JOURNAL OF MATERIALS SCIENCE 24 (1989) 3176–3179

The electrical properties of polycrystalline $ZnIn_2Te_4$ thin films

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Thin films of $ZnIn_2Te_4$ are grown onto glass substrates by the flash evaporation technique. Electrical properties such as electrical resistivity and activation energy were studied with different substrate temperatures ranging from 300 to 623 K. It is observed that the film grown at a substrate temperature of 523 K is a single phase polycrystalline stoichiometric film with minimum electrical resistivity. The effect of the film thickness on the electrical properties of $ZnIn_2Te_4$ thin films grown at a substrate temperature of 523 K has been studied. The experimental data can be satisfactorily explained on the basis of the Fuchs–Sondheimer theory.

1. Introduction

The ternary diamond-like $II–III_2–VI_4$ type semiconducting compounds (where II = Zn, Cd, Hg; III = In, Ga, Al; VI = S, Se, Te) crystallize either in the spinel structure, characteristic of oxides and sulphides, or in tetrahedral structures, typical of selenides and tellurides [1]. This group has been extensively studied in the bulk form, with reference to the electrical [2, 3], optical [4–6] and magnetic properties [7]. The promising features of some of these compounds from the point of view of their use as photoelements have been pointed out by many authors [2, 3]. Recent studies have revealed that these compounds are interesting for their applications as photoconductors [8, 9], solar cells [10–12], narrow detectors in the infrared region, temperature sensors [4], optical filters [5, 6], diodes [13, 14], switching devices [15, 16] and non-linear harmonic generators [17].

Among the semiconducting compounds of the $II–III_2–VI_4$ type, $ZnIn_2Te_4$ is of special interest. However, the thin films of this compound have not been investigated in detail so far. Therefore, we have undertaken a programme to synthesize and study the structural aspects and properties of $ZnIn_2Te_4$ thin films.

2. Experimental procedure

Thin films of $ZnIn_2Te_4$ were deposited using the flash evaporation technique. A vacuum of the order of 10^{-6} torr was maintained during the evaporation process. Evaporation of the material was carried out from a molybdenum boat maintained at a high temperature of about 1500 K in order to evaporate the charge instantaneously. Thoroughly cleaned glass slides were used as substrates. In order to study the effect of the substrate temperatures on the structure and the electrical properties of $ZnIn_2Te_4$ thin films, films with thickness of about 100 nm were grown for the electron microscopic observations as well as the electrical resistivity measurements. In all these experiments the thickness of the deposits and the deposition rate (about $1\,\mathrm{nm\,sec^{-1}}$) were maintained constant. The substrate temperatures were varied from 300 to 673 K and monitored using a chromel–alumel thermocouple mounted on the substrate surface. In order to study the affect of the film thickness on the electrical properties, films having different thicknesses of about 100 to 400 nm were grown at constant substrate temperature of 523 K. The thickness of the films was measured by the multiple beam interference technique. The measurements of the dark electrical resistivity were carried out at room temperature and in vacuum using the standard four-probe method. Silver pasted leads were used as contacts to the films.

3. Results and discussion

Our earlier studies on the growth of $ZnIn_2Te_4$ thin films [18] revealed that single-phase polycrystalline stoichiometric films of $ZnInTe_4$ have been grown in the substrate temperatures range $423 \leqslant T_s \leqslant 523$ K. The films deposited at lower substrate temperatures, ($T_{sub} < 423$ K), were amorphous in nature, while at higher substrate temperatures, ($T_{sub} > 523$ K), the films were polyphase.

The variation of the dark electrical resistivity, ϱ, of $ZnIn_2Te_4$ films (having thickness 100 nm) with the substrate temperatures T_s is shown in Fig. 1. It is observed that the electrical resistivity decreases with increasing substrate temperature and reaches a minimum value at 523 K. This decrease has been explained using Petritz's barrier model [19]. Since the crystallites do not grow sufficiently large at low temperatures, the intercrystalline regions are wide, offering a high resistance to the motion of charge carriers, while at higher substrate temperatures, the formation of fewer nucleation centres results in large crystallite sizes which ultimately decrease the number of intercrystalline barriers. The charge carriers, therefore, have to cross comparatively narrow intercrystalline barriers and

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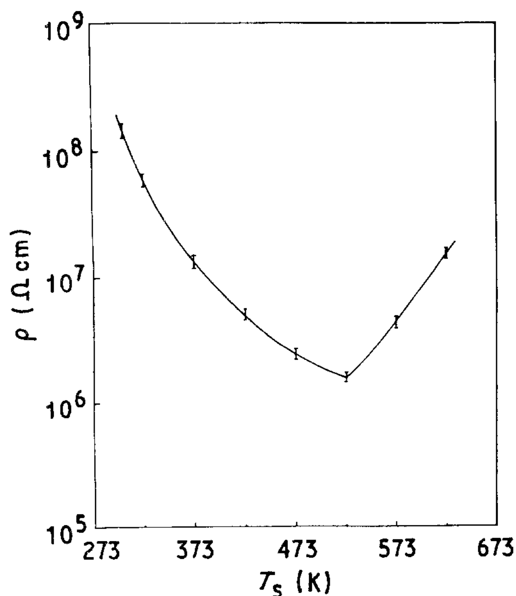

Figure 1 Variation of the dark electrical resistivity of $ZnIn_2Te_4$ thin films deposited at different substrate temperatures.

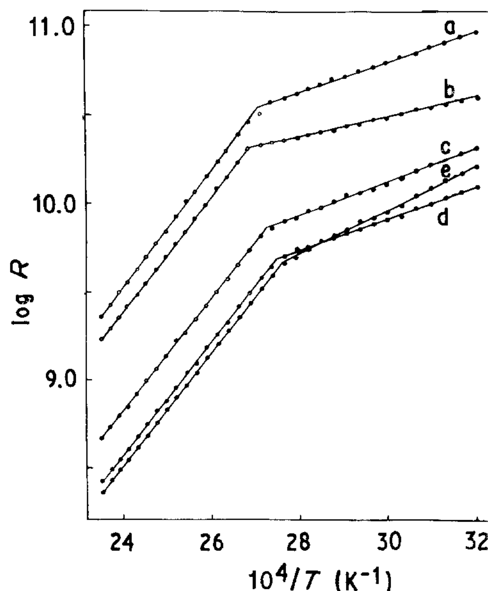

Figure 3 A plot of log of the resistance versus inverse of temperature for films deposited at 523 K with different thickness (a) 80 nm, (b) 100 nm, (c) 160 nm, (d) 240 nm and (e) 320 nm.

this may be responsible for the decrease in the resistivity. However, the resistivity of the films deposited above 523 K has increased; this may be attributed to a change in the deviation from stoichiometry of the film as well as the formation of polyphase film as reported earlier [18].

A plot of log R against $1/T$ of $ZnIn_2Te_4$ films grown under identical conditions with different substrate temperatures is shown in Fig. 2. It is seen that, as the temperature rises, the resistance decreases first slowly and then rapidly, suggesting the approach of the intrinsic region. In this region it might be expected that the average drift velocity, as well as the mobility, are different for two types of carriers in semiconductors because their mechanisms of motion under the influence of an applied field are different. Moreover, as the electrons move through the film, they are scattered by inhomogeneities present such as impurity atoms, the interstitial atoms and also the thermal vibrations of the atoms which become more prominent at higher temperatures.

The thermal activation energies were calculated from Fig. 2 and the values are shown in Table I to increase with increase of the substrate temperature. Patel and Ali [18] reported that the substrate temperature has a significant influence on the structure, orientation and stoichiometry of $ZnIn_2Te_4$ thin films. The crystallinity of the films increased with increasing substrate temperatures and the films grown at lower substrate temperatures have a random orientation and consist of dispersed microcrystallites. The films grown at higher substrate temperatures show larger grain sizes. This explains the increase of the activation energy with substrate temperature. The activation energy of the films grown at 523 K are found to be slightly less than the value reported for $ZnIn_2Te_4$ bulk. However, the activation energy of the film grown at a substrate temperature of 523 K is in good agreement with the bulk value, in spite of the film being non-

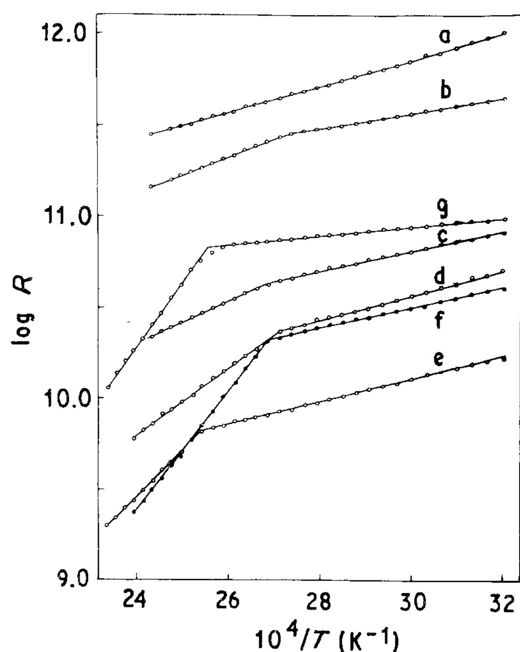

Figure 2 A plot of log of the resistance versus inverse of temperature for films deposited at (a) 300 K, (b) 323 K, (c) 373 K, (d) 423 K, (e) 473 K, (f) 523 K and (g) 573 K.

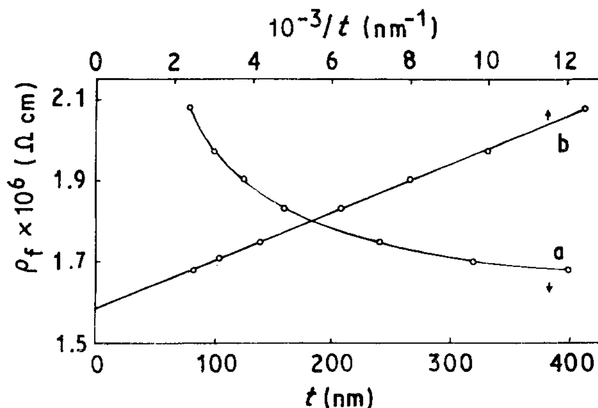

Figure 4 Variation of the resistivity of $ZnIn_2Te_4$ thin films deposited at 523 K (a) with different thicknesses, and (b) with the inverse of the thickness.

TABLE I

Substrate temperature T_s (K)	300	323	373	423	473	523	573
Activation energy E (eV)	0.284	0.384	0.462	0.711	1.025	1.305	1.403

TABLE II

Film Thickness t (nm)	80	100	160	240	320
Activation energy E (eV)	1.313	1.305	1.292	1.281	1.267

stoichiometric. Manca *et al.* [20] have reported the indirect energy gap to be 1.40 eV while the direct gap is 1.87 eV for bulk polycrystalline $ZnIn_2Te_4$ at 300 K.

Fig. 3 shows plots of the logarithm of the resistance against the inverse temperature for polycrystalline $ZnIn_2Te_4$ thin films grown at a substrate temperature of 523 K with different thickness. The activation energy, ΔE, has been calculated for different thicknesses from these plots. It was found that the activation energy decrease gradually with the increase of film thickness, as shown in Table II. This decrease may be explained by the Neugebauer theory [21, 22] for electrical conduction in ultra-thin films which in a modified form could be applied to semiconductor continuous film.

Fig. 4 (curve a) shows the variation of the dark electrical resistivity, ϱ, with the thickness, t, of $ZnIn_2Te_4$ thin films deposited at 523 K. It was observed that with an increase in film thickness, the electrical resistivity decreases, reaching an almost constant value for higher thickness. This is because in thinner films, the resistivity includes contributions from both lattice and surface scattering, the thickness of the film being comparable with the mean free path of the charge carriers, but as the thickness increases the surface scattering component decreases and the resistivity is mainly due to lattice scattering. In addition there is also the possibility of the increase of the crystallite size in thick films which may result in a decrease in the electrical resistivity. To find out the resistivity of an infinitely thick film as well as the mean free path of the conduction electrons, comparison has been made between the experimental observation and the Fuchs–Sondheimer theory for the size effect on the electron mean free path [21]. The thick film approximation of this theory can be expressed in the form

$$\varrho_f = \varrho_0[1 + 3(1 - P)/8K]$$
$$K = t/\lambda > 1 \qquad (1)$$

where ϱ_f is the film resistivity, ϱ_0 the resistivity of an infinitely thick film, P the specularity parameter and K the ratio of film thickness t to the mean free path of the conduction electrons λ. Equation 1 suggests a linear dependence of ϱ_f with the inverse of thickness, $1/t$. A graph of ϱ_f against $1/t$ is shown in Fig. 4 (curve b), where the straight line has been drawn to a least square fit of the values. The intercept of the straight line gives the resistivity of an infinitely thick film ϱ_0 as $1.585 \times 10^6\,\Omega$cm while from the slope we obtain $[(1 - P)\lambda]$ as 66.2 nm. If we assume that the resistivity arises through a total diffuse scattering ($P = 0$), the mean free path of the conduction electrons will be 66.2 nm.

A plot of (ϱ_f/ϱ_0) against K is shown in Fig. 5. The full curve represents the theoretical plot obtained from Equation 1 and the points represent the experimental observations. It is observed that, the experimental observations agree well with the Fuchs–Sondheimer theory.

4. Conclusions

The electrical resistivity and the activation energy for $ZnIn_2Te_4$ thin films deposited at constant thickness depend strongly on the substrate temperature. The decrease of the resistivity with increasing the substrate temperature up to 523 K was explained on the basis of the Petritz barrier model, while the increase in resistivity for films grown at substrate temperatures higher than 523 K was due to the formation of non-stoichiometric polyphase film. The dependence of the activation energy on the film thickness may be explained by the Neugebauer theory, while the dependence of the resistivity on the film thickness can be explained by the Fuchs-Sondheimer theory.

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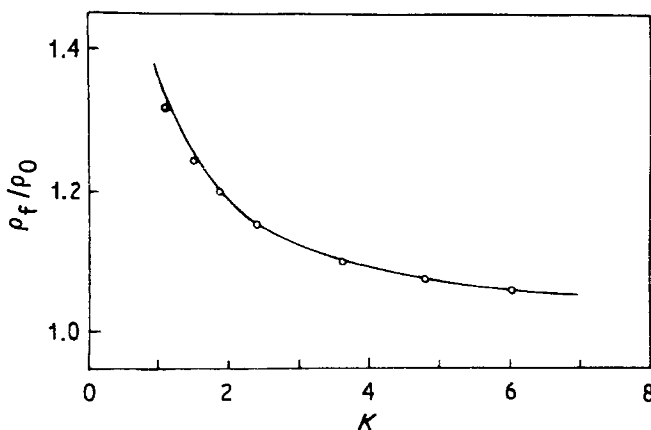

Figure 5 Plot of (ϱ_f/ϱ_o) against K. The full line represents the theoretical curve corresponding to Equation 1 and the points indicate the experimental values.

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Received 1 June
and accepted 3 November 1988