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On the stability of pseudomorphic α-Sn on InSb(001) to temperature and film thickness

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Thin films of α-Sn deposited on InSb(001) at 160°C have been studied. The films, grown to a total thickness of 80 Å, showed similar but more pronounced diffraction peaks compared to a monolayer of α-Sn on InSb grown at 30°C. A film of 80 Å was shown to change its behaviour at ~ 181°C. It is believed to collapse to β-Sn imbedded in a thin film of α-Sn.

Recently, there has been growing interest in the formation of lattice matched, substrate stabilized films of α-Sn on semiconductor surfaces for the purpose of investigating their properties for device applications [1]. Yuen et al. [1] have grown films of α-Sn on InSb(001) up to thicknesses of 2000 Å, observing structural changes with thickness as growth proceeds and finally measuring promising electrical properties of the deposited films. The α-Sn was grown at temperatures near room temperature. Earlier, work has been carried out where α-Sn films were grown on CdTe [2], in which case, as for InSb, the lattice parameter match is very close. The purpose of that effort was to measure the band gap properties of α-Sn and its variation with thickness using electron energy loss techniques. Films in the thickness range of 40–80 Å showed band offset energy dependence with thickness. Again the growth was performed near room temperature. A further study [3] indicates that the transition point of α → β Sn on InSb(001) varies inversely with film thickness but films of thickness down to 250 Å only have been studied – so that it might be anticipated that thinner films could be more stable.

Another interesting study has appeared [4] on a different system which is the formation of superlattices of α-Sn and Ge(001). There are two particularly interesting features to this study: (1) that thin layers of α-Sn can be substrate stabilized on Ge having a lattice mismatch of 13% indicating that the volume difference between α and β-Sn is a major barrier to transformation of the α to β enantiomorphs [5], and (2) that the thin layers of α-Sn are stable to high temperatures (200–300°C) during the deposition of Ge on the α-Sn.

Recently, the authors [6] showed that α-Sn grown at 30–40°C, the typical temperatures employed to date, did not show a great degree of ordering as evidenced by He atom scattering. For example, LEED indicated a reconstruction to a (1 × 1) structure for a monolayer of α-Sn adsorbed on InSb(001) but He atom scattering showed only a broad scattered distribution. However, cooling the sample to 140 K, to reduce inelastic effects showed small diffraction peaks. It was then shown that, upon annealing the α-Sn to temperatures between 100 and 200°C well defined diffraction peaks were developed in the same positions for this monolayer of α-Sn and in addition half order peaks showed up in the LEED pattern. As a result of this finding a study was made of various properties of the α-Sn films such as annealing temperatures, differences between the first and subsequent layers, growth at various temperatures and finally a 15 Å film was proven to be stable to over 200°C without any changes in structure. The present study is an extension of the previous work to investigate the stability of α-Sn as a function of thickness. It also leads the way to the investigation of higher deposition temperatures in order to better prepare films for device application. Before proceeding with the results it is useful to quote figures for α-Sn film stability as a function of thickness and temperature found by different workers. Asom et al. [7] quotes a transition temperature of 130°C for good films but does not relate this number to a specific thickness. Menendez et al. observes a transition at 115°C for a film thickness of 250 Å while thicker films (5000 Å) transform to β-Sn at ~ 75°C.

The experimental arrangement has been described previously [6] but, in brief, LEED and He atom scattering were employed to observe the growth process and changes induced by heating α-Sn films. The InSb(001) wafer was back etched to remove polishing damage in a CP-4A solution prior to insertion in the vacuum chamber. The sample was then cleaned in situ by ion bombardment (Ar^+, 500 eV, $\leq 0.4\ \mu A/cm^2$) and annealed to 300–340°C for 10–15 min. The Sn source (Cerac 99.999%) was placed in a molydenum container situated 30 cm from the sample. A single monolayer took ~ 15 min to deposit. A monolayer was measured by both He scattering and a quartz microbalance.

Before proceeding with a discussion of the results it is useful to describe briefly the surface interactions that influence atom scattering and render it a very surface sensitive tool and a useful addition to the study of deposition on semiconductors. The He atom is about 3 Å in diameter (a large probe) but scatters exclusively from the surface by the repulsive potential developed as the atoms electrons overlap the surface electronic structure. The attractive portion of this van der Waals interaction does not play a major role in deflecting the He atom except in the vicinity of a step, defect or a polarized molecule or atom on a terrace. In this latter circumstance the scattering cross section can increase considerably because of large change in trajectories. If, during reconstruction the electronic environment of the surface is changed locally, then such a situation could also change the scattering cross section and influence the peak intensity. Because of its physical dimension the probe atom is comparable to steps on the surface, kinks in steps and vacancies on terraces so that intuitively it is seen that the interplay and development of such features, during growth and recovery for instance, will influence scattering considerably. An example of such large changes in scattering, both (00) and diffraction peaks, is a similar study of the annealing of Sn on CdTe [8]. In this case Sn diffuses into the bulk and Te outwards with drastic changes to the scattering, AES signals and half width of the (00) peak. Semiconductors, as a group of materials, have basically relatively open structures so that, not only is the spacing between rows of atoms comparable to the He atom (and its wavelength ~ 1 Å) but the depth of the corrugations are relatively large. This leads to a scattering pattern with many diffraction peaks.

After cleaning the crystal the LEED showed a basic (1×4) pattern with streaks [6] in the $\times 2$ position and He scattering gave the same (1×4) with broader 1/2 order peaks in the equivalent LEED streak positions. In this study the first monolayer was deposited at ~ 0°C and annealed to 230°C while following depositions were made in 8–10 Å amounts at 160°C and checked with LEED and He scattering before proceeding. 80 Å of α-Sn was deposited in total. The presentation of the results will be as follows: (1) demonstrate the differences between the first layer, i.e., α-Sn–InSb(001) and subsequent layers, i.e., α-Sn–α-Sn using growth and anneal data, (2) show the anneal curves to indicate the region of surface temperature where growth in this study was carried out, i.e., 160°C and (3) to present the He scattering results for various film thicknesses up to the point where the film was collapsed and compare these results with that of the collapsed layer.

Fig. 1 shows evidence of the growth behaviour of α-Sn on InSb(001) and on α-Sn as monitored by the (00) He peak intensity. Fig. 1a indicates how the (00) peak falls very sharply for a coverage (θ) of $1 \rightarrow 2\%$ before showing a small maximum prior to declining to a small signal. This

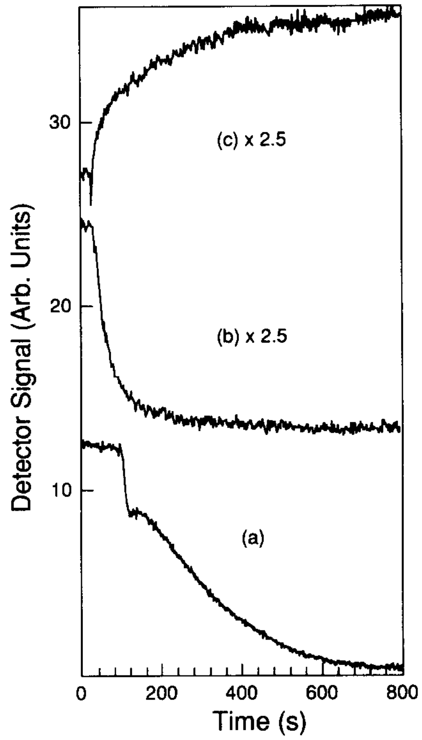

Fig. 1. Growth and recovery behaviour for α-Sn films. (a) Variation of the (00) peak height for the deposition of Sn on InSb (001). The feature at a coverage of 5–7% is indicative of a change in growth mode. Surface temperature, $T_s = 2$°C, $E_0 = 16$ meV. (b) Growth of α-Sn on 30 Å of α-Sn at 160°C, $E_0 = 16$ meV. The shape of the curve is different for this surface. (c) Recovery curve of the (00) beam for an 80 Å α-Sn film when the Sn source is switched off. $T_s = 160$°C, $E_0 = 16$ meV.

result was taken at 2°C and has been similarly demonstrated at 30–40°C previously [6]. The results taken at a slightly higher temperature (30–40°C) show a smaller initial fall and a more pronounced maximum. This is evidence of the greater mobility of adsorbed Sn atoms at the higher temperature and is in agreement with the interpretation of this feature to be a change in growth mode at low coverage. In contrast, fig. 1b shows the growth of α-Sn on 30 layers (of α-Sn) deposited at 160°C. There is a clear difference in behaviour as the signal falls rapidly (but only by about 30% of the total signal) and without showing a small maximum. The authors have previously [6] grown α-Sn layer-by-layer with the resultant same behaviour. Consequently one layer of α-Sn is sufficient to mask the effect of the InSb(001) surface as seen by this technique. This has also been carried out at 30°C where the only change is to reduce the base signal to a much lower level but retain the same shape. Fig. 1c demonstrates the mobility of the Sn atoms on α-Sn in the form of a recovery curve, i.e., the Sn source is switched off and the signal recovers over a period of 5–10 min to its previous value. The reason for the initial (00) signal decline is the presence of mobile terrace atoms of large scattering cross-section, which decrease the (00) intensity, as well as the presence of irregular 2D islands having dendritic growth properties at higher coverages. On removing the Sn flux the dendritic growth rapidly recovers and the islands subsequently slowly reach equilibrium due to less rapid inter-island Sn atom diffusion. It has been previously demonstrated that the degree of recovery increases with surface temperature.

Figs. 2a and 2b show the anneal curves for the second and first layers of α-Sn, respectively. Almost no change in the (00) signal is observed until about 80°C (dependent on the α-Sn deposition temperature, i.e., lower T_D yields earlier annealing). After this point the signal grows to a maximum at about 200–230°C depending upon the first or second layer. For the first layer, fig. 2b (where α-Sn is forming on InSb(001)) the anneal curve in the region of 200–230°C remains flat while in the case of Sn on α-Sn the signal begins to fall in this temperature region. This indicates the subtle difference between the mobility of Sn on InSb(001) and of Sn on α-Sn as well as the rigidity of the lattice. α-Sn is clearly slightly "softer" and the Debye–Waller effect is sufficient to lower the signal slightly for the second layer. At 230°C the heater is switched off and the signal increases. These observations, made in our previous study [6], precipitated experimentation of growth at different temperatures and 160°C was chosen as the present growth temperature as by so doing the outcome was similar to deposition at 30°C with subsequent annealing to 230°C. This point is about half way up the more rapid annealing region.

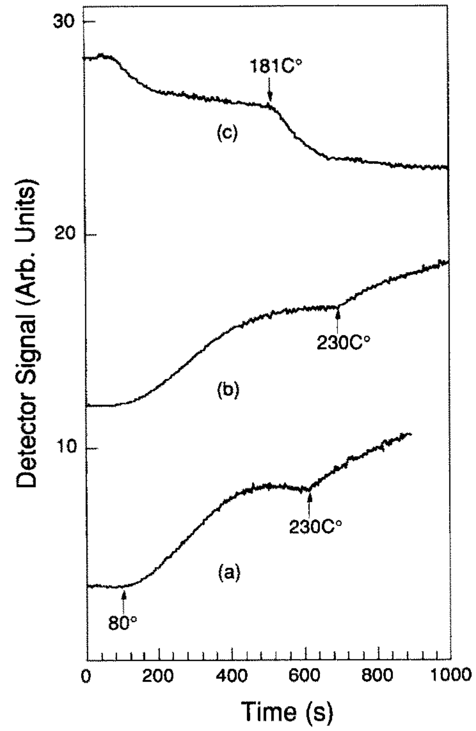

Fig. 2. Influence of temperature on α-Sn films on InSb(001). (a) Anneal curve for the second monolayer of α-Sn deposited on α-Sn. Annealing begins at ~ 80°C and is complete at 230°C. $E_0 = 16$ meV. (b) Similar anneal curve for the first layer of α-Sn on InSb(001). At the highest temperatures the curve (a) bends over indicating the Sn is more mobile on α-Sn and the Debye–Waller factor is higher, $E_0 = 16$ meV. The rise in signal at 230°C in both cases is due to the cooling of the crystal. (c) (00) signal height as a function of temperature during the collapse of an 80 Å α-Sn film. The initial decrease in signal is due to heating the crystal. At 181°C a sharp drop occurs which signifies the change in the nature of the α-sn to include nucleii of β-Sn, $E_0 = 16$ meV.

Figs. 3a–3c show the results of He diffraction scans for the second, twenty-eight and fortieth layers, i.e., 2, 56 and 80 Å thick layers. All the curves show the same basic pattern which LEED indicates to be a two domain (1 × 2) structure as found by Stradling et al. [1] for thicker layers deposited at ~ 30°C (but not for thin layers < 20 Å) and which demonstrate the influence of annealing. The half order peaks are slightly broader than the first order peaks in all cases and this trend tends to increase as the layer thickness increases. Further, there is a small decline in the diffraction peaks with thickness, otherwise the pattern remains the same. These scans were taken at about 140 K to enhance the elastic scattering but no changes were observed compared to the scans taken after each deposition (8–10 Å) at ~ 30°C. The broadening of the half order peaks are in agreement with the LEED result of a two domain (1 × 2) structure. Clearly, the film of 80 Å thickness is still α-Sn and is stable. In fact, a film of thickness 60 Å, after deposition at 160°C was slowly heated to 180°C for 15 min without any degradation of the diffraction pattern.

The final result involves the temperature stability of the 80 Å α-Sn film. Farrow et al. [4] has observed the change of α-Sn to β-Sn for thicker

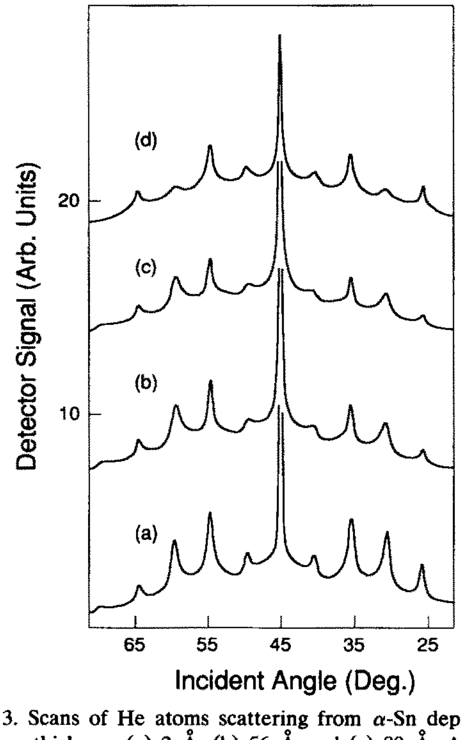

Fig. 3. Scans of He atoms scattering from α-Sn deposits of various thickness (a) 2 Å, (b) 56 Å and (c) 80 Å. All show similar features except that the thinner deposits have slightly sharper features. In particular the 1/2 order peaks broaden with thickness. $T_s = 140$ K, $E_0 = 16$ meV. (d) He scan of a collapsed 80 Å α-Sn film having been further heated to 230°C for 15 min. The (00) peak has fallen by a factor of 2.7 due to random scattering while the 1/2 order peaks have fallen probably due to a stressed film. As in a thin α-Sn film the first order peaks have increased. $T_s = 140$ K, $E_0 = 16$ meV.

films (5000 Å) where the transition temperature was ~ 80°C and higher than the enantiomorphic transition of 13.2°C. Menendez et al. observed a transition at 115°C for a 250 Å film. In the present case the thinner films are visible to the eye (but largely transparent) and on heating could be seen to change colour and become duller presumably due to the development of β-Sn nucleii. This phenomenon could be followed by measuring the (00) peak height as the deposit was slowly heated and is shown in fig. 2c. There are several slopes to the curve prior to the signal finally levelling out, the first of which is due to the Debye–Waller effect as the heating occurs. At the point shown by the arrow and over a temperature range of ~ 5°C the (00) falls rapidly and levels off. This is the point where the film has changed to nucleii of presumably β-Sn as the LEED pattern is a (1×1) pattern but of low intensity. Further, fig. 3d shows the result for the He scan for this film. There is no indication of bare InSb(001)(1×4) surface but only a pattern similar to that of α-Sn with half order peaks of much lower intensity and slightly higher first order peaks. The (00) peak is down in intensity by a factor of 2.7 and no extra peaks are observed in the He pattern (or LEED). This evidence suggests the following picture. The lowered intensity of the 1/2 order peaks tends to confirm the low contrast (1×1) LEED picture. The collapse of the film changes part of the α-Sn to nucleii of β-Sn which are random in orientation (no extra LEED spots) and in addition their bulk reduces the coherent scattering from the surface, i.e., partially by shadowing and partly from incoherence. There is no evidence of a film of this thickness facetting as seen by Asom et al. [7]. However, as has been proven earlier, a stable thinner film of α-Sn is still attainable at 180°C so that the final result resembles Stranski–Krastanow equilibrium with higher defect density at the interface between the α- and β-Sn (as the volume change is significant 5.7 and 7.39/cm^3) – a 26% change. This film was then subjected to further heat treatment of 15 min at 230°C but without further modification. The reason for this was to induce Ostwald ripening, i.e., change small nucleii to larger sizes. However, the diffusion rate at 180°C was clearly adequate to reach equilibrium. However, there is a subtle change from the as deposited α-Sn and this final condition and perhaps the reason derives from the constraint on the thin film due to the presence of dislocation around and under the β-Sn nucleii. The outcome is a greater preference for a (1×1) domain structure.

As an alternative possibility, and because chemical analysis was not part of the experiment it is necessary to point out that a very dilute alloy could form without substantially changing the scattering pattern or seriously influencing the collapse temperature of the film. In a case where diffusion across a boundary has been observed for Sn – the case of CdTe [8], very large changes were observed in the scattering behaviour as well as AES signals.

In conclusion this study strongly indicates that useful thick annealed films (and by extrapolation perhaps up to 100 Å thick) can he made at 160°C such that studies can be made of the electronic properties of the films and superlattices engineered by deposition of other materials on the α-Sn.

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