Electrical and optical properties of Indium sesquitelluride (In_2Te_3) thin films

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Indium sesquitelluride (In_2Te_3) thin films were grown on glass substrates using a flash evaporation technique. The nature of contact phenomena of Ag, Sn, In, Zn, Al-(p) In_2Te_3 junctions had been investigated. Ag, Sn, In and Zn metals were found to provide ohmic contact for In_2Te_3 thin films. The variation of DC-electrical resistivity of In_2Te_3 thin films with temperature was studied at different substrate temperatures. The optical measurements revealed that the flash evaporated In_2Te_3 thin films possessing direct energy band-gap. The variation of optical energy gap with substrate temperature was investigated. Film thickness, substrate temperature, composition and crystallinity were found to determine the optimization of electrical and optical properties of In_2Te_3 thin film.
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1. Introduction

Among the binary chalcogenide alloys of the type $A_2^{III}B_3^{VI}$ (A = Al, Ga, In and B = S, Se, Te), In_2Te_3, has been investigated for potential applications in thermoelectric power generator [1], gas sensor [2], strain gauge [3] and switching memory element [4, 5]. Indium sesquitelluride (In_2Te_3) is a layered semiconducting compound which exhibits two crystalline phases. The high temperature phase (above 523 K) is a disordered β-In_2Te_3, which has a defect zinc blende structure [6] with a lattice parameter of 0.616 nm, whereas the low temperature α-In_2Te_3 phase belongs to a defect anti-fluorite structure[7] with a lattice parameter of 1.854 nm. These two phases are characterized by one third or two thirds of the sites of the indium sub-lattice being vacant respectively. Consequently, the presence of such a large number of intrinsic defects (10^{21} cm^{-3}) affects strongly the motion and scattering of current carriers leading to observed wide variations in the electrical and optical properties of this compound [8–16]. The predominant scattering mechanism in this bulk crystalline compound of In_2Te_3 is reported to be due to neutral impurity centers caused by the cation vacancies. However, no such information is available so far as polycrystalline In_2Te_3 thin films are concerned. The room temperature (303 K) electrical resistivity reported for polycrystalline In_2Te_3 thin films was about 10^{11} ohm-cm [15], whereas it was about 1.1×10^6 ohm-cm for p-type In_2Te_3 single crystals as reported by Bose *et al.* [6, 17]. In the case of thin films, electrical resistivities of the order of 10^3 to 10^4 ohm-cm at 300 K were also reported by Zahab *et al.* [18]. In view of the confusion as well as conflicting information available on the electrical and optical phenomena in this compound, the authors have taken up a detailed investigation to study the influence of substrate temperature as well as film thickness on the electrical and optical properties of In_2Te_3 thin films. These studies, the authors believe, would be essential for the fabrication of any modern electronic thin film device based upon Indium Sesquitelluride.

2. Experimental

In_2Te_3 compound was synthesized first, by mixing and melting the high purity (99.999%) individual elements

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in stoichiometric proportions in a sealed quartz ampoule. The resultant bulk was then used as the source material for the deposition of In_2Te_3 thin films. In_2Te_3 thin films were deposited on ultrasonically cleaned glass substrates at different substrate temperatures and of different thicknesses by the flash evaporation technique. The source material was In_2Te_3 bulk powder with a grain size of about 200–300 μm and the source temperature was maintained at about 1150 K. A residual pressure of the order of 2.66×10^{-6} Torr was maintained during the deposition. The deposition rate was found to be 25 Å/sec for all the samples. The thickness and deposition rate of the films were monitored with the quartz crystal digital thickness monitor. The substrate temperature was controlled by a digital temperature controller. A digital high impedance electrometer (KEITHLEY-614) was used for the measurement of electrical properties. The optical absorption spectra (obtained from the transmittance) of the film-glass substrate combination were recorded using a BECKMAN DK-2A (UV-VIS-NIR) spectrophotometer. The substrate contribution to the optical absorption was corrected by introducing an uncoated substrate in the reference beam.

The nature of charge carriers was determined by using the hot probe technique. Conventional DC methods were employed for the measurement of electrical conductivity (σ). The variation in electrical conductivity (σ) with temperature could easily be described by the well-known relation,

$$\sigma = \sigma_O \exp\left[-\frac{\Delta E}{kT}\right] \quad (1)$$

where, 'σ_0' is the pre exponential factor and 'ΔE' is the activation energy for conduction.

3. Results and discussion

3.1. Structural characterization of In_2Te_3 thin films

Monophase and stoichiometric thin films of In_2Te_3 could be obtained by flash evaporation technique. The thin films formed on glass substrate were found to be polycrystalline and α-phase in nature. Well oriented and stoichiometric α-In_2Te_3 could be obtained on glass substrates at about 473 K. X-Ray diffraction technique was utilized for the characterization of In_2Te_3 films formed on glass substrates whereas electron diffraction technique was utilized for the films formed on the cleavage faces of NaCl. The details of growth and structural properties of In_2Te_3 thin films have already been reported elsewhere by the authors [18].

3.2. Metal-In_2Te_3 thin film coplanar structure

The flash evaporated In_2Te_3 thin films were all found to be p-type semiconductor in nature. To evaluate the electrical properties of a semiconductor material, a better under-

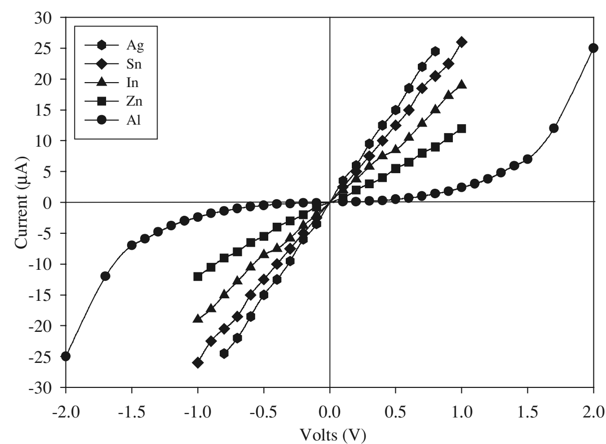

Figure 1 I-V characteristics of metal-In_2Te_3-metal contacts.

standing of the type of contacts made by different metals to the semiconductor and the effects of the contact material on it, if any, unless it is natural, is necessary when a metal-semiconductor junction is formed. Ohmic contact is a neutral contact, which offers negligible resistance to the flow of current through the semiconductor for either polarity of bias voltage and is characterized by symmetrical I-V characteristics. A rectifying contact on other hand is a blocking contact, which offers some high resistance to the flow of current through the semiconductor for either positive or negative bias voltage and characterized by asymmetrical I-V characteristics.

In the present study, contacts of Ag, Sn, In, Zn and Al metal films on In_2Te_3films grown at 473 K substrate temperature were studied as these substrate temperatures were found to yield well oriented In_2Te_3 films [18]. Fig. 1 shows the I-V characteristics of metal-In_2Te_3-metal structures obtained at room temperature (300 K). The metal contacts having approximate dimensions of 5 × 3 mm and thickness of 500 nm were vacuum deposited on α-In_2Te_3 films using proper masking arrangement in order to make the metal-semiconductor coplanar structure. The apparent resistance offered by these metal contacts increased in the order of Ag, In, Sn, Ni, Cd and Al. However, it was observed that Ag, Sn, In, Zn contacts exhibited good ohmic behaviour, whereas, Al contacts showed a non-ohmic behaviour. In the present study, vacuum deposited silver films with silver pasted leads were used for obtaining the ohmic contacts to the In_2Te_3 thin films and were subsequently utilized for the measurement of electrical properties.

3.3. Effect of substrate temperature on the resistivity of In_2Te_3 films

Fig. 2 shows the variation of electrical resistivity (ρ) of In_2Te_3 films with the substrate temperature (T_s). It is observed that the film resistivity decreases with increase in substrate temperature and reaches a minimum value at 473

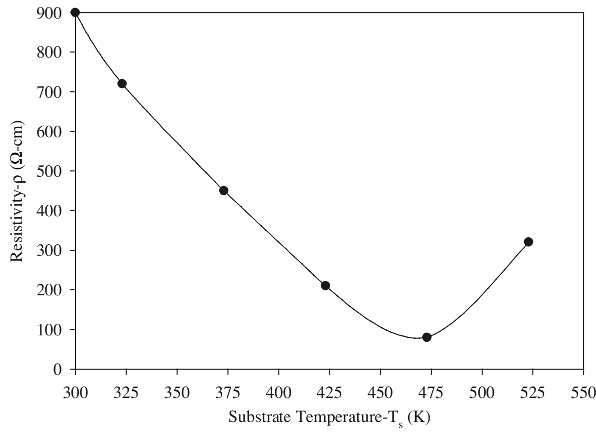

Figure 2 Variation of electrical resistivity-ρ with substrate temperature-T_s.

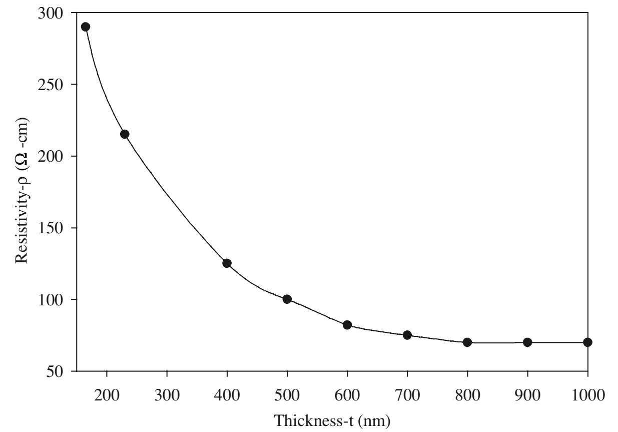

Figure 3 Variation of electrical resistivity with film thickness of In_2Te_3 films deposited at substrate temperature 473 K.

K. The authors have observed earlier [18] the formation of well oriented In_2Te_3thin films at a substrate temperature of 473 K. It was found to be due to the improvement in the crystallite sites and perfection. The resistivity has been found to increase when the substrate temperature rose above 473 K. The decrease in resistivity may also be understood on the basis of Petritz's [20] barrier model. Because the crystallites do not grow sufficiently large at low temperatures, the inter crystallite barriers are wide, offering a high resistance to the motion of charge carriers, while at higher substrate temperatures large crystallite sites are obtained which ultimately decrease the inter crystalline barriers.

The charge carriers, therefore, have to cross comparatively narrow intercrystalline barriers and these results in a decrease of resistivity. This is in agreement with the observations made from the electron microscopic studies which provided the evidence of the improvement in the crystallinity and grain size in the films with the increasing substrate temperature. The films deposited at substrate temperatures above 473 K showed an increase on the resistivity. It was observed [18] that at higher substrate temperatures In_2Te_3 films were non-stoichiometric and Tellurium deficient.

3.4. Effect of film thickness on the resistivity of In_2Te_3 films

Fig. 3 shows the variation of electrical resistivity (ρ) with thickness of the In_2Te_3 films deposited at a constant substrate temperature of 473 K. It is seen that the resistivity decreases as the thickness increases upto 800 nm. For the thickness upto 200 nm, the film consists of island structures and carrier transfer between the islands occurs by either field emission or field assisted thermionic emission. Beyond this thickness, the film is essentially continuous but resistivity changes with thickness because of appreciable surface scattering effect. Sondheimers [21] theory qualitatively explains that the scattering of carriers at the surface of the film effectively reduces the mean free path of the carriers, so that the resistivity decreases with increasing thickness. But it is inadequate to offer quantitative explanation, because during the initial stages of growth of semiconducting films, the films contain defects, voids, inter crystalline barriers and impurities, which also influence the resistivity. Beyond 800 nm thickness, the resistivity starts approaching that of bulk value since the surface scattering effect becomes negligible. It has also been observed that the resistivity of a very thick film is normally higher than that of reported value for a bulk In_2Te_3 single crystal. This may be due to the surface unevenness of thin films, as reported by Lucas [22]. Above 1000 nm thickness, the resistivity becomes nearly constant and this may be due to the saturation of grain size.

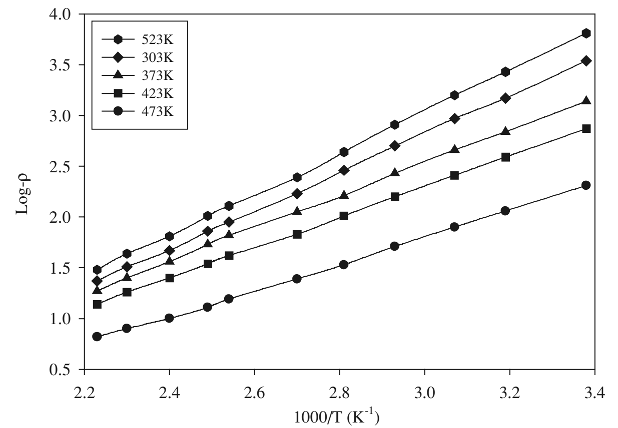

Figure 4 Variation of log-ρ with inverse of temperature-T.

3.5. Effect of substrate temperature on the electrical conductivity activation energy (ΔE) of In_2Te_3 films

The variation of DC electrical resistivity (ρ) as a function of temperature is used to determine the activation energy (ΔE). The variation of log(ρ) with inverse temperature (T) for polycrystalline In_2Te_3 thin films grown at different substrate temperatures having a near constant thickness of 100 nm is shown in Fig. 4. The obtained values of

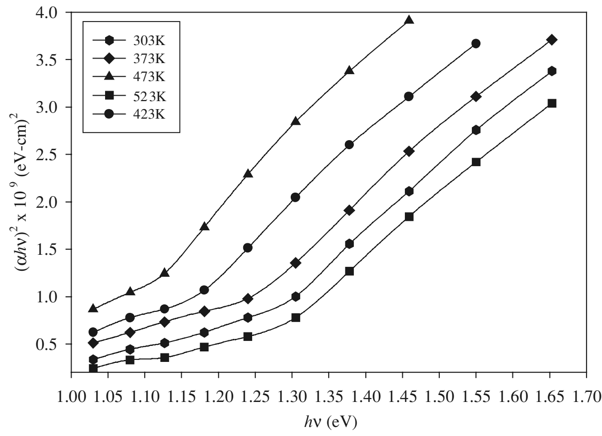

Figure 5 Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ of In_2Te_3 thin films grown at different substrate temperatures.

activation energies at different substrates temperatures for the In_2Te_3 thin films have been shown in Table I.

It is observed that the value of activation energy decreases with the increase in substrate temperature up to 473 K and then increases again. It has been mentioned earlier that at the substrate temperature of 473 K well oriented and stoichiometric α-In_2Te_3 polycrystalline thin films could be obtained. However, the small value of the observed activation energy at this substrate temperature indicates only the extrinsic conduction. It is to be noted here that the films were not subjected to any post-deposition thermal annealing.

3.6. Optical absorption in In_2Te_3 thin films

The intrinsic absorption edge of the flash evaporated In_2Te_3 thin films was examined using the relation given by Bardeen *et al.* [23] which states that the absorption coefficient α is related to the incident photon energy $(h\nu)$ as

$$\alpha h\nu = \beta(h\nu - Eg)^x \qquad (2)$$

where E_g is the energy gap and $x = 1/2$ for a direct allowed transition. β is the parameter that depends on the transition probability. A plot of the average value of $(\alpha h\nu)^2$ against $h\nu$ was found to be a straight line for the films deposited at different substrate temperatures (Fig. 5).

TABLE I Values of electrical conductivity activation energy (ΔE) at different substrate temperatures for the In_2Te_3 thin films

Substrate temperature (K)	Activation energy ΔE (eV)
303	0.35
373	0.34
423	0.32
473	0.30
523	0.36

TABLE II Values of optical energy gap (E_g) at different substrate temperatures for the In_2Te_3 thin films

Substrate temperature (T_s K)	Optical energy gap E_g (eV)
303	1.18
373	1.13
423	1.05
473	1.00
523	1.22

The intercepts of these linear plots on the energy axis at $(\alpha h\nu)^2 = 0$ gave the direct band gap energies at different substrate temperatures. The values of the optical band gap energy determined for In_2Te_3 thin films deposited at different substrate temperatures are shown in Table II.

The optical energy gap was found to decrease with increasing substrate temperature and reached an optimum value of 1.00 eV at 473 K. Above 473 K the optical energy gap was found to increase as observed in the variation of conductivity activation energy with substrate temperature. The substrate temperature 473 K was found to be the optimum value for good quality poly crystalline In_2Te_3 thin films. Hence, α-In_2Te_3 thin films deposited at 473 K are being utilized by the authors for device applications.

4. Conclusions

The flash evaporated In_2Te_3 thin films were found to be *p*-type semiconductor in nature. Metal contacts such as Ag, Sn, In and Zn were found to provide good ohmic contacts to In_2Te_3 thin films, whereas, Al contact was found to be non-ohmic. The influence of substrate temperature on the conductivity activation energy and the optical band gap was investigated. The observed change in the electrical and optical properties with substrate temperatures can be attributed to the changes in the structural perfection of the films. A substrate temperature of 473 K was found to provide a direct optical energy gap of 1.00 eV indicating the possible utility of these films as absorbers in thin film solar cells.

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