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Optical and electrical properties of pure and doped amorphous thin selenium films

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Thin amorphous selenium (a-Se) films and Se films doped with indium have been prepared by thermal evaporation under high vacuum and controlled deposition conditions. Measurement of DC conductivity made *in situ* as a function of temperature (in the range room temperature to 400 K) and absorption in the photon energy range 1·5 to 6·5 eV are reported. The effects of film thickness from 50 to 760 nm and vacuum annealing on these properties are considered. Our specimens showed low conductivity and two activation energies indicating different conduction mechanisms in the gap. Furthermore, the conductivity is found to be independent of thickness but sensitive to doping and oxygen incorporation. The value of the optical energy gap (E_{opt}) is (2·0 and 1·93) eV for (a-Se) and (a-Se : In) films, respectively. From the Urbach edge, the value of E_e, the width of the tail of the localized states in the gap, is estimated. The values of both E_{opt} and E_e are nearly independent of thickness. A preliminary study of the infra-red transmission is also investigated. The value of the refractive index is in the range 2·40–2·65.

1. Introduction

Amorphous selenium (a-Se) has become a material of commercial importance since the advent of electrophotography. Selenium occurs in two crystalline phases. The normal haxagonal phase in metallic Se (or grey) and has a high conductivity with respect to other semiconducting phases ($\approx 10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$). Monoclinic (or red) Se has a low conductivity ($\approx 10^{-11}$–$10^{-12}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) and is a less stable phase. The red phase is thought to be based on a structure of Se rings while grey Se consists of long chains of atoms allowing a path for carrier migration. The third phase, a-Se, can be obtained by quenching the liquid, but most electrical measurements have been made on evaporated films. Because of its attractive properties, a-Se in thin film form has various device applications, such as rectifiers, photocells, vidicons and switching and memory devices (Mott and Davis 1979, Homma *et al.* 1980). Like many other amorphous semiconductors having band gaps larger than 2 eV, the conductivity (Hartke 1962) of pure a-Se at room temperature is very low $\approx 10^{-16}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. Unfortunately the temperature range over which conductivity measurements can be made is limited by the high resistivity at low temperature and the low crystallization temperature. The temperature dependences of the optical absorption edge in amorphous and liquid Se have been measured by Siemsen and Fenton (1967).

Since, for all the devices mentioned above, amorphous films of specific electrical and optical properties are required, it becomes necessary to find an appropriate experimental technique by which films having the required specifications can be

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obtained. Doping is one of the usual methods but it was suggested by Mott (1970) and Mott *et al.* (1975) that this is not applicable in a-Se because of the pinning of the Fermi level (E_F) by D^+ and D^- states in the band gap. However, in this paper an attempt is made to study the possibility of preparing pure and doped a-Se thin films and further to study their optical and electrical properties in some detail.

2. Experimental details

Thin a-Se films and films doped with In (99·9999%) have been prepared by thermal evaporation under high vacuum and controlled deposition conditions. The indium was accurately weighted with an electronic balance and thoroughly mixed with pure a-Se (99·999%) and both were evaporated from molybdenum boats in an Edwards coating unit to form pure and doped a-Se films. The lowest attainable pressure was $\approx 3 \times 10^{-6}$ Torr rising to $\approx 7 \times 10^{-6}$ Torr during evaporation. Different thicknesses of film were prepared at a substrate temperature of approximately room temperature. Transparent glass slides were used for electrical and optical properties and were thoroughly cleaned in a series of well-known steps before use. The actual thickness (t) of the films studied was determined by multiple beam interferometry using Fizeau fringes of equal thickness.

A PE 1450 DC power supply, a PM 2517 digital multimeter and a Keithly 616 digital electrometer, were use for RMS electrical conductivity.

The optical absorbance A and transmittance were taken at room temperature in the wavelength range ($\lambda = 200$–900 nm) using a Pye-Unicam SP 1800 Pye Unicam/Philips spectrophotometer.

After correcting for reflection at the first surface, the absorption coefficient (α) at an angular frequency of radiation (ω) was calculated using the relation:

$$\alpha(\omega) = 2{\cdot}303A/t \tag{1}$$

while measurements of IR absorption at $\lambda = 2{\cdot}5$–$50\,\mu m$ were made using a modified technique (Al-Ani 1984). The structure of our films was measured by X-ray diffraction using a Siemens D 500 diffractometer.

3. Results and discussion

3.1. *Optical properties*

X-ray investigations at room temperature have been carried out for the specimens and a typical diffractogram showed the absence of peaks, which reveals that those films possessed amorphous structure.

At high absorption levels ($\alpha(\omega) \geqslant 10^4\,\mathrm{cm}^{-1}$) the absorption coefficient in amorphous semiconductors has the following frequency dependence (Tauc 1970, Davis and Mott 1970)

$$\hbar\omega\alpha(\omega) = B(\hbar\omega - E_{\mathrm{opt}})^r \tag{2}$$

where B is a constant, $\hbar\omega$ is the incident photon energy and r is an exponent which can assume values of 1, 2, 3, 1/2 and 3/2, depending on the nature of the electronic transitions responsible for the absorption.

Equation (2) with $r = 2$ is normally suggested to fit the optical results and infer a non-direct transition in k-space. Thus, from the spectrum of the optical absorbance

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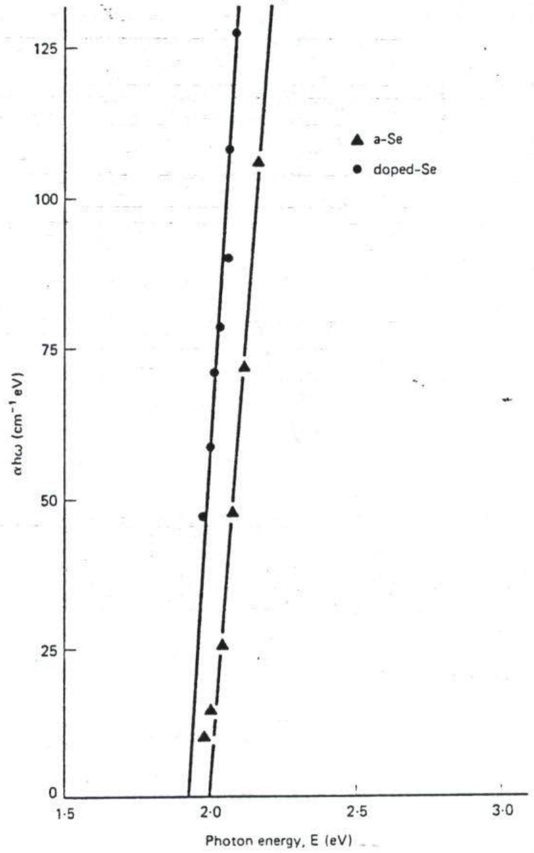

Figure 1. Variation of $(\alpha\hbar\omega)$ with $\hbar\omega$ for a-Se and a-Se : In.

the data is replotted in Fig. 1 in terms of an equation which is appropriate when, for an amorphous non-metallic material, there is a sharp rise in the density of states close to the band edge, i.e. (2) with $r = 1$. A good straight line is obtained with values of $E_{\text{opt}} = 2{\cdot}0$ and $1{\cdot}93$ eV for pure and doped a-Se, respectively. The application of this equation to a-Se is appropriate because of the chain-like structure which exists in many Se specimens and may give rise to a one-dimensional system.

The values are in excellent agreement with previous results (Al-Ani and Hogarth 1984). The addition of In to the network has reduced the value of E_{opt}. Similarly, it was found that E_{opt} gets smaller in evaporated a-Si film when it is doped by 3% (by weight) indium or phosphorus (Makadsi *et al.* 1989).

In the absorption coefficient range $1\,\text{cm}^{-1}$ to $\approx 10^{-4}\,\text{cm}^{-1}$, $\alpha(\omega)$ is described by the Urbach (1953) formula:

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/E_e) \tag{3}$$

where α_0 is a constant and E_e is an energy which is interpreted as the width of the tail of localized states in the forbidden band gap which are associated with the amorphous nature of the material. Figure 2 shows the Urbach behaviour of the optical absorption data for both a-Se and a-Se : In films. The exponential dependence of $\alpha(\omega)$ on $\hbar\omega$ for those films indicates that they obey Urbach's rule. The values of E_e were $0{\cdot}07$ eV and $0{\cdot}1$ eV for a-Se and a-Se : In films, respectively (Table 1) and it does not vary significantly with dopants. Hartke and Regensburger (1965)

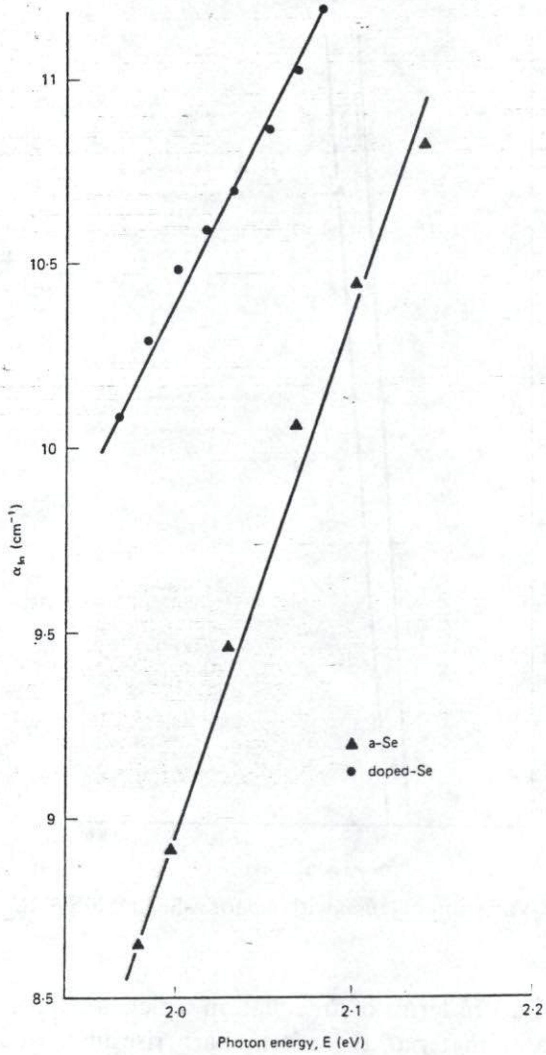

Figure 2. Urbach behaviour of optical absorption data of a-Se and a-Se: In thin films.

and Mott and Davis (1979) found the value $E_e \approx 0{\cdot}058$ eV, whereas Al-Ani and Hogarth (1984) obtained $E_e \approx 0{\cdot}11$ eV.

In view of the likely presence of strong internal fields in amorphous semiconductors and the accurately exponential behaviour predicted by the Dow and Redfield theory (1970) for the field broadening of an exciton line, this model is attractive as an explanation of the type of edge shown in Fig. 2. Table 1 summarizes

Specimen thickness (nm)	E_{opt} (eV)	E_e (eV)
100	2·00	0·154
115	2·05	0·154
200	2·05	0·123
760	2·00	0·070
730 (a-Se : In)	1·93	0·100

Table 1. Values of E_{opt} obtained from $(\alpha\hbar\omega)$ versus $\hbar\omega$ and E_e calculated from the Urbach rule for a-Se thin films prepared by thermal evaporation.

the optical parameters obtained for other a-Se specimens. It is observed that the ≈ 100 nm thick sample had the largest value of E_e while it becomes lower and reaches its limiting value at high thickness. This may be interpreted as follows.

At the beginning of the deposition process, some dangling bonds are likely to be created and these would be expected to act as structural defects, which are responsible for the localized states in the material. As the thickness is increased a more homogeneous a-network is built up thus reducing the proportion of defects and the concentration of localized states. The infra-red spectra of a-Se films deposited on KBr are presented in Fig. 3. Those spectra did not actually detect any clear band. Available literature (Lucovsky and Knights 1974) on IR and Raman spectra is only for the far IR region, i.e. at wavenumber 0–300 cm^{-1}, since a-Se was considered as an example of a molecular material (Mott and Davis 1979) in which dominant vibrational modes are retained on disordering. Indeed further IR measurements are needed to reach a better insight into the type of chain and local modes available in this material.

The refractive indices (n_f) of the films were estimated from the interference fringes which occur on the long-wavelength side of the absorption edge and by using the equation (Al-Ani and Beynon 1985).

$$2n_f t = \frac{1}{\lambda_2} - \frac{1}{\lambda_1}$$

where λ_1 and λ_2 are the wavelengths of neighbouring dark fringes in the interference pattern. Those values were in the range 2·40–2·65, in good agreement with the measurements of Koehler *et al.* (1959).

3.2. *Electrical properties*

Figure 4 shows the temperature dependence of the (*in situ*) DC conductivity (σ) of pure a-Se film to be in accordance with the equation

$$\sigma = \sigma_0 \exp\left(-E_a/kT\right) \tag{4}$$

where σ_0 is constant, E_a is the activation energy of conduction, k is Boltzmann's constant and T is the absolute temperature. This equation is plotted as $\ln \sigma$ versus $1000/T$ which yields straight lines. Two straight lines are presented; the first stage from room temperature up to 356 K gives $E_{a1} \approx 0{\cdot}111$ eV, the second stage at higher than 356 K rises sharply to 411 K with $E_{a2} \approx 0{\cdot}668$ eV. The other sample thickness

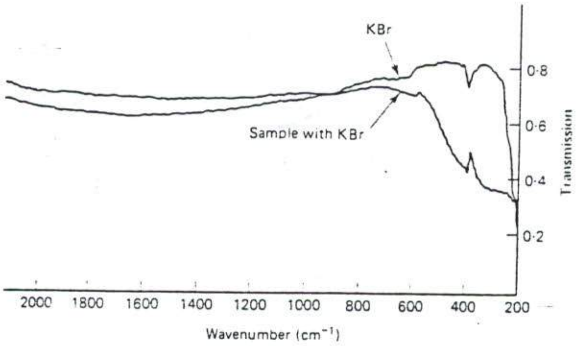

Figure 3. Infrared transmission spectrum for both a KBr disc and an a-Se film.

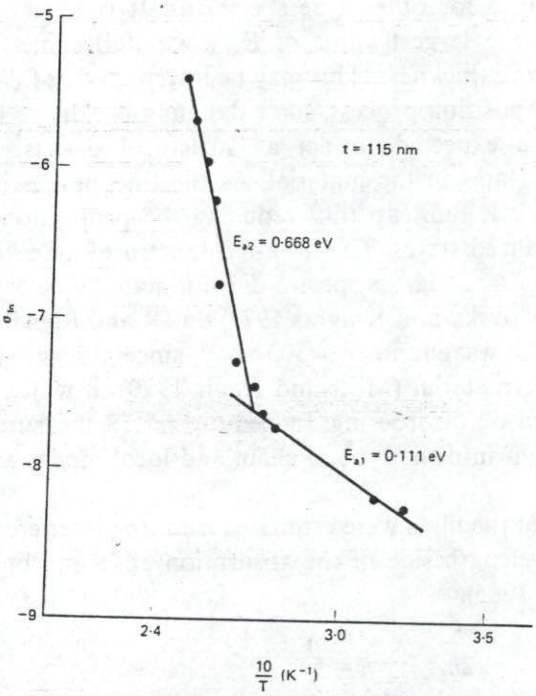

Figure 4. Variation of DC conductivity with temperature for an a-Se thin film of $t = 115$ nm.

(≈ 260 nm) also shows two regions (Fig. 5). The first stage, from room temperature to, 341 K shows $E_{a1} \approx 0{\cdot}095$ eV and the second, from 341 to 416 K, shows $E_{a2} \approx 0{\cdot}798$ eV. As may be seen, there is a clear increase in the conductivity in comparison to the previous sample. Figure 6 presents the conductivity for an a-Se : 3% In film.

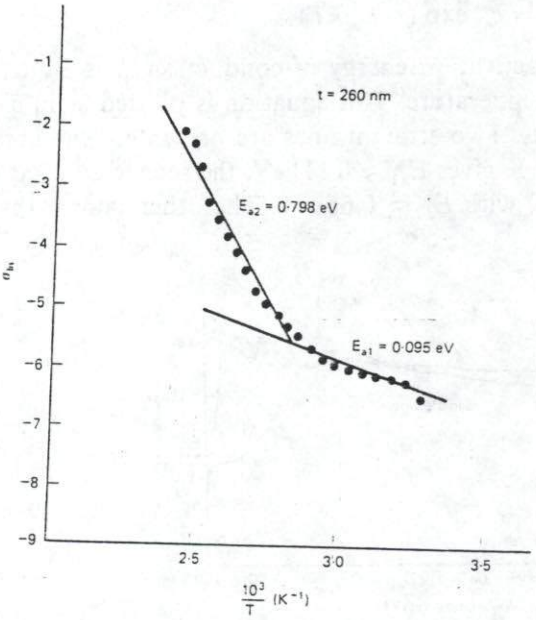

Figure 5. Variation of DC conductivity with temperature for an a-Se thin film of $t = 260$ nm.

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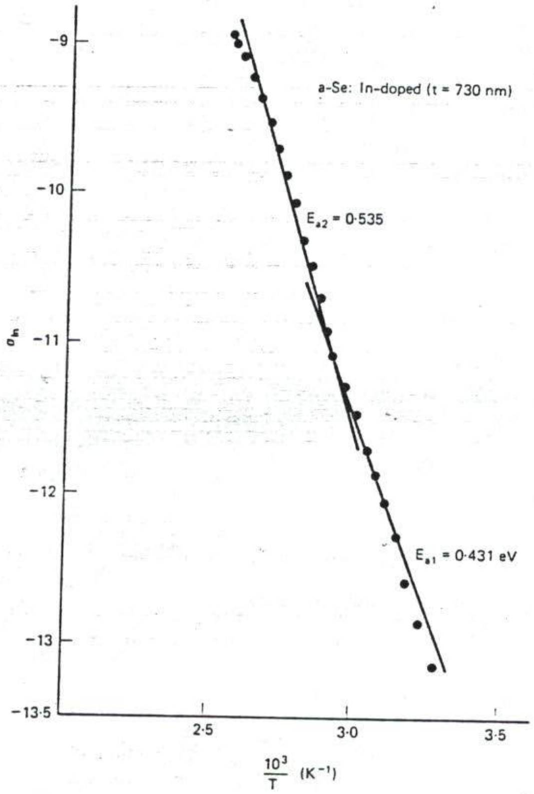

Figure 6. Variation of DC conductivity with temperature for an a-Se : In thin film of $t = 730$ nm.

The first stage, from 303 to 342 K, shows $E_{a1} \approx 0{\cdot}43$ eV, and the second stage, at higher temperature up to 385 K, shows $E_{a2} \approx 0{\cdot}535$ eV. Table 2 summarizes our electrical results.

Here the change in activation energy is lower from one stage to another compared to those presented earlier. When the temperature rises above 343 K, one expects a transfer to the crystalline state of Se film. This may explain the sudden change in the density of states in the gap which led to a sharp rise in the value of E_a when moving from one stage to the next.

Any difference between the reported values of the DC conductivity of a-Se films may be attributed to sensitivity to the presence of impurities, particularly oxygen. The room temperature resitivity of pure deoxygenated Se (< 2 ppm O_2) according to Twaddel *et al.* (1972) is $10^{17}\,\Omega$ cm, which drops by more than six orders of magnitude with the presence of ≈ 50 ppm O_2.

From the calculated values of E_a and σ_0, it has been suggested (Mehra *et al.* 1984) that conduction in a-Se and binary a-Se films is due to the thermally-assisted

Thickness (nm)	E_{a1} (eV)	E_{a2} (eV)
115	0·111	0·668
260	0·095	0·798
730 (a-Se : In)	0·431	0·535

Table 2. Electrical activation energies of a-Se and a-Se : In thin films obtained from high temperature conductivity.

tunnelling of charge carriers in the localized states in the band tails. We should remember that the Hall effect did not confirm whether the conduction is due to holes or electrons. The calculated values of the thermal activation energies further show that the Fermi level is well away from the band edges in the forbidden gap.

The activation energy alone, however, does not indicate where conduction occurs, i.e. in the extended states above the mobility edge or by hopping in the localized states. This is because both mechanisms may occur simultaneously, but the dominating conduction at low temperature is via localized states. Thus from Figs 5 and 6 both extended state and localized state conduction is confirmed. The high-temperature conductivity data verify the thermally assisted tunnelling of charge carriers in the localized states of band tails. On the other hand, the decrease in the value of E_a from 0·535 eV to 0·431 eV in Fig. 6 is probably due to the addition of impurity levels in the energy gap.

3.3. *Concluding remarks*

The present investigation showed that a-Se thin films could be doped and thus possess different electrical and optical properties from pure a-Se. The optical constants ($\alpha(\omega)$, $n(\lambda)$) for both pure and doped specimens have been evaluated. The value of E_{opt} was obtained from a relation which is believed to arise from a sharp increase in the density of states at the band edge, a possibility suggested by the one-dimensional nature of the chain-like structure. The order of $E_{opt} \approx 2{\cdot}0$ eV for an a-Se thin film is in agreement with earlier data. The addition of dopants lowered E_{opt}. The electrical conductivity showed two activation energies due to the thermally assisted tunnelling of charge carriers in localized states of the band tails.

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