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OPTICAL PROPERTIES OF AMORPHOUS Se FILMS PREPARED BY PECVD

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The optical transmission spectrum of amorphous Se films prepared by plasma-enhanced chemical vapour deposition was measured over the 500 to 2000 nm spectral region. The absorption coefficient values plotted vs photon energy according to Tauc's law yielded an optical gap, E_g, of 1.94 eV. The temperature dependence of E_g was measured between 13 K and 300 K and was found to be well described within Fan's one-phonon approximation. Photo-induced darkening of the optical gap was studied by illumination at 13 K and 77 K. © 1997 Elsevier Science Ltd

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1. INTRODUCTION

A decrease in the optical gap (photodarkening) for amorphous chalcogenides after bandgap illumination is a well-known effect. In amorphous Se (*a*-Se) reversible photodarkening is observed only if the material is illuminated below room temperature, in fact, at a temperature close to that of liquid nitrogen. Most studies on *a*-Se, a simple twofold coordinated material, have dealt with thin films prepared by thermal evaporation. In our study we have prepared films of amorphous selenium by plasma-enhanced chemical vapour deposition (PECVD).

The optical transmission was measured as a function of the photon energy in order to derive the refractive index and absorption coefficient of these films. The procedures that have been proposed by Swanepoel [1] for this optical characterization have been applied here. This involves the construction of continuous envelopes around the extremes of the interference fringes. The optical gap of *a*-Se was determined from the calculated values of the absorption coefficient. We also studied the temperature dependence of the optical gap, $E_g(T)$. Furthermore, we summarize our results of the investigation of the influence of temperature on the shift of the optical absorption edge induced by illumination. The aim is to show that the light-induced red shift of the gap is connected with an increase of localized states at the band edges.

2. EXPERIMENTAL PROCEDURES

Amorphous Se thin films were prepared by PECVD using the hydride H_2Se as precursor gas. Details of the deposition conditions have been described by us in previous papers [2, 3]. Information concerning the structure of the films was obtained from Raman spectroscopy. The spectra indicated that the dominant molecular structure is the eight-membered ring and/or a chain with Se_8 molecular fragments [2]. The optical transmission was measured in the temperature region 13–300 K, using an optical cryostat fixed in the sample compartment of the spectrophotometer. The sample illumination was made at 13, 77 and 300 K by a halogen lamp equipped with an infrared-cut filter. During illumination, the lamp was fixed in the sample compartment of the spectrophotometer, so that the position of the beam was always the same. We also recorded the reflectivity spectrum at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows a typical optical transmission spectrum of an as-deposited amorphous Se film recorded at room temperature. Two features are immediately apparent:

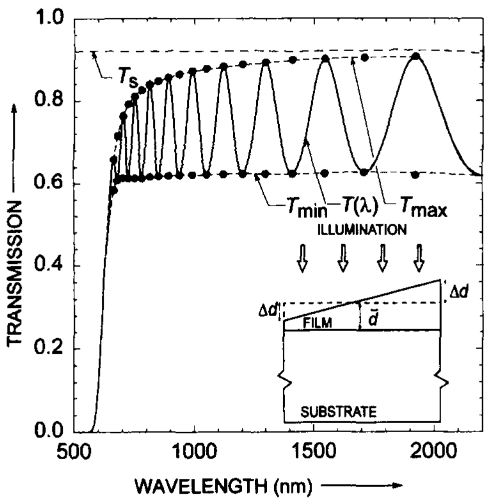

Fig. 1. Optical transmission spectrum of an *a*-Se film at 300 K. Also, diagram showing an absorbing thin film with a linear variation in thickness on a thick transparent substrate.

the spectrum shows strong interference fringes and the transmission drops markedly around 650 nm. We applied the procedure suggested by Swanepoel [1] to calculate the average thickness, thickness variation and refractive index from the transmission spectrum alone. This method entails constructing envelopes around the interference maxima and minima as described in detail elsewhere [4].

The calculation procedures of the refractive index, n, and average film thickness, $\bar{d}$, will now be presented. First of all, the optical transmission $T_{\Delta d}$, in the transparent region at a specific wavelength λ, for the case of non-uniform thickness, can be obtained by the expression [1].

$$T_{\Delta d} = \frac{1}{\varphi_2 - \varphi_1} \int_{\varphi_1}^{\varphi_2} \frac{A}{B - C\cos\varphi + D} \mathrm{d}\varphi \tag{1}$$

$A = 16n^2 s$, $B = (n+1)^3(n+s)^2$, $C = 2(n^2-1)(n^2-s^2)$, $D = (n-1)^3(n-s^2)$, $\varphi = 4\pi nd/\lambda$, with $\varphi_1 = 4\pi n(\bar{d} - \Delta d)\lambda$ and $\varphi_2 = 4\pi n(\bar{d} + \Delta d)/\lambda$. It is assumed that the thickness varies linearly over the illuminated area, so that the thickness is: $d = \bar{d} \pm \Delta d$ (see Fig. 1). Δd refers to the actual variation in thickness from the average thickness and s is the refractive index of the substrate. The expressions for the envelopes around the interference maxima and minima of the optical transmission spectrum are the following [1]:

$$T_{\max} = \frac{2a}{\Delta\varphi(1-b^2)^{1/2}} \tan^{-1}\left[\frac{1+b}{(1-b^2)^{1/2}} \tan\left(\frac{\Delta\varphi}{2}\right)\right] \tag{2}$$

$$T_{\min} = \frac{2a}{\Delta\varphi(1-b^2)^{1/2}} \tan^{-1}\left[\frac{1-b}{(1-b^2)^{1/2}} \tan\left(\frac{\Delta\varphi}{2}\right)\right] \tag{3}$$

where $a = A/(B+D)$, $b = C/(B+D)$ and $\Delta\varphi = \varphi_2 - \varphi_1$. The range of validity of equations (2) and (3) is: $0 < \Delta d < \lambda/4n$. In addition, equations (2) and (3) are two independent transcendental equations with only two unknown parameters, n and Δd. They have been successfully solved for the experimental values using a standard computer method (Newton–Raphson iteration). Firstly, the values of the maximum and minimum transmission,

Table 1. Values of λ, $T_{\max}$ and $T_{\min}$ for the amorphous Se transmission spectrum shown in Fig. 1; the underlined transmittance values are those derived by the envelope computer program [5]. Also, the accuracy improvement procedure for the refractive indices yields n_2 values

λ (nm)	s	$T_{\max}$	$T_{\min}$	n_1	Δd (nm)	m	n_2
1923	1.507	0.906	0.620	2.490	39.4	4.0	2.486
1710	1.511	0.903	0.626	2.474	38.2	4.5	2.487
1546	1.514	0.901	0.624	2.488	36.2	5.0	2.498
1411	1.520	0.897	0.623	2.497	34.4	5.5	2.508
1298	1.514	0.892	0.623	2.506	36.1	6.0	2.517
1202	1.515	0.887	0.622	2.516	36.4	6.5	2.525
1122	1.515	0.882	0.622	2.528	36.3	7.0	2.538
1052	1.515	0.877	0.621	2.540	36.3	7.5	2.550
992	1.514	0.870	0.620	2.554	36.6	8.0	2.565
938	1.511	0.863	0.619	2.572	37.2	8.5	2.577
892	1.506	0.855	0.618	2.588	37.6	9.0	2.595
850	1.478	0.847	0.617	2.599	39.1	9.5	2.610
814	1.507	0.839	0.616	2.629	37.8	10.0	2.631
781	1.514	0.825	0.612	2.674	38.2	10.5	2.650
752	1.515	0.810	0.613	2.708	39.3	11.0	2.674
725	1.514	0.791	0.613	2.752	40.6	11.5	2.695

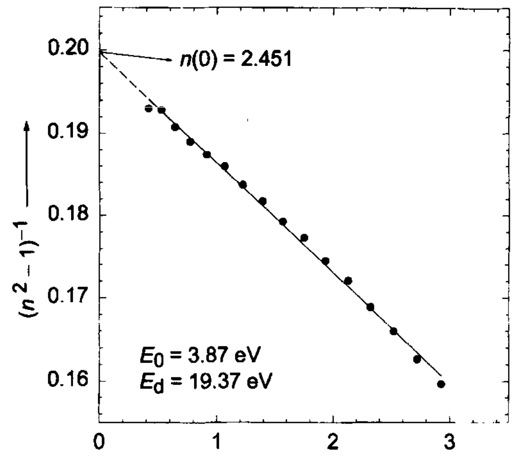

Fig. 2. Plot of the refractive-index factor $(n^2 - 1)^{-1}$ vs E^2 for an a-Se film; the $n(0)$ value is the refractive index extrapolated to $E = 0$.

$T_{\max}$ and $T_{\min}$, are used in equations (2) and (3) to derive the values of the refractive index and thickness variation, shown as n_1 and Δd in Table 1. From the values of Δd in Table 1 it seems reasonable to suggest a value for the thickness variation of ≈ 37 nm. In addition, the values of n_1 can be used to derive $\bar{d}$ from the basic equation for the interference fringes, $2n\bar{d} = m\lambda$ (m is the order number of the interference extrema) and also improved values for n, shown as n_2, as described in detail in our previous work [4]. If this is carried out, the value of $\bar{d}$ obtained in this particular case is 1547 ± 12 nm (the accuracy is 0.8%).

Next, the spectral dependence of the refractive index is fitted to the Wemple–DiDomenico dispersion relationship [6], that is, the single-oscillator model

$$\epsilon_1(E) = n^2(E) = 1 + \frac{E_0 E_d}{E_0^2 - E^2} \tag{4}$$

where E_0 is the single-oscillator energy and E_d is the dispersion energy. By plotting $(n^2 - 1)^{-1}$ against E^2 and fitting a straight line as shown in Fig. 2, E_0 and E_d are determined directly from the slope, $(E_0 E_d)^{-1}$ and the intercept, E_0/E_d, on the vertical axis. The values of the dispersion parameters E_0 and E_d for the as-deposited a-Se film under analysis are 3.87 eV and 19.37 eV, respectively.

Since the values of the refractive index are already known over the spectral region studied, from the above-mentioned optical dispersion relationship, the absorbance, x, is now calculated using an expression suggested by Swanepoel [1]. In the region of strong absorption (where the interference fringes disappear), the absorbance can be written as

$$x \approx \frac{(n+1)^2(n+s^2)}{16n^2 s} T \tag{5}$$

and, therefore, the optical absorption coefficient, α, is given by the following equation

$$\alpha \approx \frac{1}{d} \ln\left[\frac{16n^2 s}{(n+1)^2(n+s^2)T}\right]. \tag{6}$$

In the region of strong absorption, the absorption coefficient α was estimated in a second way by using a combined set of transmission and reflectance R data; α was determined from the expression

$$\alpha = \frac{1}{d} \ln\left(\frac{1 - R^2 + [(1-R)^4 + 4R^2T^2]^{1/2}}{2T}\right). \tag{7}$$

The α values are very close to those calculated from the above mentioned optical dispersion relationship [equation (4)].

The optical gap E_g is determined from the calculated values of α. In the strong absorption region, involving interband optical transitions between valence and conduction bands, α is given according to Tauc by the equation

$$\alpha h\nu = B(h\nu - E_g)^2 \tag{8}$$

where E_g is defined as the optical gap and B is a constant related to the parameter ΔE(tail), which is a measure of the extent of band tailing. The optical gap, derived from the Tauc plots was equal to 1.94 eV and 2.12 eV at 300 K and 13 K, respectively.

Since our interest in this work was the role of the temperature in the photo-induced shift of the gap we also studied the temperature shift of the gap $E_g(T)$ in the range 13–300 K. The results are summarized in Fig. 3. The

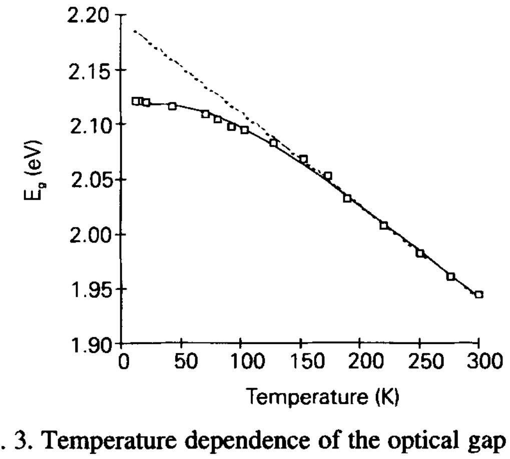

Fig. 3. Temperature dependence of the optical gap E_g of a-Se.

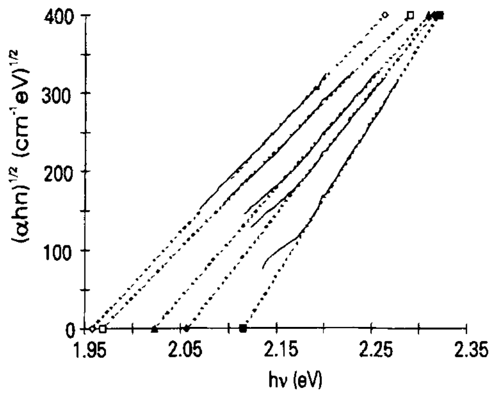

Fig. 4. Tauc curves before (■) and after illumination of *a*-Se at 13 K.: (♦) 5 min; (▲) 15 min; (□) 60 min; (◇) 120 min.

solid curve represents a fit to the experimental data (open squares) using Fan's one-phonon approximation [7]:

$$E_g(T) = E_g(0) - A[\exp(h\nu/kt) - 1]^{-1} \qquad (9)$$

$E_g(0) = 2.12$ eV, $A = 0.22$ eV and $h\nu = 0.021$ eV. The dashed line in Fig. 3 indicates a fit of the experimental data to the standard linear equation $E_g(T) = E_g(0) - \beta T$ with $\beta = 8.4 \times 10^{-4}$ eV K^{-1}.

We illuminated the *a*-Se films with white light (light intensity 80 mW cm^{-2}) and recorded the transmission spectra after illumination at 13 K and 77 K for an increasing period from 5 to 120 min. The results of photo-induced changes (photodarkening) of the optical properties induced by illumination at 13 K are shown in Fig. 4. The saturated values of the shift ΔE_g was 0.157 eV at 13 K and 0.108 eV at 77 K, which demonstrates that the magnitude of the shift of the absorption edge increases with decreasing temperature. The spectrum caused by illumination at low temperature (13 and 77 K) cannot be characterized by a simple parallel shift of the absorption edge, but is accompanied by a strong decrease in the slope of the Tauc curve. The change of the $B^{1/2}$ value [equation (8)] was equal to 629 and 316 cm$^{-1/2}$ eV$^{-1/2}$ after 120 min of illumination at 13 K and 77 K, respectively. Since in the Mott–Davis interpretation B is inversely proportional to ΔE(tail), i.e. proportional to the width of localized states at band edges, a decrease of $B^{1/2}$ values induced by illumination indicates an increase of localized states at the band edges.

An amorphous Se film photodarkened at 13 and 77 K has its initial absorption restored when heated up to room temperature. The process was completely reversible. An isochronal annealing experiment using a constant heating rate yielded a low activation energy for the bleaching process of the order of 0.07 eV. The ease of recovery at temperatures below 300 K can be understood if one takes into account that the twofold-coordinated Se matrix is very flexible and that the glass transition temperature is around 50°C.

We speculate that broadening of the localized tails can occur if dihedral angle distortions give rise to localized states in the gap close to the band edges [8]. This process was proposed by Nagels *et al.* [2] as a possible origin of photo-induced darkening in *a*-Se. The band tailing parameter B in equation (8) is given by the equation (9)

$$B = \frac{4\pi\sigma_{\min}}{nc\Delta E} \qquad (10)$$

where $\sigma_{\min}$ is the minimum metallic conductivity, n the refractive index, c the light velocity and ΔE the width of the band tails. With $\sigma_{\min} = 300\,\Omega^{-1}\,\text{cm}^{-1}$, $n = 2.5$, the experimental $B^{1/2}$ value equal to 1944 and 1315 cm$^{-1/2}$ eV$^{-1/2}$ before and after illumination, respectively, we derive $\Delta E = 0.15$ and 0.32 eV before and after illumination at 13 K. The difference is 0.17 eV which is very close to the value found for the photo-induced optical shift. The influence of the charge of the refractive index n ($\approx 2\%$) on B is very small. This means that models proposed by other authors based on changes in refractive index cannot explain our experimental results.

4. CONCLUSIONS

The procedure suggested by Swanepoel using the envelope of the extremes of the interference fringes was applied to calculate the average thickness and the refractive index of an *a*-Se film prepared by PECVD. The refractive index values were used for calculating the spectral dependence of the optical absorption coefficient α in the strong absorption region. A second method using a combined set of transmittance and reflectance data yielded similar results for the α values. The temperature shift of the optical gap of *a*-Se was found to be well described within Fan's one-phonon approximation. An increase of localized states at band edges could be responsible for the observed photodarkening at low temperature. Broadening of the localized tails could occur it dihedral angle distortions give rise to localized states in the gap close to the band edges.

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