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X-ray studies on the structure of p-$(Pb_{1-x}Sn_x)_{1-y}Te_y$ thin films

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Thin films were deposited by vacuum evaporation of p-$(Pb_{1-x}Sn_x)_{1-y}Te_y$ powders (where $x \simeq 0.71$ and $y \simeq 0.508$) on to glass, mica and natural NaCl substrates heated to various temperatures. X-ray diffractograms show that films deposited on colder substrates exhibit inferior crystalline quality. Films deposited at $T_{sub} \simeq 457 \pm 5$ K are polycrystalline, showing strong (2 0 0) or (2 2 2) peaks along with weaker (2 2 0), (4 0 0) or (4 2 0) peaks. Variance analyses performed on intense line profiles show that the crystallite size, r.m.s. strain and dislocation density are fairly high even in polycrystalline films. PbSnTe crystallites show a preference for (1 0 0)-oriented growth on heated glass and (1 0 0)-cleaved NaCl substrates; but on equally heated mica, their growth shows an initial preference for the (1 1 1) orientation, which gradually switches over to the (1 0 0) orientation for higher thicknesses. Probably due to a higher SnTe content, PbSnTe crystallites show evidence of misorientation on heated glass and natural NaCl substrates.

1. Introduction

Thin films of PbSnTe have high prospects for applications in various IR-sensitive as well as thermoelectric, Hall effect and piezo resistive devices because of the material's narrow and controllable energy gap. But thin films usually contain high concentrations of various structural defects, namely grain boundaries, isolated dislocations, stacking faults, inhomogeneities, lattice strains etc. These defects, along with the size and orientation of the grains, markedly influence the physical properties of the films. Hence, an estimation of the grain size and various defect parameters is essential for a proper understanding of the film behaviour. Since the broadening of an X-ray diffraction peak primarily depends on these defects and sizes of the crystallites, the former provides estimates for the latter.

Assuming the defects to be uncorrelated with each other, the observed diffraction profile is the result of convolution of the profiles due to different defects present in the sample. To separate out individual defect profiles by deconvolution is a difficult task. It is better to find out the effect of various defect types on some parameter of broadening. The method of line profile analysis suggested by Wilson [1] and based on variance, which follows the law of addition, is a very convenient technique. An extension of the method by Mitra and Misra [2, 3] for application to a single line is more advantageous, particularly for thin films, where multiple reflections are often weak or absent because of the limited amounts of scattering material involved. Several workers have applied this method successfully for thin films of PbS [4], PbTe [5] and SnTe [6], but no worker seems to have reported similar studies on PbSnTe thin films, as performed in this investigation.

2. Experimental procedure

A polycrystalline ingot of p-$(Pb_{1-x}Sn_x)_{1-y}Te_y$, where $y \simeq 0.508$ and $x \simeq 0.71$, was prepared by synthesizing p-PbTe and p-SnTe in a vacuum [7]. The single-phase nature and polycrystallinity of bulk PbSnTe were established by observing X-ray diffraction peaks in a Norelco (Philips) diffractometer (35 kV, 10 mA, Cu$K\alpha$ radiation). Thin films were deposited on glass, freshly cleaved amber mica and naturally grown NaCl substrates by vacuum evaporation of PbSnTe powder from a molybdenum boat at base vacua $\sim 4 \times 10^{-3}$ Pa. Substrates were supported on a metallic holder heated to various temperatures by radiant heating. The rate of deposition was kept low ($\sim$2 to 5 nm min^{-1}) for ensuring uniformity of deposition and minimum molecular dissociation. Moreover, a low deposition rate and a high substrate temperature are required to achieve a lower density of structural defects in the films. Thicknesses were measured by Fizeau's interference method. Compositions of the bulk and the films were analysed by energy-dispersive X-ray analysis (EDAX) (Camscan Series 2 DV with Link analytical system) and the films were found to have a reduced tin content (x) and enhanced tellurium excess ($y - 0.5$) compared with the bulk.

Diffractograms of the films were similarly recorded in the Norelco unit (35 kV, 10 mA, Cu$K\alpha$) at a scanning speed of $0.25°(2\theta)$ min^{-1}. Films deposited at a

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substrate temperature of $\sim 457 \pm 5$ K were selected for variance analysis and most of them exhibited strong (2 0 0) or (2 2 2) peaks along with relatively weak (2 2 0), (4 0 0) or (4 2 0) peaks. Since the variance of a line profile depends considerably on the error in the assumed background of the profile, background corrections were carefully done following Mitra and Misra [8]. Relative intensities were then estimated at 2θ intervals of 3.456×10^{-4} rad. Corresponding ranges and variances were calculated with the help of a computer (HP 9836) by suitable programming. Variance analyses were performed mostly on (2 0 0) or (2 2 2) peaks and sometimes on (2 2 0) peaks simultaneously.

3. Variance analysis

The variance or the second moment about the mean of a line profile, corrected for background, varies linearly with the range (in 2θ) in a region where the intensity decreases as the inverse square of the range (i.e. near the tails). Further, since the variances are additive, the profiles were corrected for instrumental broadening by subtracting the variances of the corresponding profiles for a well-annealed SnTe powder. After making these corrections, if it is assumed that the broadening of a profile is due entirely to the finite size of the crystallites and strains in them and if the faults are zero, the variance ($W_{2\theta}$) of a pure line profile in 2θ can be expressed as [9]

$$W_{2\theta} = \frac{\lambda\alpha}{2\pi^2 p \cos\theta} + 4\tan^2\theta \langle e^2 \rangle \qquad (1)$$

where p is the particle size, α is the angular range over which the intensity distribution is appreciable, $\langle e^2 \rangle$ is the mean-square strain, λ is the wavelength of the X-rays and θ is the Bragg angle. Thus, if the graphs of $W_{2\theta}$ against α are plotted, their slopes and the intercepts on the $W_{2\theta}$ axis will give p and $\langle e^2 \rangle$, respectively.

Since both the particle size (p) and microstrain are manifestations of the dislocation network in the films, the dislocation density (ρ), as shown by Williamson and Smallman [10], can be written (under certain simplified assumptions) as

$$\rho \simeq \frac{2(3\langle e^2 \rangle)^{1/2}}{bp} \qquad (2)$$

where b is the Burgers vector associated with the Burgers circuit. If it is further assumed that $\boldsymbol{b} = a_0$, the lattice parameter of the bulk sample, ρ can be easily calculated, which, according to Hirsch [11], gives the length of the dislocation line per unit volume.

4. Results and discussion

Graphs were plotted using $W_{2\theta}$ as ordinate and α (range) as abscissa, and only three or four points corresponding to the tails were considered for the reasons mentioned above. Fig. 1 shows the plots for three representative samples. The graphs are straight lines as expected, showing the correctness of the data collection and the background correction. Intercepts and slopes were calculated by least-squares fitting. Dislocation densities were calculated from the same data using Equation 2. Table I shows the results thus obtained.

The crystallite size (p) determined by the X-ray method gives the apparent dimension of the crystallites perpendicular to the reflecting planes producing the given profile, and averaged over all domains. The real crystallite size can be deduced from the well-known relation $t = p/K$, where K is the Scherrer constant, which is equal to unity for cubic and spherical crystallites. Hence for cubic-shaped crystallites, analysis of (2 0 0), (2 2 0) or (2 2 2) reflections gives the particle sizes along [2 0 0], [2 2 0] or [2 2 2] directions, respectively.

All the films analysed have been found to be polycrystalline, having sufficiently large crystallite sizes ($p \approx 55$ to 90 nm) along [2 0 0] and [2 2 2] directions, but they are smaller along [2 2 0] directions. As pointed out by Zemel [12], the films deposited even on glass substrates exhibited fairly large single-crystal grains along the [2 0 0] axis. This fact, and a comparison of the ratio of the integrated intensities ($I_{200}:I_{220}$) with that of the bulk, lead us to conclude that PbSnTe crystallites prefer to have (1 0 0)-oriented growth, which is a characteristic property of the lead salts. When, however, the glass substrates were initially kept at room temperature and they were not appreciably heated during deposition, the films did not show any peak, implying that the films were amorphous. Results obtained with heated NaCl sub-

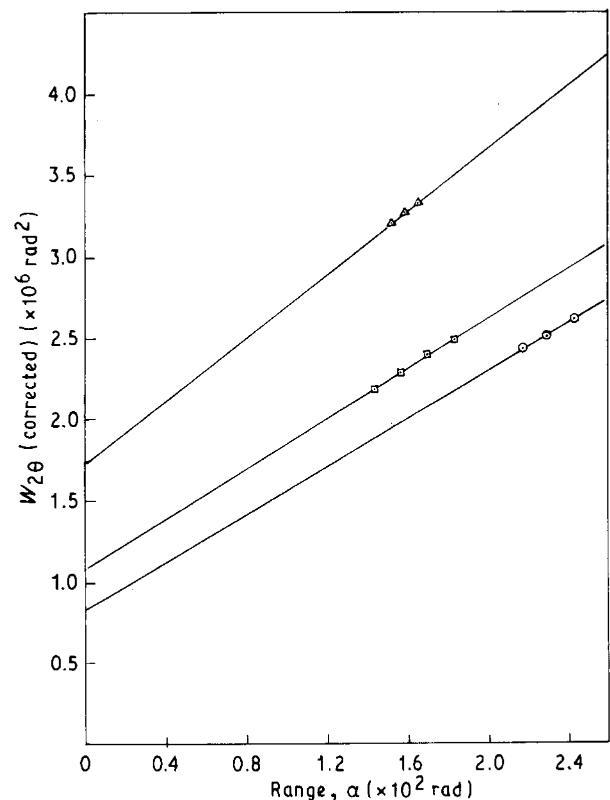

Figure 1 Plots of variance (corrected) against range for PbSnTe thin films. (⊙) Deposited on glass, thickness 125.0 nm, (2 0 0) peak. (⊡) Deposited on mica, 125.0 nm, (2 0 0) peak. (△) Deposited on mica, 164.0 nm, (2 2 2) peak.

TABLE I Crystalline and some structural-defect parameters of vacuum-evaporated PbSnTe thin films

Substrate and sample No.	Average substrate temperature (K)	Film thickness (nm)	Visible peaks	Peak analysed	Apparent particle size(nm)	R.m.s. strain, $\langle e^2 \rangle^{1/2}$	Dislocation density $\rho(m^{-2})$
Mica (133/M)	457 ± 5	150.0	(2 2 0)(2 2 2)[a] (4 0 0)	(2 2 2) (2 2 0)	83.4 31.8	3.53×10^{-3} 0.46×10^{-3}	2.31×10^{14} 0.78×10^{14}
Mica (131/M)	457 ± 5	164.0	(2 0 0)(2 2 0) (2 2 2)[a](4 0 0) (4 2 0)	(2 2 2)	88.3	1.43×10^{-3}	0.88×10^{14}
Glass ($132/G_2$)	457 ± 5	157.5	(2 0 0)[a](2 2 0) (2 2 2)(4 2 0)	(2 0 0)	56.9	1.61×10^{-3}	1.54×10^{14}
Glass ($132/G_3$)	457 ± 5	157.5	(2 0 0)[a](2 2 0) (2 2 2)	(2 0 0)	73.2	1.65×10^{-3}	1.23×10^{14}
Natural NaCl (130/NCL)	457 ± 5	168.0	(2 0 0)(2 2 0) (4 0 0)(4 2 0)[a]	(2 0 0)	78.7	1.75×10^{-3}	1.21×10^{14}

[a] Peaks marked are the most intense peaks.

strates (naturally grown) were similar to those obtained with equally heated glass substrates, barring two exceptions that in the former case the (2 2 2) peak did not appear at all, while the (2 0 0) peak became much stronger. This can be understood in view of the facts that (i) the NaCl substrate was (1 0 0)-cleaved and PbSnTe crystallites prefer (1 0 0)-oriented growth, and (ii) PbSnTe and NaCl are isostructural, having small lattice mismatches (less than 13% for our sample).

On heated mica substrates, however, the films were observed to show a preference for (1 1 1)-oriented growth. This is quite expected, because both mica (monoclinic) and the lead salts (rock salt f c c) have pseudo-hexagonal symmetry. However, with increasing thickness, the growth of PbSnTe films shows a tendency to switch over to the (1 0 0)-oriented growth usually preferred by the lead salts. This conclusion is arrived at by comparing the ratio of integrated intensities ($I_{222}:I_{200}$) for two films of thicknesses 150 and 164 nm (Table I), deposited under identical conditions; the ratio is much higher for the film having a smaller thickness.

The r.m.s. strain values are nearly equal ($\sim 10^{-3}$) for all the films and are much higher than those observed ($\sim 10^{-4}$ to 10^{-5}) in cold-worked metals. Higher microstrains are mainly due to the mismatch – both as regards thermal expansion and lattice parameter – at the film–substrate interface.

Dislocation densities are also of the same order ($\sim 10^{14}$ lines m^{-2}) in all the films examined, irrespective of the substrate. These values are sufficiently higher than those found in PbSnTe crystals ($\sim 10^7$ lines m^{-2}) having a tellurium excess [13]. It is also observed that similar analyses performed on similarly deposited films of the PbTe and SnTe yielded similar results for all these three parameters [5, 6].

High-energy electron diffraction (HEED) photographs (Figs 2 and 3) taken in an AEI EM6 electron microscope (100 kV, 0.40 m) clearly depict the crystallinity of the films deposited under identical conditions ($T_{sub} \approx 457$ K) on glass (Fig. 2) and mica (Fig. 3). Though bright spots only appear, the films are truly polycrystalline, as established by X-ray diffraction.

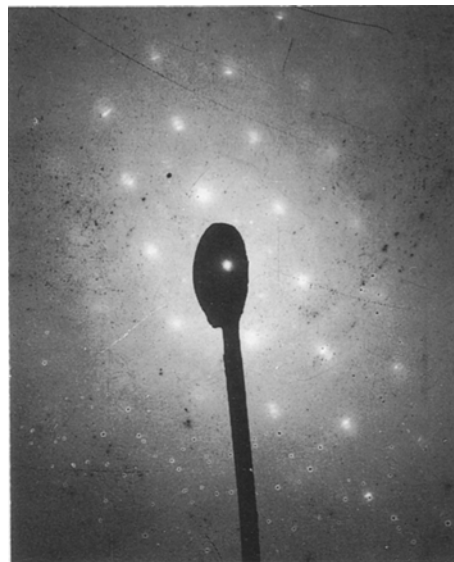

Figure 2 HEED (transmission) photographs for PbSnTe films deposited on heated ($\sim$457 K) glass.

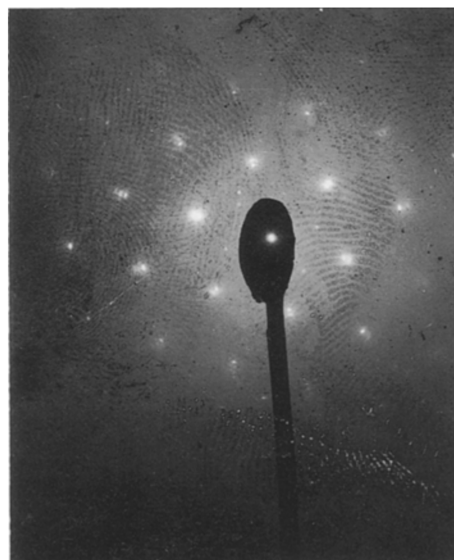

Figure 3 HEED (transmission) photographs for PbSnTe films deposited on heated ($\sim$457 K) mica.

Since the electron beam has a very small cross-section and the sizes of the crystallites oriented parallel to the surface of the substrates are fairly large, these photographs correspond to individual crystallites only.

However, two peculiar results have been observed. Firstly, the film $132/G_3$ deposited on glass (Table I) exhibited (2 0 0) and (2 2 0) peaks as doublets having $\Delta(2\theta) = 0.18$ and $0.20°$, respectively, while its (2 2 2) peak appeared as a singlet in the same diffractogram. No other film has depicted such a feature, and this may have the following explanation. Since SnTe has a higher volatility than PbTe [14], pseudo-binary PbSnTe evaporates mainly as PbTe and SnTe molecules. These molecules recrystallize after condensation on the substrates to form PbSnTe again, which may have a different stoichiometry compared to that of the evaporant. In that case, all visible peaks will be uniformly displaced. If, otherwise, two different phases of PbSnTe having slightly different compositions are formed during recrystallization, all the peaks will appear as doublets. Hence the doublets along [2 0 0] and [2 2 0] axes only are possibly due to two slightly mismatched orientations of the PbSnTe nuclei perpendicular to the respective directions. This may be treated as an example of incomplete recrystallization.

Secondly, upon heated NaCl (naturally grown) substrates, PbSnTe film (film 130/NCL, Table I) exhibited a strong (4 2 0) doublet ($CuK\alpha_1$–$K\alpha_2$ pair), which was (i) much stronger than that exhibited by the bulk powder or any other film similarly deposited on other substrates (film $132/G_2$, Table I) and (ii) stronger than even the (2 0 0) peak of the same sample. This means that the total number of PbSnTe crystallites oriented parallel to the (4 2 0) plane and/or their sizes along [4 2 0] axes are larger than those for any other direction of the same film or in the same direction for the bulk. Since the substrates (NaCl) are (1 0 0)-cleaved and PbSnTe crystallites prefer (1 0 0)-oriented growth, the above results deviate considerably from the expected ones. However, it is highly probable that a good number of crystallites suffer misorientation from the preferred (4 0 0) arrangement (corresponding to $2\theta \simeq 57.7°$) to the adjacent (4 2 0) one ($2\theta \simeq 64.8°$) and strengthen the corresponding diffraction maxima; our sample contains an excess of SnTe, and there is evidence [15] for SnTe films deposited on (1 0 0) planes of NaCl, KCl and KBr showing azimuthal grain misorientations in the range 4 to 6°.

5. Conclusions

The results obtained in this investigation may be summarized as follows:

1. PbSnTe film grown on substrates (glass, mica and NaCl) heated to 457 ± 5 K are polycrystalline, while those deposited on colder substrates show inferior crystalline quality.
2. PbSnTe crystallites prefer to have the usually expected (1 0 0)-oriented growth on heated glass and (1 0 0)-cleaved NaCl substrates; but on equally heated (amber) mica, their growth shows an initial preference for the (1 1 1) orientation (as required by the symmetry matching), which with increasing thickness gradually switches over to the (1 0 0) orientation.
3. Variance analyses yield quite satisfactory results, that the crystallites have fairly large sizes even in polycrystalline films; the microstrain and dislocation density are also sufficiently high, principally due to the thermal expansion and lattice constant mismatch at the film–substrate interface.
4. Due to a higher SnTe content in the sample, PbSnTe crystallites probably show evidence of misorientations on heated glass and NaCl substrates.

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