ag is highly unlikely due to their size mismatch. In fact, at the growth temperature (473 K), the diffusion constant of Sn into Ag lattice is found [166] to be $1.9 \times 10^{-23} \text{m}^2/\text{s}$. However, the Ag atoms can diffuse into the Sn layers much faster as it occurs via an interstitial mechanism with a small activation energy [167]. This helps the migration of Ag atoms to Sn layer and facilitate the formation of Ag-Sn alloy as well as an ordered Ag overlayer, also confirmed by our ARPES studies. In fact, during the growth at 473 K, both Sn and Ag atoms have increased mobility and this helps to form the surface alloy.

3.4.2 XPS study

![Figure 3.9](image)

**Figure 3.9:** (a) XPS of Sn 3d core level for different Sn coverages with relative magnification factor. (b) Relative area under the curve for Sn 3d$_{5/2}$ and Ag 3d$_{5/2}$ for different Sn coverages. (c) Shift in binding energy with coverage for Sn 3d$_{5/2}$ (left axis) and Ag 3d$_{5/2}$ (right axis) with increasing Sn coverage.

In Fig. 3.9(a), the Sn 3d core-level spectra measured for different Sn coverages on Ag(001), grown at 473 K is shown. Sn 3d spectra shows a doublet corresponding to
Sn 3d_{5/2} and Sn 3d_{5/2} with a spin-orbit splitting of about 8.3 eV. Here the Ag 3d spectra is not shown as there is no change in the spectral characteristics compared to the clean Ag(001) substrate. However, the important information such as the change in the peak area as well as shift in the binding energy are shown in Fig. 3.9(b) and (c), respectively. In order to study the growth of Sn on Ag(001), we plot the relative area under the Ag 3d_{5/2} and Sn 3d_{5/2} XPS peaks as a function of the Sn coverage by taking into account the relative sensitivity factor in Fig. 3.9(b). The Sn (Ag) signal intensity increases (decreases) as the Sn coverage increases. It is clear from the data that the substrate intensity does not get suppressed substantially despite the deposition of ML coverages of Sn. Moreover, the slow increment of the Sn 3d_{5/2} intensity with the Sn coverage is also not consistent with the layer-by-layer growth of Sn on the Ag(001) substrate (for details see the discussion section). In Fig. 3.9(c), the binding energy (BE) shifts of Sn 3d_{5/2} as well as Ag 3d_{5/2} core-level peak position with Sn coverage can be seen. The BE of Sn 3d_{5/2} peak position increases in a near-linear manner up to 0.5 ML while for higher coverages the BE further increases towards a saturation value. The higher binding energy shifting of both Sn 3d_{5/2} and Ag 3d_{5/2} peaks is an indication of Ag-Sn alloy formation within the film, as discussed in the next paragraph.

The XPS data provide some insights into the growth of Sn on Ag(001) at 473 K. The relative area under the curve for Sn 3d_{5/2} increases almost linearly up to 2 ML. In case of a typical layer-by-layer growth mode, one expects to have breaks in the slope during completion of each monolayer or when the growth mode changes from one to another [182], similar to the RT growth case. Thus, the smooth intensity variation with the absence of any sharp breaks in the slope suggests a similar growth mode at least above Sn coverage of 0.5 ML. This is also consistent with our LEED observations that there is no structural evolution above 0.5 ML Sn coverage. Moreover, the relative intensity variation of Sn 3d_{5/2} and Ag 3d_{5/2} observed in Fig. 2(b) also appears to differ from the layer-by-layer growth mode as neither the substrate Ag 3d_{5/2} intensity drops
substantially nor the Sn $3d_{5/2}$ intensity grows substantially even after deposition of 3 ML coverage of Sn. These are strong indications of alloy formation between Ag and Sn atoms during growth at 473 K. In order to understand the detailed growth mode, it is possible to estimate the XPS intensity variation based on the attenuation length of the photoemitted electrons with a model [182]. However in the present case, the alloy phase diagram of Ag-Sn [149] is rather complicated with many possible phases. Even for a known Sn coverage, the exact thickness of the film depends on the concentration or concentration gradient of the alloy film. The observation of an ordered Ag overlayer on top of the alloy film further complicates these efforts. In absence of crucial information such as film thickness and alloy composition, we have not attempted such quantification of the XPS data as this could lead to erroneous results. Further microscopic characterization of the system will be required to understand the detailed growth mechanism at play here.

The known BE position of the bulk Sn $3d_{5/2}$ peak is at 485.0 eV [168], which is marked in Fig. 2(c) as a dotted line. For very low coverages of Sn, the Sn atoms are isolated (impurity atoms) on Ag(001) substrate and show lower BE position due to the reduced coordination at the surface. It is well-known that there is surface core level shift of few hundred meV observed for metal surface due to reduced coordination number [183–185]. By 0.5 ML Sn, the BE reaches near bulk value indicating a near bulk coordination for the Sn atoms. For higher coverages of Sn, the BE increases beyond the bulk value indicating alloy formation with Ag. Here, it is interesting to note the behaviour of Ag $3d_{5/2}$ BE position [see Fig.3.9(c)] with Sn coverage can be explained with the same argument discussed for RT growth case. In case of 3D island growth of Sn on Ag(001) substrate, the Sn $3d$ is expected to shift towards the bulk value for small coverages as the 3D clusters are formed and the Ag $3d$ is not expected to shift at all. Thus, the shift of both Ag $3d$ and Sn $3d$ towards higher binding energy confirms the formation of Ag-Sn alloy in the film.
3.4. High temperature study

3.4.3 ARPES study

Figure 3.10: ARPES spectra at $\overline{M}$ point of Ag(001) for different coverages of Sn taken with He I$_\alpha$. Tamm-like surface state for Ag(001) (SS) at a binding energy of 3.8 eV and modified surface state at a binding energy of 4.0 eV for top Ag layer are marked with dashed lines in the figure.

The electronic structure of Sn films grown on Ag(001) substrates at 473 K were studied using ARPES. In Fig. 3.10, the ARPES spectra collected at $\overline{M}$ position of surface Brillouin zone using He I$_\alpha$ photons is shown. The spectrum for clean Ag(001) substrate is already discussed in the RT growth case. With deposition of even 0.1 ML Sn, the intensity of the Tamm SS drops drastically while it is completely absent for 0.25 ML, suggesting complete destruction of the (1×1) translational symmetry of the Ag(001) surface. The feature observed at 3.9 eV for 0.1 and 0.25 MLs (near the SS position) is the characteristics of the bulk band (B1) of silver [151] [see Fig. 3.11(b)].
For Sn coverages of 0.5 ML and more, the growth of a sharp feature at 4.0 eV with similar width and dispersions as that of the Ag(001) Tamm surface state is observed.

\[ \Gamma \]
\[ M \]
Ag(001)
(a)
\[ \Gamma \]
\[ M \]
0.25 ML
(b)
\[ \Gamma \]
\[ M \]
1 ML
(c)
\[ \Gamma \]
\[ M \]
2 ML
(d)

Figure 3.11: Band dispersion near \( \overline{M} \) point of (a) clean Ag(001) with Tamm surface state (marked SS and denoted by black dashed line). (b) 0.25 ML Sn coverage. (c) 1 ML Sn coverage. (d) 2 ML Sn coverage. Blue dashed lines in (c)-(d) mark the position of the modified surface state (resonance). Dashed lines are guide to the eye. The data were taken with He I\( _{\alpha} \) photons.

ARPES band dispersion images close to \( \overline{M} \) point measured using He I\( _{\alpha} \) photons can be seen in Fig. 3.11 for clean Ag(001), 0.25 ML, 1 ML and 2 ML Sn coverages. Fig. 3.10 displays the ARPES spectra extracted from the Fig. 3.11 at \( \overline{M} \) position. The high intensity Tamm SS [marked by black dotted line in Fig. 3.11(a)] can be seen in case of clean Ag(001) surface. The other features at higher binding energy for Ag(001) are due to the three bulk bands of Ag at 3.9 eV, 4.1 eV and 4.5 eV, respectively, as described by A. Goldmann et al. [151]. The band at 3.9 eV almost overlaps with the Tamm SS while the other two bands are barely resolved in Fig. 3.11(a). In case of 0.25 ML, the strong intensity at \( \overline{M} \) point vanishes as the Tamm SS gets destroyed.

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3.4. High temperature study

[see Fig. 3.11(b)]. However in case of 1 and 2 ML Sn coverages, as mentioned earlier, there appears a sharp Tamm-like SS feature at about 4.0 eV (marked by blue dashed line) slightly below the original Tamm SS.

The complete destruction of Tamm SS state by 0.25 ML Sn coverage is consistent with the observation of $p(2\times2)$ LEED pattern which can be attributed to the formation of uniformly distributed substitutional $(2\times2)$ ordered Ag-Sn surface alloy. This also rules out the possible formation of 3D Sn clusters on Ag(001) substrate which would have exposed some bare Ag(001) surface resulting in the observation of Tamm SS features in the ARPES spectrum. The appearance of modified Tamm-like surface state for higher Sn coverage suggests that Ag atoms diffuses to the top of the Sn layers forming $(1\times1)$ ordered Ag layer. The Tamm-like surface state observed from this Ag layer is shifted in energy to 4.0 eV due to the different surface potential experienced by these Ag atoms sitting on top of Ag-Sn alloy layer. Similar shifted Tamm-like SS have been reported in case of Cr/Ag(001) also [174,175]. In case of 3D cluster growth for higher Sn coverages, this will expose some bare Ag(001) surface leading to the presence of Tamm SS (with BE 3.8 eV). The absence of any SS feature at 3.8 eV for higher Sn coverages (see Fig. 3.10) confirms that no cluster growth of Sn occurs on Ag(001). For all the Sn coverages, we can observe a strong intensity at 4.5 eV which is the contribution from Ag 4$d$ states. This indicates that the Ag atoms have a substantial presence within the Sn film even for the highest film coverage studied. In case of 0.1 ML Sn coverage, two peaks at 5.7 eV and 6.3 eV are observed (see Fig. 3.10) which are absent for clean Ag(001), indicating their surface origin. The peak at 5.7 eV is prominent for 0.25 ML and possibly indicating the origin of this feature from the $p(2\times2)$ Ag-Sn alloy surface. For higher Sn coverages, the peak at 5.7 eV gets broader and merges with the valence band possibly indicating the formation of bulk Ag-Sn alloy at Ag(001) surface.

The band dispersions observed in Fig. 3.11 near $\overline{M}$ helps to understand the top layer structure of the Sn/Ag(001) system. The modified Tamm SS band observed

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at 4.0 eV in Fig. 3.11(c)-(d) originates from the ordered Ag overlayer on the Ag-Sn alloy film as its binding energy is shifted to higher energies due to the different surface potential but with similar width as well as dispersions. As observed in Fig. 3.11(c)-(d), the bulk bands of Ag(001) are also clearly present in the ARPES spectra for higher Sn coverages. However, it is unlikely that these bulk Ag bands originate from the underlying Ag(001) substrate, as the thickness of the alloy layers are expected to be much higher than the inelastic mean free path of electrons, as discussed earlier. Thus, our ARPES measurements strongly suggest the presence of an ordered Ag overlayer on top of the Ag-Sn alloy layers forming a sandwich structure, also consistent with our LEED and XPS results. Presence of this Ag overlayer is also possibly the reason along with the Ag-Sn alloy formation for the persistent Ag $3d_{5/2}$ intensity with increasing Sn coverage, as observed in Fig. 3.9(b).

The valence bands for Sn-Ag alloy grown on Ag(001) at 473 K was probed by He I$_\alpha$ ($\hbar\omega = 21.2$ eV) and data was recorded along $\Gamma - \mathbf{X}$ direction as can be viewed in Fig. 6.11. The overall band structure is similar to the band structure observed for RT growth. The bands are comparatively more sharp and intense due to the better ordering than the RT growth sample. The images are presented for 0-4 eV BE window due to same reason as to avoid intense Ag $4d$ bands. The Ag $sp$ bands can be clearly seen for bare Ag(001) at $\mathbf{X}$ in Fig. 6.11(a) where the two bands meet at the Fermi level making a inverted 'V' like shape. In a similar manner as in RT growth case, the crossing is shifted to the higher BE side with increase in coverage. The crossing shifted to -1 eV for 0.1 ML to -3.3 eV for 3 ML through -1.8 eV (for 0.5 ML), -2.7 eV (for 1 ML). The other bands appeared in case of RT growth around the $sp$ bands near the $\mathbf{X}$ point is missing in this case. Two metallic bands can be observed in Fig. 6.11(f) for the highest coverage studied i.e. 3 ML originating from the crossing point near -3.3 eV disperse linearly in the upward direction and finally cross the Fermi level at -1.4 Å$^{-1}$ and -0.78Å$^{-1}$. A faint thick feature, crossing the Fermi level at -0.9Å$^{-1}$ is noticed near this linearly dispersing bands. We have also
3.5. Comparison of room temperature and high temperature growth

Figure 3.12: ARPES data probing the valence bands along $\Gamma - X$ direction for (a) bare Ag(001) (b) 0.1 ML (c) 0.25 ML (d) 0.5 ML (e) 1 ML (f) 3 ML coverage of Sn.

performed the band structure along the $\Gamma - M$ direction, but not shown here. Similar to the case of RT case, the evolution of the electronic band structure is complex and a complete understanding of the electronic structure of the system require a detailed surface electronic structure calculations, which will be the subject of a future study.

3.5 Comparison of room temperature and high temperature growth

In this section, the growth of Sn on Ag(001) for RT and 473 K is compared. For higher growth temperature, the surface mobility of Sn and Ag atoms are expected to be considerably enhanced along with the enhancement of the Ag diffusion through the
Sn layers. Moreover, high temperature growth is expected to facilitate the formation of Ag₃Sn alloy as it is close to the bulk alloying temperature [149]. For a minute amount of Sn coverage (0.1 ML), a faint $c(2\times2)$ LEED pattern was observed at 473 K [173], while no such ordering was observed at RT. Here, the amount of Sn deposited is likely too small to form patches of ordered Sn domains at RT, due to the reduced mobility. Even though for 0.25 ML, both RT and 473 K growth produces $p(2\times2)$ substitutionally ordered surface, the LEED patterns and the surface ordering are found to be superior for the RT growth. This is likely due to the larger intermixing (disorder) between the Sn and Ag atoms at 473 K due to the enhanced mobilities. However, for 473 K growth, no surface reconstructions or surface structure evolution was observed beyond 0.5 ML Sn coverage and a constant $p(1\times1)$ LEED pattern was observed. Here, bulk Ag-Sn alloying occurs beyond 0.5 ML Sn coverage, while for RT growth, Ag-Sn alloying occurs beyond the 1 ML Sn coverage. No bulk alloying is found to occur for the RT growth up to the completion of pseudomorphic Sn monolayer on Ag(001). The formation of this Sn layer could be attributed to thermodynamic competition between different surface parameters such as the surface energy, Ag-Sn alloy formation energy and surface mobilities. Detailed theoretical calculations would be very helpful to understand the detailed mechanism behind the monolayer stabilization. For higher Sn coverages, bulk Ag-Sn alloy film is found to form for both RT and 473 K growth on Ag(001) with an ordered Ag monolayer coating. The difference in the growth mode between RT and 473 K can be clearly observed in the XPS growth curves, where a progressive layer growth occurs at RT till Sn monolayer is completed while alloy formation takes place beyond 0.25 ML, in the case of 473 K growth. The BE variation of the XPS core-levels confirms the Ag-Sn alloy formation for higher Sn coverages. The ARPES spectra at the $\overline{M}$ position shows the modified Tamm-like surface states for both RT and 473 K growth. For RT growth, this clearly shows the Ag layer on Sn monolayer as well as that on the Ag-Sn alloy film, while in case of 473 K growth, only one shifted Tamm-like SS
state corresponding to Ag layer on the Ag-Sn alloy film is observed. Even though we confirm the alloy formation, we could not clearly identify the chemical composition of the alloy phases due to absence of crucial information such as film thickness and alloy composition. We have not attempted such quantification of the XPS data as this could lead to erroneous results. Further microscopic characterization of the system will be required to understand the detailed growth mechanism at play here.

3.6 Summary

Growth of Sn on Ag(001) substrate at RT as well as HT (473 K) from submonolayer coverages to near-bulk limit was investigated using LEED, XPS and ARPES techniques. For RT growth, surface structural evolution was observed, from substitutional $p(2\times2)$ Ag-Sn ordered surface to different reconstructed surface structures and further to pseudomorphic Sn layer on Ag(001). Above ML coverage of Sn, the surface structure showed a $c(2\times2)$ pattern superimposed on the $p(1\times1)$ LEED pattern, which did not further evolve with increased Sn coverage. XPS studies showed that the growth mode for submonolayer region and above ML region to be very different. For submonolayer coverages, Sn atoms progressively formed the monolayer without alloying with Ag, while for thicker Sn coverages, it formed Ag$_3$Sn-like bulk alloy with an ordered Ag overlayer coating, consistent with the LEED results. On the other hand for growth at elevated temperature, for very small (0.1 ML) Sn coverages, a $c(2\times2)$ LEED pattern was observed which modifies into a $p(2\times2)$ pattern by 0.5 ML Sn coverage, suggesting the formation of a substitutional $(2\times2)$ ordered Ag-Sn surface alloy. For higher Sn coverages the Sn atoms form a bulk alloy with the substrate atoms, as confirmed by the XPS results. ARPES experiments indicated, both for RT and HT the presence of segregated Ag atoms for submonolayer coverages and established the formation of a monoatomic Ag overlayer on Ag-Sn bulk alloy for higher Sn coverages. These studies confirmed that Ag atoms can diffuse into the Sn
layers via interstitial sites with a small activation energy and facilitate the formation of Ag-Sn alloy. The band structure shows the shifting of Ag $sp$ bands crossing with rise in coverage for both RT and HT with some extra surface bands for RT growth case. Further microscopic and LEED IV studies along with detailed surface electronic structure calculations are required in order to understand the detailed growth mechanism, morphology and electronic structure of the Ag-Sn alloy system on Ag(001) surface.