Electron microscopic studies of vacuum-evaporated $(\text{Pb}_{1-x}\text{Sn}_x)_{1-y}\text{Te}_y$ thin films

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Abstract. Thin films of $(\text{Pb}_{1-x}\text{Sn}_x)_{1-y}\text{Te}_y$ have been deposited by vacuum evaporation onto glass, mica, CaF_2 and NaCl substrates heated to various temperatures at low deposition rates. Transmission HEED, TEM and SEM studies have been carried out for as-grown films. HEED photographs show that (i) the degree of crystallinity of the films improves at higher substrate temperatures and (ii) the crystallites have smaller dimensions on CaF_2 than on NaCl , mica and even glass, under identical conditions of deposition. SEM studies reveal that with increasing T_{sub} , grains tend to form clusters through mobility coalescence. Needle-shaped grains are formed when the deposition rate exceeds a certain critical value. Formation of needle-like grains has been attributed to the excess Te atoms possessing trigonal structure so that such grains can be observed only in *p*-type PbSnTe films.

Keywords. Pb-Sn-Te films; vacuum evaporation; electron microscopy.

1. Introduction

PbSnTe is a useful IR-sensitive narrow gap semiconductor. The physical properties of thin films depend significantly on their crystallinity and lattice imperfections—both structural and chemical. We had earlier adopted the variance analysis method of X-ray line profiles to determine the crystallinity and certain structural defect parameters of some PbSnTe films deposited by single-boat vacuum evaporation onto heated (457 K) mica, glass and NaCl substrates (Das *et al* 1991). However, such analysis could not be performed on films similarly deposited on polished and (111)-cleaved CaF_2 , because the prominent peaks of PbSnTe were masked either completely or partially by those from the CaF_2 itself. This difficulty is largely obviated in transmission electron micrograph which gives the crystallite size in the plane of the films by direct observations (Wissmann 1975). In contrast, measurements from X line profiles give the average crystallite size perpendicular to the corresponding reflecting planes, the individual microcrystals being capable of diffracting X-rays coherently. On the other hand, TEM photographs show the type of islands, which may or may not be a single crystal.

Since high energy electrons having smaller wavelengths interact with a substance more intensively than X-rays, microcrystalline structure of thin films can be ascertained from transmission high energy electron diffraction (HEED) experiments. Scanning electron micrographs (SEM) permit efficient observation of three-dimensional structures on the surface of thin films. Electron microscopic studies have therefore become imperative not only for microstructural analysis of PbSnTe layers on CaF_2

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in particular but may supplement the results of X-ray analysis already performed (Das *et al* 1991) for layers on glass, mica and NaCl substrates.

2. Experiments

Powdered samples of *p*-PbTe (obtained from BARC, Trombay, India) and *p*-SnTe (synthesized in vacuum) were taken in a mass ratio—1.0013:1.7357, the masses being measured in a Mettler balance. The corresponding mole fraction (x') of SnTe in the mixed compound $(\text{PbTe})_{1-x}(\text{SnTe})_x$ was equal to 0.702. The mixture was fused at ~ 1248 K in a quartz tube in vacuum ($\sim 6.66 \times 10^{-3}$ Pa) to produce a pseudo-binary *p*-PbSnTe in polycrystalline form. Its composition, as determined by energy-dispersive analysis by X-rays (EDAX-model Camscan, series 2 DV with link analytical systems) is given by $(\text{Pb}_{1-x}\text{Sn}_x)_{1-y}\text{Te}_y$, where $x \simeq 0.71$ and $y \simeq 0.51$. Thus the sample was found to be Te-rich (or metal-deficient). This is consistent with its phase diagram (Herman and Melngailis 1974), which shows that the composition of PbTe at the maximum melting point is Te-rich and shifts to become still richer in Te as Sn replaces Pb in the lattice.

Thin layers of the above material were deposited on glass, freshly cleaved mica (amber), polished and (111)-cleaved CaF_2 and (naturally grown) NaCl substrates by vacuum evaporation in a Hind Hivac coating unit (base vacua $\sim 4 \times 10^{-3}$ Pa). Substrates were maintained at different temperatures (~ 300 – 457 K) during different depositions. The deposition rate was always kept low (~ 2 – 5 nm/min) (Das *et al* 1991). Thicknesses of the films were measured by Fizeau's interference method. Results of EDAX analysis showed that the films possessed higher Te-excesses ($y - 0.5$) and lower Sn-contents (x) than those in the bulk.

Transmission HEED and TEM studies were performed in an electron microscope (AEI-EM6) operated at 100 kV with a maximum resolution of 1.0 nm. Samples were prepared following the carbon replica technique. However, the carbon-coated specimens had to be made thinner by dissolving the film material in dilute (10–15%) nitric acid. Photographs were taken on diapositive plates (0.095×0.08 m²), the exposure times being about 10–20 s. SEM photographs were taken for the as-grown films in another electron microscope (Philips, PSEM-500) operated at 50 kV. Thin gold layers (~ 3 – 5 nm) were deposited on the samples and photographs taken at suitable tilt angles.

3. Results and discussion

3.1 HEED studies

These studies were carried out on as-deposited (but thinned) films grown on different substrates at various temperatures. Growth of crystallinity in the films was better revealed by transmission HEED photographs (figures 1a to d). Figure 1a shows that at lower substrate (glass) temperatures ($T_{\text{sub}} \sim 373$ K), small spots as well as diffuse rings appear. Though the diffuse rings characterize the amorphous nature of the film-material, a degree of short-range order may also be associated with them. When T_{sub} was increased to (457 ± 5) K, the order of vacuum and the deposition rate being nearly similar, the diffuse rings disappear and the spots become larger and brighter

Figure 1. Transmission HEED (100 kV) patterns for PbSnTe thin films as-deposited on (a) glass (~ 373 K), (b) glass (~ 457 K), (c) mica (~ 457 K) and (d) (111)-cleaved and polished CaF_2 (~ 457 K).

(figure 1b). This implies that the degree of crystallinity of the films improves at a higher substrate temperature (kept below a certain optimum value that is not determined in this analysis) at the expense of disorder. Similar results have been obtained with mica (figure 1c) and NaCl substrates.

Though only spots appear in HEED photographs (figure 1b,c) the films concerned are not truly mono-crystalline; they are actually polycrystalline as revealed by XRD (Das *et al* 1991). Since the electron beam has a very small cross-section and the sizes of the crystallites parallel to the substrates, surfaces are likely to be fairly large (Das *et al* 1991), the spots in the said HEED photographs correspond to individual monocrystallites only.

Figure 1d shows halves of the Debye rings obtained with PbSnTe films deposited onto (111)-cleaved and polished CaF_2 . These films were deposited along with those on glass and mica for which HEED photographs (figure 1b,c) show only spots. Thus, T_{sub} (~ 457 K) and other deposition parameters were identical for the films corresponding to figures 1b,c,d. Indexing of figure 1d reveals that a large number of rings corresponding to reflections having indices (200), (220), (222), (420), (422), (600), (620), (622), (640) and (642) appear with appreciable intensities. Also, some more rings having weaker intensities and corresponding to intermediate or still higher order of reflections

appear in the negative of the photograph, while with XRD, peaks corresponding to the highest sets of indices (420) only could be noticed with similar films on other substrates (Das *et al* 1991). This establishes a greater efficacy of the TED technique in micro-diffractions.

An analysis of the said photograph leads to the following conclusions: (i) thin films of PbSnTe, deposited on polished and (111)-cleaved CaF_2 are polycrystalline at $T_{\text{sub}} = (457 \pm 5) \text{ K}$. Similar results have been obtained with CaF_2 by other workers using single-boat evaporation (as in this work) for $T_{\text{sub}} = 473\text{--}573 \text{ K}$ (Farinre 1970) and even with flash evaporation (Kasai 1970) for $T_{\text{sub}} < 488 \text{ K}$, (ii) the sizes of the PbSnTe-crystallites are much smaller on CaF_2 than on identically maintained glass, mica or NaCl, because with the same analysing electron beam, the grains formed on glass and mica are monocrystalline (figure 1b,c) while those on CaF_2 are polycrystalline (figure 1d); (iii) PbSnTe-microcrystals show preferences for certain orientations on CaF_2 , which can be arranged in a descending order as (200), (220), (420), (222) and (422). This is revealed by the stronger intensities of the corresponding rings. The sizes of the grains in the plane of the substrates also vary in the same order from a higher to a lower value.

Thus, in general, the degree of crystallinity of PbSnTe films deposited on heated ($\sim 457 \text{ K}$) mica, glass or NaCl (natural) substrates is superior to that of the films deposited on (111)-cleaved CaF_2 under identical conditions. This may be viewed upon as the combined effect of the following factors: (i) PbSnTe is not isostructural with CaF_2 , though it (PbSnTe) is so with NaCl, (ii) while CaF_2 cleaves along the (111)-planes, PbSnTe-crystallites prefer (100)-oriented growth even on glass (Das *et al* 1991) and (iii) the lattice-misfit ($\Delta a/a_{\text{PbSnTe}}$) that PbSnTe (bulk) has with CaF_2 is 15.1% which is greater than the value of the same parameter (viz 11.3%) for NaCl substrates and also the Royer's limit (viz. 15%) for the occurrence of epitaxy.

Though the thermal expansion coefficients of $\text{CaF}_2 (= 19 \times 10^{-6} \text{ K}^{-1})$ (Kasai 1970) and $\text{PbTe} (= 16.3 \times 10^{-6} \text{ K}^{-1})$ — $\text{SnTe} (= 17.6 \times 10^{-6} \text{ K}^{-1})$ solid solutions (Friek *et al* 1980) are quite closer than to those of glass [$= (46\text{--}71) \times 10^{-7} \text{ K}^{-1}$], mica ($36 \times 10^{-6} \text{ K}^{-1}$) and NaCl ($39 \times 10^{-6} \text{ K}^{-1}$) (Holloway and Walpole 1980) respectively, the effect of thermal expansion matching seems to be outweighed by effects of the above factors.

3.2 SEM and TEM studies

SEM photographs have been taken for as-grown films only (i.e. without etching, doping or heat treatment). Hence they reveal mainly the morphology of growing film-surfaces under various conditions of deposition. Figures 2a–c are the SE micrographs of films deposited onto glass substrates heated to 320 K, $(400 \pm 5) \text{ K}$ and $(457 \pm 5) \text{ K}$ respectively, the other deposition parameters being nearly identical. It is observed that as T_{sub} is raised from 320 K to $\sim 400 \text{ K}$, the particles grow in size (viz from $\sim 0.1 \mu\text{m}$ to $\sim 0.2 \mu\text{m}$ or more). That this growth in size occurs through coalescence is evident from their tendency to form necks and clusters (figure 2b). At a still higher substrate temperature (viz $\sim 457 \text{ K}$), coalescence is enhanced and the grains on the surface fail to exhibit any regular shape (figure 2c).

Almost similar results were obtained with mica (figures 3a, b) and NaCl (figure 3c) substrates, except that the particle size and microrelief are relatively small on mica at all substrate temperatures (cf. figures 2a and 2c with figures 3a and 3b respectively).

Figure 2. SEM photographs for PbSnTe films as-deposited on glass substrates heated to (a) 320 K ($20,000\times$, 30° tilt), (b) (400 ± 5) K ($10,000\times$, 50° tilt), and (c) (457 ± 5) K ($20,000\times$, 50° tilt) (scale = $1 \mu\text{m}$).

Figure 3. SEM photographs for PbSnTe films as-deposited on (a) mica (~ 310 K) ($20,000\times$, 65° tilt), (b) mica (~ 457 K) ($20,000\times$, 65° tilt) and (c) NaCl (~ 457 K) ($40,000\times$, 0° tilt) (scale = $1\ \mu\text{m}$).

Figure 4. TEM micrograph of a PbSnTe film as-deposited on (111)-cleaved and polished CaF_2 (~ 457 K) ($50,000\times$, scale = $0.5\text{ }\mu\text{m}$).

Therefore, higher tilt-angles had to be used always for films grown on mica. A comparison of figures 2c and 3c shows that the surface pattern of PbSnTe films deposited under identical conditions (viz. $T_{\text{sub}} \sim 457$ K) on glass and NaCl (natural) is almost similar.

TE micrographs were taken for some of the films and they illustrate almost similar results as do the SEM photographs. Figure 4 is a TE micrograph of a PbSnTe film deposited on CaF_2 heated to (457 ± 5) K. It represents a surface morphology which is very similar to that of a film deposited on glass under identical conditions (cf. figure 2c). But the two-dimensional nature of the TEM photographs is their inherent limitation, because of which micro-reliefs on film-surfaces are not clearly revealed.

The results discussed so far may be explained in the following way. The condensing atoms/molecules receive additional thermal energies on a substrate depending on the latter's temperature and nature (viz. thermal conductivity, thickness etc.). Therefore the deposited atoms/molecules have (i) higher mobilities at higher substrate temperatures (for a given substrate) and (ii) different mobilities on different substrates kept at similar temperatures. Improved crystallinity of the films at higher substrate temperatures, as observed in our HEED analysis, is also consistent with the above observations. Because of higher mobilities, the atoms/molecules deposited on substrates kept at higher temperatures move with greater freedom, finally coalescing to form larger coherent domains which can scatter X-rays or electrons coherently. This may be termed as the "mobility coalescence" (Puskeppel and Harsdoff 1976). Moreover, the above observations seem to find justification in the results of our subsequent Hall measurements that majority carriers (i.e. holes in our films) possess (a) higher mobilities in films of similar thicknesses deposited on a given substrate but kept at higher temperatures (investigated up to ~ 457 K) and (b) different mobilities on different substrates kept at similar temperatures during depositions. For example, for films deposited simultaneously onto mica, NaCl (natural), CaF_2 and glass substrates at a given substrate temperature, the hole mobility has been found to have lowest values on mica and gradually higher values on NaCl, CaF_2 and glass respectively.

Figures 5a, b, c represent a set of three SEM photographs for three PbSnTe films deposited under identical conditions on glass (figures 5a, b) and mica (figure 5c) respectively. Here, the substrates were initially kept at the ambient temperature

Figure 5. SEM micrographs showing needle-like grains on PbSnTe films as-deposited under identical conditions (Final $T_{\text{sub}} \sim 373 \text{ K}$, rate of deposition $\sim 4.5 \text{ nm/min}$) onto glass (**a, b**) ($10,000\times$, 50° tilt) and mica (**c**) ($20,000\times$, 50° tilt), (scale = $1 \mu\text{m}$).

(300 K); but when the deposition started, the temperature of the substrates gradually rose to 373 K, the average rate of deposition being ~ 4.5 nm/min. The needle-like grains are seen strewn throughout the uppermost surfaces of the films. Figures 5a, c correspond to glass and mica substrates respectively, which were placed vertically above the source (open M_o -boat) and figure 5b to that placed horizontally but away from the vertical axis. Two distinct features can be noted from a close examination of the photographs: (i) the needles are much smaller in number as well as in length on surfaces of layers grown on mica than on glass, and (ii) they are more elongated on obliquely placed substrates (both on glass and mica).

Under almost similar conditions of deposition as mentioned above, when T_{sub} gradually rises from 300 K to 363 K in 32 min, the average deposition rate being ~ 3.0 nm/min, spherical grains are observed (figure 6) on film-surfaces deposited on glass, which are as noticed earlier for $T_{\text{sub}} = 320$ K and at an average deposition ~ 2.5 nm/min (figure 2a). But in this case, the number of grains per unit area is larger. Moreover, from the photograph (figure 6), it is seen that very few needle-shaped grains have been formed. Thus, it can be inferred that under nearly similar conditions of deposition, needle-like grains are formed on our PbSnTe films, when the deposition rate exceeds a certain critical value (viz. ~ 3.0 nm/min, as in this case). However, for films deposited on mica under identical conditions as those mentioned above (corresponding to figures 2a and 6), the micro-reliefs on film-surfaces were so small that no SEM photographs could be taken.

Such needle-like topography is also evident from TEM for a thicker PbSnTe film deposited on CaF_2 heated to (457 ± 5) K (figure 4) and from the SE micrographs for similarly deposited films on glass (figure 2c) and on NaCl (figure 3c). However, it appears that the needles have, to some extent, melted away due to the higher temperature (~ 457 K) of the substrates. But SEM of an identically deposited film on mica (figure 3b) does not show any needle-like surface morphology.

The formation of needle-like grains at higher deposition rate can be understood as follows: At higher deposition rate, the source temperature and so the final substrate temperature become higher due to radiant heating, particularly when the deposition continues for a sufficient time. At the same time, the surface density of condensed

Figure 6. SEM micrograph showing the beginning of needle formation over PbSnTe films as-grown on glass (rate of deposition ~ 3.0 nm/min) ($20,000\times$, tilt = 45° , Scale = $1\ \mu\text{m}$).

(but unsettled) molecules/atoms increases, all of which have higher mobilities because of increased T_{sub} . The particles therefore touch one another more frequently and form larger grains below a critical deposition rate (viz. ~ 3 nm/min in this case) and needles above it.

However, a question may be raised at this stage as to why the grains develop preferentially into needles. The most probable answer may be found in the following arguments. Since the films have been observed (by EDAX) to have varied Te-excesses and since Te has the trigonal (A 8) structure (Barrett and Massalski) consisting of atoms arranged in hexagonal arrays of helical chains along the c -axis with each atom having two neighbours, the needle-like grains may be said to be Te-microcrystals (grown from excess Te), their c -axes being parallel to the length of the needles (Shih and Champness 1979). Again, the partial pressures of Te_2 , Pb and Sn being in a progressively decreasing order, a certain ($\sim 14\%$) fraction (Brebrick and Strauss 1964a, b) of PbTe and SnTe molecules dissociate during evaporations in a scheme:

While the dissociated fraction of PbTe evaporates congruently, that of SnTe does not because of lower Sn volatility. Moreover, the tendency of dissociation is greater for higher evaporation temperatures. Since our bulk PbSnTe contained a higher mole fraction of SnTe, the films are likely to contain higher Te-excesses at higher evaporation temperatures.

The excess Te in PbSnTe makes it a p -type semiconductor and both Hall and thermoelectric measurements made subsequently have confirmed that ours is also a p -type material. So, it can be said that needle-shaped grains can be observed only in p -type films of PbSnTe and that too under certain conditions of deposition as discussed above. Moreover, the origin of needle-shaped grains observed in the TE micrographs of SnTe films (Santhanam 1982) can be understood in the same way, because undoped SnTe is always p -type as a result of its Sn-deficiency (i.e. relatively excess Te).

The reason for smaller grain sizes/micro reliefs on mica than on glass is not clearly understood. However, two probable explanations based on some assumptions have been attempted here. If the mobility of deposited atoms or molecules on mica is assumed to be less than that on glass (as for the hole mobility), then it may be said that the atoms or molecules incident on mica settle more quickly at numerous preferred sites provided by the crystalline structure of mica; but on glass, the atoms/molecules having greater mobility, move through longer distances to form larger droplets of irregular sizes through 'mobility coalescence', while the grains are almost of equal sizes on mica (cf. figures 2a and 6 with figure 3a).

An alternative and more probable explanation is based on the modes of growth of the films. From the SEM photographs, it appears that the growth of PbSnTe films on glass follows either Volmer-Weber (i.e. particle growth) or Stranski-Krastonov (i.e. initial monolayer growth succeeded by particle growth) modes. But on mica, PbSnTe films most probably follow the Stranski-Krastonov mode in which the Frank van der Merwe (i.e. monolayer) part plays the dominant role. As a result, the sizes of the particles or needles on upper surfaces of the films deposited on mica are always smaller.

Lastly, figure 7 shows the dislocation network on a PbSnTe film (300 nm) deposited on mica heated gradually to 368 K during depositions (25 min) from an initial

Figure 7. SEM photograph showing the dislocation network on a PbSnTe film as-grown on mica (Final $T_{\text{sub}} \sim 368$ K, and rate of deposition ~ 12 nm/min).

temperature of 323 K. Here, the deposition was performed following Holloway and Walpole (1980) to see if thin film of our pseudo-binary alloy could be deposited without a compositional drift. In addition to using an open M_0 -boat as in previous depositions, the powdered and homogenized source material was compressed to form a tablet. The rate of deposition was much higher viz. about 12 nm/min, the order of vacuum being $\sim 5 \times 10^{-3}$ Pa. However, subsequent compositional analyses of the films by EDAX revealed that they did suffer stoichiometric shifts. But thin films thus deposited on glass showed no dislocation network or microrelief up to highest available magnifications (viz 80,000 $\times$) in SEM (camscan-series 2DV with Link analytical system). Films on mica also showed no microrelief between/within dislocation lines/loops.

4. Conclusions

The results discussed can be summarized as follows:

- (i) The crystallinity of the films is strongly affected by the substrate temperature. As the latter is increased, the former improves at the expense of disorder and the deposited atoms show gradually increasing tendency of cluster-formation and coalescence to produce larger grains, which can be explained on the basis of higher mobilities of deposited atoms/molecules at higher substrate temperatures.
- (ii) PbSnTe crystallites have smaller dimensions on CaF_2 than on NaCl, mica or even ordinary glass substrates—all kept under identical conditions.
- (iii) Needle-like grains are formed for rates of deposition exceeding a certain critical value viz. ~ 3 nm/min in this case, below which the grains are spherical. Moreover, the needles can be observed only in *p*-type PbSnTe films which have excess Te possessing trigonal (A8) structure.
- (iv) Sizes of the grains (both spherical and needle-like) and their microreliefs are much smaller on films grown from powdered materials on mica at all substrate temperatures compared to those on the other three substrates used in this investigation.

References

- Barrett C S and Massalski T B *Structure of metals, crystallographic methods, principles and data*, (New York: McGraw Hill) Indian reprint (New Delhi: Eurasia Pub. House) 3rd edn. 229
- Brebrick R F and Strauss A J 1964a *J. Chem. Phys.* **40** 3230
- Brebrick R F and Strauss A J 1964b *J. Chem. Phys.* **41** 197
- Das S C, Samantaray B K, Bhattacharjee S and Chaudhuri A K 1991 *J. Mater. Sci.* **26** 2595
- Farinre T O 1970 Ph D Thesis, Pennsylvania University, USA
- Frick D M, Rarenko I M, Solonichnyi Ya V and Shperun V M 1980 *Inorg. Mater.* **16** 278
- Harman T C and Melngailis I 1974 *Narrow gap semiconductor in applied solid state science*, (ed.) R Wolfe **4** 1
- Holloway H and Walpole J N 1980 in *Molecular beam epitaxy* (ed) B R Pamplin (Pergamon) pp. 49–94
- Kasai I 1970 Ph D Thesis, California University, Los Angeles
- Puskeppel A and Harsdorff M 1976 *Thin Solid Films* **35** 99
- Santhanam S 1982 Ph D Thesis, Dept. of Phys., IIT, Kharagpur, India
- Shih I and Champness C H 1979 in *The physics of tellurium and selenium, Springer Series in Solid St. Sci.*, (eds) E Gerlach and P Grosse **13** 267
- Wissmann P 1975 *Surface physics, springer tracts in modern physics*, (ed) G Hohler (Springer-Verlag) **77** 1