JOURNAL OF MATERIALS SCIENCE 30 (1995) 4890–4895

Transport properties of InSe$_x$ flash evaporated thin films

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Thin films of InSe$_x$ were obtained by vacuum evaporation of polycrystalline materials onto substrates at moderate temperatures, T_s. Electrical properties of films grown from different stoichiometries of flash source materials are reported in this work. The temperature dependence of the conductivities shows two conduction regimes. The low temperature regime exhibits a $T^{-1/4}$ conductivity dependence which fits well, using the Mott model, with an average localized states density value of $N(E_F) \approx 8 \times 10^{18}\ \mathrm{cm^{-3}\,eV^{-1}}$. Hall measurements as a function of temperature show that the predominant conduction mechanism is scattering by grain boundaries in polycystalline films.

1. Introduction

The growth and characterization of polycrystalline thin films of layered semiconducting compounds of the binary In–Se system, e.g. InSe and In$_2$Se$_3$, are of particular interest because of their applicability in semiconductor technology [1, 2], electrochemical and photovoltaic cells [3–7] and switching devices [8]. The main difficulty confronted in the preparation of these compounds in a single evaporation is the coexistence of several kinds of compounds with different stoichiometries [9] and, in addition, InSe is thermally less stable than In$_2$Se$_3$. Several authors have studied amorphous and/or polycrystalline InSe films for which the presence of a small amount of In$_4$Se$_3$ has been reported [10–12]. This phase frequently coexists with InSe owing to loss of the more volatile selenium during the film growth. It has been recently reported that films with adequate stoichiometry can be prepared by flash evaporation of presynthesized compound [13]. The crystallinity and morphology of films have been studied as a function of the starting material composition for which reproducible polycrystalline InSe films are formed.

Flash evaporated InSe$_x$ thin films grown using different stoichiometries of source materials exhibit structural properties which originate from either single phases, such as In$_4$Se$_3$, InSe or In$_2$Se$_3$, or a mixture of these compounds [14, 15]. The electrical properties of these films are reported as a function of the material source stoichiometry. The conduction mechanisms of polycrystalline films are investigated in the temperature range 77–300 K. Furthermore, the density of localized states in the vicinity of the Fermi level are determined.

2. Experimental procedure

InSe$_x$ films were grown by flash evaporation of presynthesized indium–selenide powders of various stoichiometries on silica glass substrates maintained in the temperature range 300–653 K. The source materials for films were polycrystalline materials In$_{1-y}$Se$_y$ with compositions range between $0.49 \leqslant y \leqslant 0.62$. The presynthesized powder was prepared by direct fusion of elements in atomic proportions in a vacuum sealed quartz tube heated up to a temperature of 1200 K for 24 h. The ampoule was slowly cooled down to room temperature and the procedure was repeated two times to improve homogeneity of the material.

Films of dimensions $15 \times 10\ \mathrm{mm^2}$ were evaporated using tantalum masks and a molybdenum boat in a vacuum of below 10^{-3} Pa. In the flash evaporation technique the source materials were powdered and evaporated from a homemade system described elsewhere [16], in which the controlled boat temperature was about 1500 K. The evaporation speed was about $25\ \mathrm{nm\,s^{-1}}$. The thickness of evaporated films was in the range 0.3–0.9 μm and was controlled by a quartz crystal monitor which was calibrated with the aid of a Tensor profilometer. The film composition was determined by X-ray photoelectron spectroscopy (XPS) using an ISA-Riber Mac-2 electron spectrometer. The structure of polycrystalline films has been investigated using X-ray diffraction (XRD) and Raman scattering (RS) spectroscopy.

Electrical resistivity and Hall measurements were carried out using a five probe technique. Evaporated indium contact films with indium-pasted leads provided ohmic contacts to the films. Film resistivity and

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Hall coefficient were measured as a function of temperature ranging from 77 to 300 K in a SMC-TBT cryostat using a computerized homemade apparatus.

3. Results and discussion

3.1. Composition and structure of InSe$_x$ films

The chemical analysis of InSe$_x$ films grown at moderate substrate temperatures, T_s, ($433 \leqslant T_s \leqslant 653$ K) was carried out by XPS measurement. Quantitative studies were based on the determination of the In(4d) and Se(3d) peak areas [17]. The XPS spectra of InSe and In_2Se_3 single crystals were recorded as references. They show an energy separation of 35.6 eV between the In(4d) and Se(3d) states. A summary of the results of six typical samples subjected to estimation is given in Table I. Fig. 1 shows the atomic compositional ratio x = Se/In in flash evaporated films as a function of the selenium content in the source material.

These results were confirmed by structural investigations using both XRD and RS techniques. At low selenium contents when the source stoichiometry ratio is $R = 0.96$, spectrum (with intense peaks located at 104, 131 and 150 cm^{-1}) related to a film having a single phase In_4Se_3 is recorded. For higher values of R the film characterizations exhibit a rather complex structure, and a mixture of either InSe + In_4Se_3 or InSe + In_2Se_3 is detected. At $R \approx 1.17$ an InSe polycrystalline phase appears and well resolved lines due to the polar modes of InSe are observed in the RS spectrum of the film grown above $T_s = 473$ K. Indexing the X-ray peaks shows that the InSe films grow in the γ-polytype with rhombohedral symmetry [18]. Further increase of R produces an In_2Se_3 film. The γ-modification of this phase is clearly identified by means of the Raman lines at 153 and 232 cm^{-1} [19]. It is worth noting that the formation of a single phase InSe film involves an over-stoichiometry of the starting powder; the role of excess selenium in film growth is the formation of a higher partial pressure of selenium for surface reactions onto the substrate [20].

TABLE I Estimation of selenium–indium ratio in flash evaporated InSe$_x$ films as a function of the selenium content in the source materials

Flash-source		InSe$_x$ film	
Composition	Atomic ratio R = Se/In	Atomic ratio x = Se/In	Nearest formula representation
$In_{0.51}Se_{0.49}$	0.96	0.75	In_4Se_3
$In_{0.50}Se_{0.50}$	1.00	0.85	$0.6In_4Se_3 + 0.4InSe$
$In_{0.47}Se_{0.53}$	1.13	0.90	$0.6InSe + In_4Se_3$
$In_{0.46}Se_{0.54}$	1.17	1.00	InSe
$In_{0.40}Se_{0.60}$	1.50	1.38	$0.76In_2Se_3 + 0.24InSe$
$In_{0.38}Se_{0.62}$	1.63	1.50	In_2Se_3

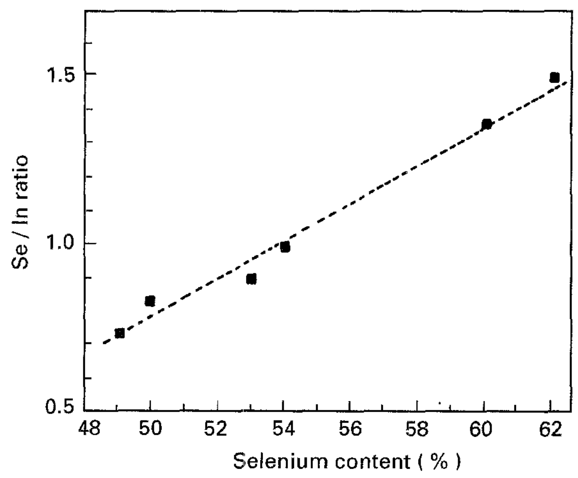

Figure 1 Atomic compositional ratio Se/In in thin film as a function of selenium content in the source deposition materials.

3.2. Electrical properties of InSe$_x$ films

Results of experimental studies are presented concerning d.c. conductivity to obtain additional information about the nature of the conduction mechanism in InSe$_x$ films. The electrical measurements have been carried out in the temperature range 77–300 K on polycrystalline films which exhibit semiconducting n-type conductivity. Fig. 2 shows the Arrhenius plot of the electrical conductivity of polycrystalline InSe$_x$ thin films grown from various source materials: (a) $In_{0.51}Se_{0.49}$, (b) $In_{0.50}Se_{0.50}$, (c) $In_{0.47}Se_{0.53}$, (d) $In_{0.46}Se_{0.54}$ and (e) $In_{0.40}Se_{0.60}$.

Electrical conduction can take place by two parallel processes

1. by band conduction, and
2. by hopping conduction in the localized states.

The former tends to occur at high temperatures, where carriers excited beyond the mobility edges into non-localized states dominate the transport, while the latter may be due to carriers excited into localized states at band edges [21], i.e.

$$\sigma = \sigma_i + \sigma_h \qquad (1)$$

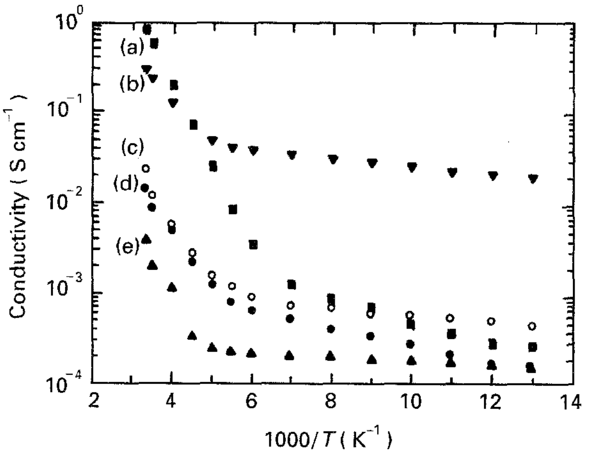

Figure 2 Arrhenius plot of the electrical conductivity of polycrystalline InSe$_x$ thin films grown from various source materials: (a) $In_{0.51}Se_{0.49}$, (b) $In_{0.50}Se_{0.50}$, (c) $In_{0.47}Se_{0.53}$, (d) $In_{0.46}Se_{0.54}$, and (e) $In_{0.40}Se_{0.60}$.

TABLE II Electrical properties of polycrystalline $InSe_x$ films at room temperature

Film composition	$\sigma_{300\,K}$ $(S\,cm^{-1})$	E_a (meV)	$\mu_{300\,K}$ $(cm^2\,V\,s^{-1})$
$InSe_{0.75}$	8.0×10^{-1}	172	83.3
$InSe_{0.85}$	3.0×10^{-1}	105	51.5
$InSe_{0.9}$	2.5×10^{-2}	128	14.2
$InSe_{1.0}$	2.0×10^{-2}	133	5.0
$InSe_{1.38}$	4.0×10^{-3}	162	3.1

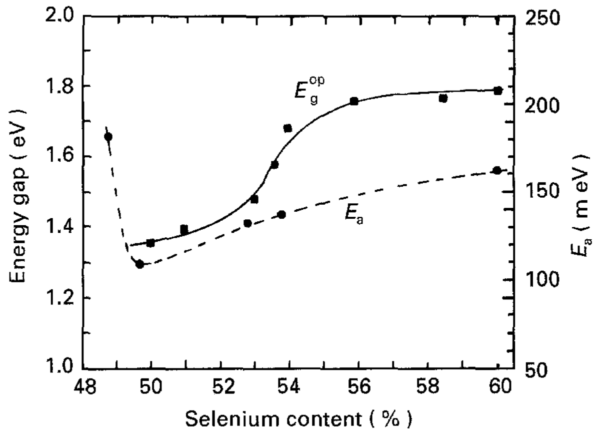

Figure 3 (a) Optical energy gap and (b) conductivity activation energy of polycrystalline $InSe_x$ thin films as a function of selenium content in the source material.

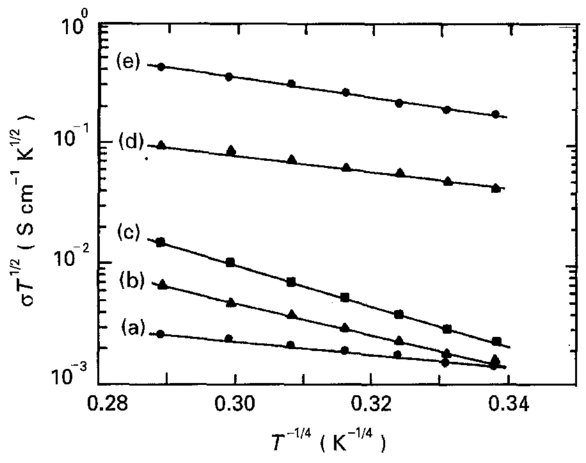

Figure 4 Dependence of $\sigma T^{1/2}$ against $T^{1/4}$ for polycrystalline $InSe_x$ thin films grown from various source materials as in Fig. 2.

where σ_i is the intrinsic conductivity and σ_h the hopping conductivity. The intrinsic conductivity is of Arrhenius type expressed as

$$\sigma_i = \sigma_0 \exp(-E_a/k_B T) \qquad (2)$$

where E_a is the thermal activation energy for conductivity and k_B the Boltzman constant. A plot of $\ln \sigma_i$ versus $1/T$ gives the thermal activation energy, E_a. The intrinsic conduction gives the thermal activation energy, E_a, according to Equation 2, whose values as a function of film composition are listed in Table II. As shown in Fig. 2 the conductivity of polycrystalline $InSe_x$ films grown at $T_s \geqslant 433$ K varies with composition from 1 to $10^{-4}\,S\,cm^{-1}$ in the temperature range 300–77 K. The activation energy, E_a, determined was lower than the band gap of the films. This observed difference is presented in Fig. 3, where the optical energy band gap, E_g^{op}, was determined by absorption measurements. This may be due to the defects or gap states present in large number in the films [21]. These states are localized at the Fermi level which is pinned near the conduction band.

The hopping conduction is observed at low temperature in the range below 200 K. Replots of the conductivity curves in Fig. 2 lead to Mott's relation for thermally assisted hopping conduction [22]

$$\sigma_h = \sigma_2 T^{-1/2} \exp(-B/T^{1/4}) \qquad (3)$$

where σ_2 and B are constants. This relation holds quite well at low temperatures as shown in Fig. 4. The close linear fit which extends up to 200 K suggests that conduction at low temperature is due to hopping of the carriers in the localized states at the Fermi level [23]. A marked increase in conductivity over two orders of magnitude is observed when the selenium content in the source material decreases from $y = 0.6$ to 0.49. There have been few investigations on the low temperature conduction regime in indium–selenide films to date. Wood *et al.* [24] observed variable range hopping type conduction for amorphous In_xSe_{1-x} films with $x > 0.46$. Watanabe and Sekiya [25] have studied the $T^{-1/4}$ dependence of conductivity for amorphous In_2Se_3 films. The temperature dependence of conductivity in amorphous In_4Se_3 films grown at $T_s = 300$ K has been investigated [26]. Measurements show that the conductivity is in the order 10^{-5}–$10^{-2}\,S\,cm^{-1}$ in the temperature range 300–430 K. Experimental plots of $\ln(\sigma T^{1/2})$ against $T^{-1/4}$ exhibit a straight line. The conductivity is lowered by a few orders of magnitude, and the slope is increased (with $B = 1.5\times10^2\,K^4$) in comparison with data obtained from films grown on heated substrates. These results suggest that the density of localized states is strongly dependent on the substrate temperature in In_4Se_3 films.

To gain a good understanding of the electronic structure of the $InSe_x$ system, it is important to study the density of localized states in these films. The density of states at the Fermi level, $N(E_F)$, was calculated using the expression

$$B = [16\alpha^3/k_B N(E_F)]^{1/4} \qquad (4)$$

where B is obtained from the slope of $\log \sigma$ versus $T^{-1/4}$ plots, α is the coefficient of exponential decay of the localized state wave function, which is assumed to be given by $\alpha^{-1} = 0.6$ nm for the region where Mott's equation is valid [27]. Values of $N(E_F)$ obtained from Equation 4 are listed in Table III. Fig. 5 shows the density of localized states plotted against the composition of selenium at the thermal equilibrium Fermi level, E_F. One finds that $N(E_F)$ is influenced by composition. Experimental results show that the density of states is lower for In_4Se_3 films. These values are in

TABLE III Density of localized states in polycrystalline $InSe_x$ films

Film composition	$N(E_F)$ ($cm^{-3} eV^{-1}$)
$InSe_{0.75}$	7×10^{17}
$InSe_{0.85}$	6×10^{18}
$InSe_{0.9}$	6×10^{18}
$InSe_{1.0}$	6×10^{18}
$InSe_{1.38}$	1×10^{19}

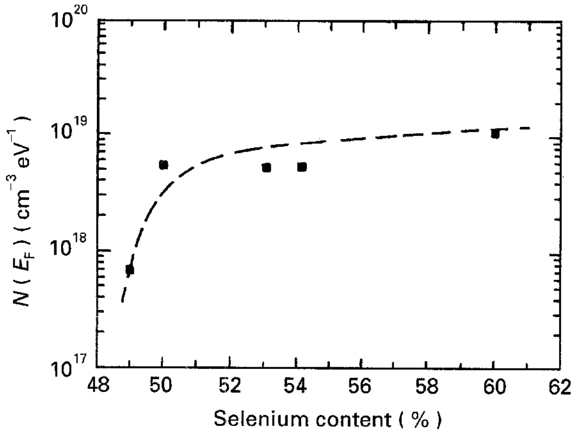

Figure 5 Density of states at the Fermi level of polycrystalline $InSe_x$ thin films as a function of selenium content in the source material.

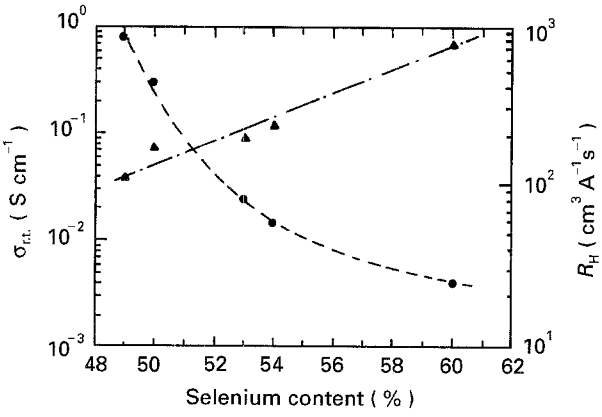

Figure 6 Room temperature, r.t., conductivity and Hall coefficient, R_H, of polycrystalline $InSe_x$ thin films as a function of selenium content in the source material.

good agreement with those of other In–Se films reported in the literature [28, 29].

Fig. 6 shows variations in the room temperature conductivity and in the Hall coefficient of polycrystalline $InSe_x$ films as a function of selenium content. It can be seen from these observations that in the films formed at moderate deposition temperatures (in the range 433–653 K) carrier mobility decreases as the selenium content increases in $InSe_x$ films. The carriers show appreciable mobility in the indium-rich films. The Hall mobility, μ_H, reaches a value of 83.3 $cm^2 V^{-1} s$ in In_4Se_3 films grown at $T_s = 520$ K, whereas μ_H is only 5 $cm^2 V^{-1} s$ in InSe polycrystalline film grown at $T_s = 653$ K. Data for the above measurements are listed in Table II. It is worth noting that the increase of localized states in the band gap is responsible for decreasing the carrier mobility and the carrier life time in $InSe_x$ films.

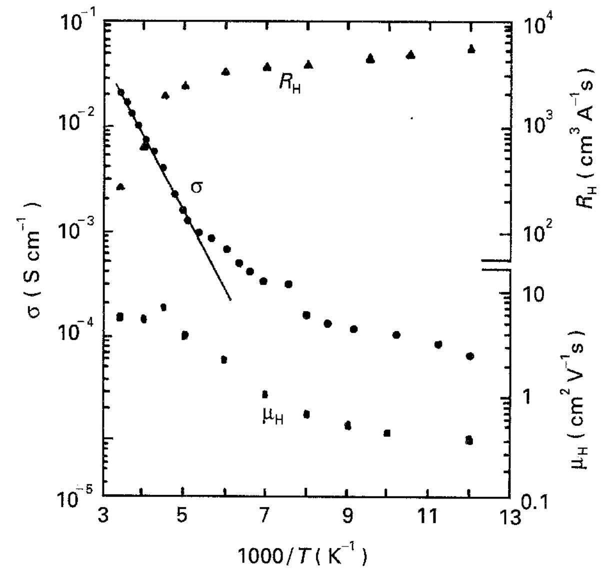

Figure 7 Conductivity, σ, mobility, μ_H, and Hall coefficient, R_H, of a flash evaporated InSe film (0.6 μm thick) as a function of the reciprocal temperature.

Fig. 7 shows the temperature dependence of the electrical properties of an InSe polycrystalline film deposited at 653 K. One observes that the carrier mobility decreases by one order of magnitude in the temperature range 300–77 K. The plot $\ln(\mu_H)$ against $\ln(T)$ does not fit any classical scattering mechanism which occurs in bulk semiconductors (here one observes a $T^{0.8}$ dependence of the carrier mobility). Consequently, the transport properties of polycrystalline InSe and In_4Se_3 films are examined and interpreted as follows.

In polycrystalline semiconductors the transport of carriers is driven by scattering mechanisms at intercrystallite boundaries, rather than by intracrystallite characteristics. Moreover, for compound materials the grain boundaries can be a region of non-stoichiometry, which influences the transport properties. By combining the grain boundary trapping model with a thermionic-emission mechanism through created potential barriers, Seto [30] has developed a comprehensive theory of transport phenomena in polycrystalline materials which explains most of their electrical properties. The electrical transport properties of $InSe_x$ films are governed by monovalent trapping states at the grain boundaries able to capture, and therefore immobilize, free carriers [5, 31]. To simplify the model one assumes that polycrystalline indium–selenide films are composed of identical crystallites having a grain size, L. One also assumes that there is only one type of donor state present and uniformly distributed with a donor state density, N_D. Intrinsic defects are electrically active in this type of compound and probably dominate conduction mechanisms. The concentration traps, N_t, are assumed to be initially neutral and become charged by trapping a carrier. Using the above assumptions, an abrupt depletion approximation is used to calculate the

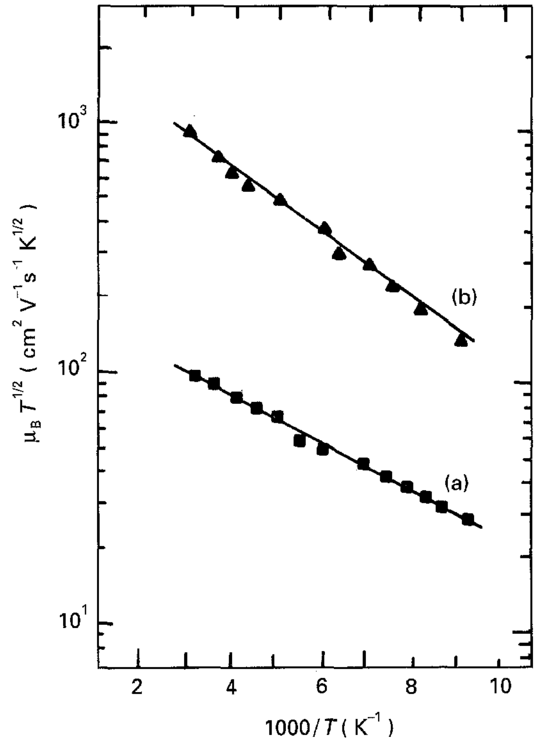

Figure 8 Petritz mobility as a function of the reciprocal temperature in (a) In_4Se_3 and (b) InSe thin films.

TABLE IV Electrical parameters deduced from the model of monovalent trapping states at the grain boundaries in polycrystalline $InSe_x$ films

Film	Φ_B (meV)	N_D (cm^{-3})	N_t (cm^{-2})	L (nm)
InSe	20	8.6×10^{16}	4×10^{11}	17
In_4Se_3	35	1.5×10^{17}	9×10^{12}	23

energy band diagram in the crystallites. In this approximation all the mobile carriers in a region of width, W, from the grain boundary are trapped by the trapping states, resulting in a depletion zone. A logarithmic plot of $\mu_B T^{1/2}$ against the reciprocal temperature shows that the mobility, μ_B, follows approximately an exponential law represented by

$$\mu_B = eL(2\pi m^* k_B T)^{-1/2} \exp(\Phi_B / k_B T) \qquad (5)$$

where Φ_B is the potential barrier height at grain boundary, m^* is the effective mass of carrier, e is the electron charge, and k_B is the Boltzman constant. This law indicates that charge carriers in $InSe_x$ films are scattered by a potential barrier associated with the intergrain boundaries as proposed by Petritz [32]. Fig. 8 shows the variations in $\ln(\mu_B T^{1/2})$ for InSe and In_4Se_3 polycrystalline films grown at 653 and 433 K substrate temperatures, respectively. Using the model of potential barriers, Equation 5, for these films one obtains the values listed in Table IV. The grain size of $InSe_x$ obtained from the theoretical Petritz mobility is comparable with the depletion zone width which increases with increasing substrate temperature resulting in a decrease of the potential barrier height.

4. Conclusions

$InSe_x$ thin films grown at moderate substrate temperatures ($433 \leqslant T_s \leqslant 653$ K) have a polycrystalline structure. The electrical properties of these films prepared by flash evaporation have been investigated. Electrical properties have been studied in the two regimes of conduction by band conduction and by hopping conduction in the localized states. Intrinsic conductivity is of Arrhenius type, with a thermal activation energy, E_a, in the range 0.1–0.2 eV, which is a function of selenium content. Hopping conduction is observed at low temperature in a range below 200 K, which exhibits a $T^{-1/4}$ conductivity dependence. The conduction occurs by carrier hopping between localized states near the Fermi level, E_F, an average value of $N(E_F) = 8 \times 10^{18}$ cm^{-3} eV^{-1} was obtained, which is in good agreement with those of other In–Se films reported in the literature.

The Hall mobility reaches a value of 83 cm^2 V^{-1} s^{-1} in In_4Se_3 films grown at $T_s = 520$ K. The electrical transport properties of $InSe_x$ films are governed by carrier trapping at the grain boundaries. Using the model of potential barriers for InSe and In_4Se_3 films grown at moderate temperature, one obtains the potential barrier height, the impurity concentration, the trapping density and the width of the depletion zone in the crystallites.

Acknowledgements

The authors are very grateful to Mr M. Lemal for the XRD measurements. They wish to thank Dr J. Y. Emery for his technical assistance in carrying out the XPS measurements. One of the authors (N. B.) would like to thank Professor M. Balkanski for his encouragement during the course of this work.

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Received 26 July 1994
and accepted 22 March 1995