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PREPARATION AND CHARACTERIZATION

STUDY OF THE PHASE TRANSITION IN HETEROEPITAXIALLY GROWN FILMS OF α-Sn BY RAMAN SPECTROSCOPY

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The transition in heteroepitaxially grown films of tin from the semiconducting (α) phase to the metallic (β) phase depends on the film thickness and the surface orientation. Investigations of the optical Raman phonon of α-Sn demonstrate that α-Sn films grown on InSb(001) surfaces show a sharp α ↔ β transition at a temperature T^* which depends on the film thickness. For a film thickness of less than 60 nm the transformation occurs at $T^* = 115\,°\mathrm{C}$, which is much higher than the bulk T^* value of 13.2 °C. Evidence for the formation of β-Sn on (110) and (111) surfaces is given from Raman and reflection high energy electron diffraction investigations.

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1. INTRODUCTION

Tin can undergo a phase transition from its metallic (β) phase to a lower temperature semiconducting (α) phase. For the bulk material this phase transition occurs below 13.2 °C and was reported for the first time by Erdman[1] in 1851. The transformation is accompanied by a 27% increase in volume leading to powdery α-Sn or at least to highly strained α-Sn crystals with a large number of cracks. A preparative method of recrystallizing α-Sn from a mercury solution was invented by Ewald and Tufte[2]. With this method it was not possible to grow crystals of high perfection and some of the results obtained for samples prepared with this method are claimed nowadays to be influenced by a fairly high degree of mercury doping[3]. Recently, a new method of growing high quality α-Sn films has been reported by Farrow *et al.*[4] These researchers used molecular beam epitaxy (MBE) of tin atoms onto clean (001) surfaces of CdTe and InSb substrates at room temperatures. Films of α-Sn could be prepared at room temperature up to a thickness of 0.5 μm. Another remarkable finding was that these films showed a much higher transformation temperature of approximately 70 °C which was ascribed to a substrate stabilization effect.

To investigate the substrate effects in more detail we grew α-Sn films of various thicknesses by MBE on top of InSb substrates of different orientations. The phase transition α ↔ β was studied by Raman spectroscopy.

In the following section the preparation of α-Sn and the experimental set-up are described. Experimental results are discussed in Section 3.

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2. EXPERIMENTAL DETAILS

Oriented and polished crystal plates of InSb of area 7 mm × 7 mm and thickness 1.2 mm were cleaned by sputtering with argon ions of energy 500 eV. After the sputter damage had been annealed these surfaces showed well-developed reflection high energy electron diffraction (RHEED) patterns. The cleanness of the substrate was checked by measuring the photoemission 4d core line spectra of indium and antimony and by angularly resolved photoemission spectroscopy (ARUPS) of the InSb valence band[5]. All peaks appearing in the latter spectra could be explained as transitions from the InSb band structure. No additional peaks originating from hydrocarbon contamination could be detected.

Films of tin were grown by MBE on top of InSb substrates using a Knudsen effusion cell. During growth the vacuum was 3×10^{-10} Torr. The growth, at a typical rate of about 0.2 nm s^{-1}, was monitored by RHEED. Further details concerning the growth conditions and the reconstruction of the various surfaces are given in ref. 6.

Raman experiments were performed with the MBE-grown tin films using the 752.5 nm line of a Kr$^+$ laser. The sample was mounted in a glass oven in which the pressure was kept below 10^{-5} Torr. Special care was taken to prevent any laser annealing of the samples. Focusing of the laser beam with spherical lenses induced a local $\alpha \leftrightarrow \beta$ transformation. This laser-induced transformation could be suppressed by using cylindrical lenses and keeping the laser power below 100 mW. Under these conditions we estimate a power density of 10 W cm^{-2}. All measurements were performed in the backscattering configuration, which is usual for opaque materials. The scattered light was analysed with a 1 m Jarrell Ash double monochromator and detected by photon counting.

3. RESULTS AND DISCUSSION

Figure 1 shows typical Raman spectra for an α-Sn(001) film as a function of temperature. The signal corresponding to the optical Raman phonon of α-Sn is observed at temperatures much higher than the bulk $\alpha \leftrightarrow \beta$ transition temperature, indicating the stabilizing influence of the substrate. The selection rules for phonons with the $\Gamma_{25'}$ symmetry are well observed.

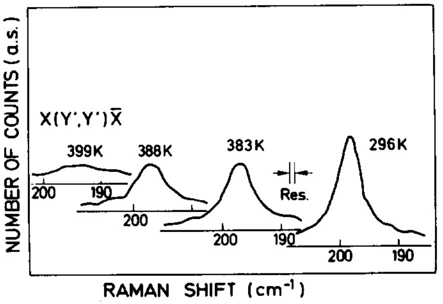

Fig. 1. Typical Raman spectra for an α-Sn(001) film (500 Å thick) obtained with the 7524 Å line of a continuous wave Kr$^+$ laser (substrate, InSb(001)). The incident and scattered wavevectors are parallel to ⟨001⟩ (X // ⟨001⟩). The incident and scattered polarization vectors are parallel to ⟨011⟩ (Y' // ⟨011⟩).

The observed Raman peak cannot be attributed to the longitudinal optical Raman phonon of InSb because, in agreement with the data obtained for bulk α-Sn [7], its frequency is about 10 cm^{-1} higher. Also the disappearance of the peak at temperatures of the order of 100 °C shows that it must originate from the epitaxial film.

The room temperature Raman frequency ω of 197.4(1) cm^{-1} for (001) films is higher than the frequency reported by Buchenauer *et al.*[7] for bulk α-Sn ($\omega = 196.7$ cm^{-1}). The frequency for (111) films is 197.2(2) cm^{-1}. A similar value of 198(1) cm^{-1} is obtained for (110) surfaces. The full width at half-maximum (FWHM) of the Raman line is 3.3(5) cm^{-1} at room temperature. This value is similar for all surfaces.

Electrical measurements by Farrow *et al.*[4] indicate a p-type carrier concentration in their films of up to 4×10^{19} cm^{-3} at 77 K. Similar carrier concentrations produce significant changes in the Raman spectra of silicon and germanium[8]: the Raman peaks shift to lower frequencies, broaden and become asymmetric. None of these effects was observed in our α-Sn samples. The linewidth is similar to that reported in ref. 7. It is larger than that for germanium (FWHM is 2.2(2) cm^{-1} for germanium at 300 K), but this difference can be qualitatively understood in terms of the anharmonic properties of both materials[9]. The Raman peak position of α-Sn films is not shifted to lower frequencies, as would be expected for a strongly doped p-type film, but to higher frequencies. We therefore conclude that our films do not have the strong p-type character reported by Farrow *et al.*[4] We must also rule out the formation of microcrystallites or amorphous α-Sn. This would lead to violation of the Raman selection rules, to a lower Raman frequency and to a line broadening[10], in a similar way to the effect of the p-type doping.

The higher Raman frequency can be explained as due to compression of the film resulting from lattice mismatch between α-Sn and InSb. The change in the phonon frequency produced by the compression of the film can be calculated from the model of Bell[11]. The input data are the distorted lattice parameter (measured by Farrow *et al.*[4]) and the anharmonicity parameters defined by Bell[11]. Since no measurements of the anharmonicity parameters of α-Sn have been published, we used those determined for InSb [11], a reasonable assumption considering the similarities in the lattice dynamical properties of both materials. The value obtained for the frequency shift between the film and the bulk is 0.6 cm^{-1}, which is in good agreement with the experimentally obtained shift of 0.7 cm^{-1}. The fact that the Raman frequency of the (111) films is slightly lower can also be understood with Bell's model. For this surface the hydrostatic and uniaxial components of the line shift make opposite contributions[11].

Figure 2 shows the temperature dependence of the integrated Raman signal for α-Sn(001) films obtained at various thicknesses. All (001) samples show a similar temperature dependence of the Raman signal, characterized by a sharp decrease in intensity around a temperature T^* which indicates the $\alpha \leftrightarrow \beta$ transformation. The values for T^* depend on the film thickness. For films thinner than 60 nm, $T^* = 115$ °C. For the 190 nm thick film, $T^* = 70$ °C, in agreement with the value reported by Farrow *et al.*[4] for films 200 nm thick. The slight linear decrease in the intensity at temperatures well below the transition temperature T^* can be explained as due to a decrease in the Raman susceptibility as a result of the red shift in the E_1 and $E_1 + \Delta_1$ gaps with temperature[12].

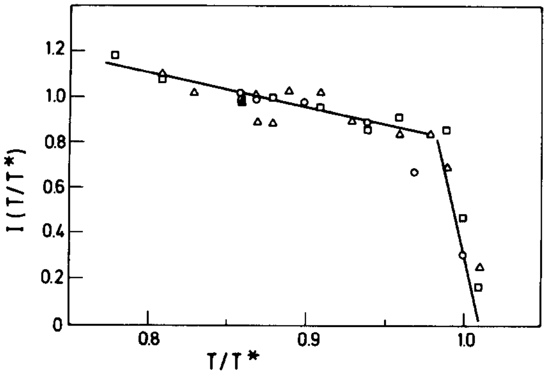

Fig. 2. Temperature dependence of the integrated Raman peak of α-Sn for (001) films (substrate, InSb(001)): □, $d = 250$ Å, $T^* = 388$ K; △, $d = 600$ Å, $T^* = 388$ K; ○, $d = 1900$ Å, $T^* = 344$ K; T^*(bulk) = 286 K. The vertical scale has been chosen to normalize $I(T/T^*)$ to 1.0 for $T/T^* = 0.85$.

The α ↔ β phase transition observed in the films is partially reversible. When the (001) samples in the β-Sn phase were cooled from 120 °C to room temperature, the original α-Sn peak was again observed, but with a reduced intensity of about 25% compared with that for the freshly grown α-Sn sample.

A quite different temperature behaviour is observed for tin films grown on the (110) and (111) surfaces of InSb. In Fig. 3 we show the integrated Raman signal as a function of temperature for (110) and (111) films 30 nm thick. No sharp α ↔ β transition can be found for these samples. The Raman intensity decreases continuously as a function of temperature. The transformation is only partially reversible, similar to the situation found for the (100) face. A very weak peak at about 180 cm^{-1} can be seen in (110) films. This peak may be attributed to the transverse optical Raman phonon of InSb.

The observed differences between the (100) films and the (111) and (110) films may be explained by assuming that the latter films contain β-Sn regions which favour the α → β transformation. The linear decrease in the α-Sn Raman signal would indicate an increase in the amount of β-Sn in the film. Auger electron spectra and electron energy loss spectra taken by Mattern and Lüth[13] seem to confirm this assumption for the (110) films. Above a coverage of 1 nm of tin their films transform

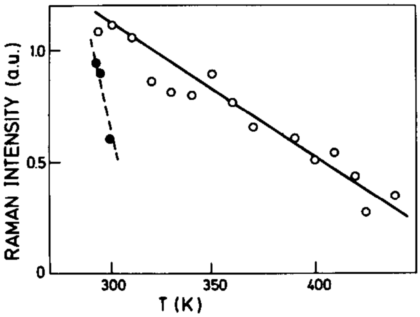

Fig. 3. Temperature dependence of the integrated Raman peak of α-Sn for (110) (○) and (111) (●) films (300 Å thick) on InSb. The relative scale between the (110) and (111) films is arbitrary.

to the β-Sn phase. Angle-resolved photoemission experiments[5] indicate that no β-Sn regions are present in (001) films below T^*, explaining also the abrupt α → β transformation. However, once the films has been heated above its transformation temperature, the β-Sn prevents the full recrystallization of the original α-Sn film, accounting for the only partial reversibility of the transformation.

The observation of the transverse optical phonon of InSb in (110) films can be explained by assuming discontinuities in these films, *i.e.* regions of lower tin coverage which allow the detection of the substrate Raman peaks. RHEED[6] experiments carried out during the growth of the α-Sn films show weak reflection spots due to volume diffraction, indicating island growth.

It remains to be determined whether the marked differences in film growth for various orientations are of an intrinsic nature, *i.e.* depend on the different physical properties of the interfaces under consideration, or rather are due to differences in the surface quality of the InSb substrate. Further investigations by RHEED and ARUPS are in progress. Studies starting from submonolayer coverages may give additional information about the growth mode and the observed differences in the thermal stability of the α-Sn films.

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