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ON THE OPTICAL PROPERTIES OF VACUUM-DEPOSITED SELENIUM FILMS

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In the present work, the direct transmission spectrum of selenium thin films deposited on different substrates has been measured at 300 K. The measurements were made using a Beckman double beam spectrophotometer IR 4220 and double beam UV-300 difference/dual wavelength spectrophotometer. The transmission data yielded the real (n) and imaginary (k) parts of the complex index of refraction, the imaginary (ε_2) part of the complex dielectric constant and the absorption coefficient (α) over the energy range. All the observed shoulder have been interpreted in terms of transitions at symmetry points in K-space. Based on the observed transition energies, a band structure for selenium thin film is proposed and is compared with published theoretical calculations.

1. Introduction

Se and Te belong to group VI in the periodic table. Characteristic of elements in this row is their tendency to have twofold coordination in their elemental forms. In their trigonal crystalline forms, the atoms are arranged in spiral chains oriented along the C-axis. These chains are located at the centre and six corners of a hexagon. Se can also be found in α and β monoclinic forms, in which Se_8 rings form the basic structural unit[1].

The difference in the optical and electrical properties of the amorphous and crystalline forms of selenium as recently reviewed by Stuke[2] and Alder[3], suggests that the electronic spectra of the two forms differ significantly. The absorption spectra for amorphous and crystalline Se were identical, indicating no major differences in the conduction bands of the two forms. However, it is not clear whether such absorptions are due to one-electron transitions into the conduction band or are affected by coulomb interaction in the final state (excitonic effects). The ε_2 spectrum of amorphous Se has two broad peaks at 4 and 8 eV[2,4].

In the last few years, there has been a growing interest in the interpretation of optical and electrical properties of amorphous semiconductors[5]. Most of the work in this field is more or less concerned with the band-edge region, the occurrance of band tails, and the particular character of electron states in this region. The concern of this note will be the form of the optical spectrum of amorphous Se well above the fundamental threshold, i. e. in the region from 2 to 10 eV. Selenium can serve as a rather promising test model, since there are two well-distinguished regions of the optical absorption belonging to two different band triples[6], one extending from 2 to 5.5 eV, the other from 6 to 10 eV.

Many investigators have dealt with the measurement of optical constants of Se thin films, namely the refractive index (n) and extinction coefficient (k) in the visible region[7–18].

Merdy and Baldi[19] studied the absorption and reflecting power of thin films Se, not exposed to air, in the fundamental absorption region. The transmission has been measured between 2 and 11 eV and the reflecting power between 4 and 13 eV. The optical properties of trigonal Se single crystals between 4 and 14.4 eV have been determined for radiant energy polarized parallel to ($E//C$) and perpendicular to ($E \perp C$) the C-axis of the crystal. The reflectivity spectrum for polarization $E \perp C$ calculated from the ellipsometric measurements are determined[20]. The authors also show the relation of the fine structures to possible transitions in the band structure[21].

2. *Experimental techniques*

Thin selenium films were prepared by thermal evaporation of spec pure (99.999%) selenium in a vacuum of approximately 10^{-4} Pa at an evaporation rate of about 5 nm/s. Deposition was carried out on different substrates suitable for measuring the optical transmission in the required spectrum region (mica sheet discs for IR and a fused silica for visible region). For optical transmission measurements a Beckman double beam spectrophotometer IR 4220 and double beam UV-300 difference/dual wavelength spectrophotometer was used in the infrared and visible region, respectively. The thickness of the film was measured by Tolansky's technique[22].

Data analysis

Using classical electromagnetic theory, it is possible to obtain the following expression for the transmittance of an absorbing film of refractive index $N = n_2 + \mathrm{i}\, k_2$, deposited on a transmitting substrate of refractive index, n_1, and the refractive index of the surrounding medium n_3[23,24],

$$T = \frac{16 n_1 n_2 (n_2^2 + k_2^2)}{[(n_1 + n_2)^2 + k_2^2]\,[(n_3 + n_2)^2 + k_2^2]} \exp^{-4\pi k_2 d/\lambda} \qquad (1)$$

where λ is the wavelength of the incident light and d is the film thickness. This expression is valid on the condition that $4\pi k_2 d > \lambda$. Plotting ln T versus d at each specified results in a straight line, the slope of which can be used to determine k. Knowing k, the value of n can be calculated by solving the fourth order equation resulting after substituting the values of T, n_1, n_3, k_2 and d at the specified λ in Eq. (1).

3. *Results and discussion*

In the present work, Fig. 1 shows the direct transmission spectra of selenium thin films deposited onto a fused silica at room temperature. For comparison it has been plotted together with the results of Mokhtar and Osman[17] and Petrov[25] taken at 300 K. The transmittance in Fig. 1 increases gradually as the wavelength increases, however, the transmittance decreases as increasing the film thickness. Earlier measurements of the visible transmission of Se films has shown that the transmission increased with increasing wavelength[17-25]. As would be expected with discontinuous films they are transparent at long wavelengths. This phenomenon has been noted by other workers. The condensates consist of very fine (< 2 nm), barely discernible particles, grouped in separate aggregates of different shape and dimensions. The very fine particles are formed close to the evaporator of the off during evaporation of the metal[26,27] and are not produced from individual atoms at the surface of the glass, as is usually assumed.

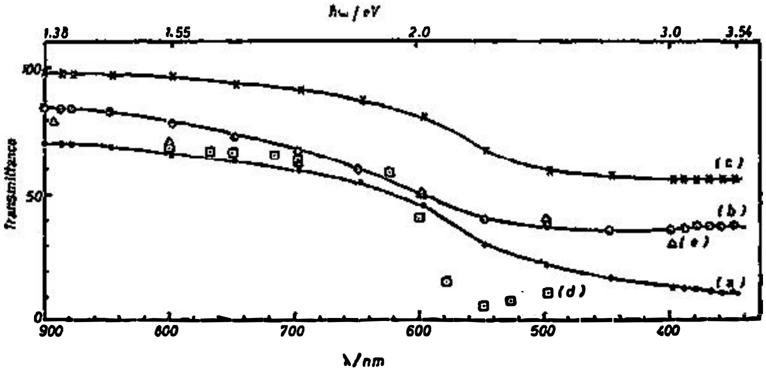

Fig. 1. Spectral dependence of the transmission of selenium films in the visible range.
(a) $d = 42$ nm; (b) $d = 32$ nm; (c) $d = 25$ nm; (d) From Ref. 17; (e) From Ref. 25.

The spectral behaviour of the real, n, and imaginary, k, parts of the refractive index of Se films is shown in Fig. 2. Se is rather high index material in this spectral region with an index of refraction between about 2.0 to 0.75 and an absorption index between about 2.5 to 0.75[20]. The present results of the optical constants obtained are in a good agreement with previously published data on Se[17,20].

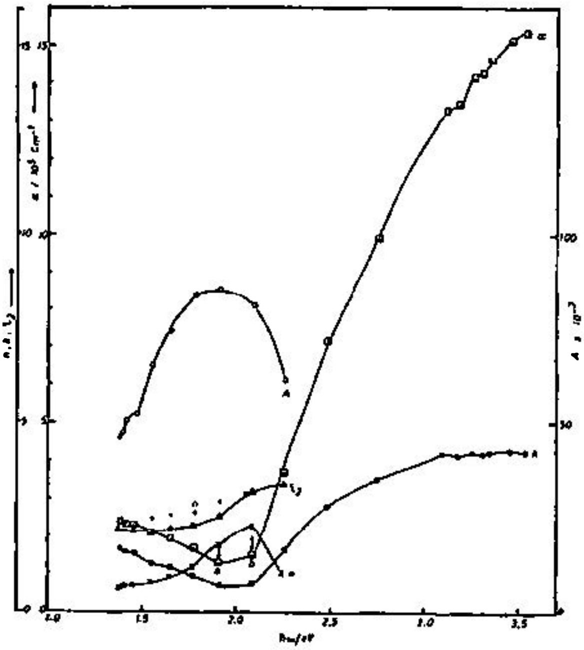

Fig. 2. The dependence of the extinction coefficient (k), refractive index (n), absorption coefficient (a), coefficient of energy absorption (A) and imaginary part of dielectric constant (ε_2) on the photon energy are shown compared with refractive index (n) from Ref. 17.

Once n and k have been calculated, then the imaginary part of the dielectric constant ε_2, the absorption coefficient a and the coefficient of the energy absorption A, can be calculated

$$\begin{aligned} \varepsilon_2 &= 2nk \\ a &= 4\pi k/\lambda \\ A &= \frac{4n}{(n+1)^2 + k^2}. \end{aligned} \qquad (2)$$

The same Fig. 2 shows the results for ε_2, the imaginary part of the dielectric constant. The curve of ε_2 rise gradually as the photon energy increases, but according to the results of Tutihasi and Chen[11], they reach a peak at 3.5 eV for $E//C$ and 3.8 eV for $E \perp C$. Since ε_2 is directly related to the density of states for band-to-band transitions, the results should be useful for checking theoretical models of the energy-band structure of selenium.

The determination of the absorption coefficient for normal incidence indicated the presence of a sharp peak. From the position of the maximum A (Fig. 2) the quantity of the energy gap between bands which corresponds to the quantum transition

$$\Delta E = \frac{hc}{\lambda} \qquad (3)$$

where h is the Planck's constant, c is the speed of light and λ is the wavelength of the maximum absorption. The value of ΔE equals 1.907 eV for thickness 43 nm.

From these values of k the absorption coefficient α of Se was calculated and is shown in Fig. 2 also. It is interesting to note that the absorption exhibits considerable structure in this region as expected from the transmission curve and rises to a value of 1.54×10^6 cm^{-1} at about 3.543 eV. Even at the minimum at 1.907 eV it is still very strong, with a value of 1.32×10^5 cm^{-1}. The most important features of the curve is:

The absorption is almost independent of energy up to 1.907 eV. The structure found in this region is ascribed to interference phenomena. A linear rise begins at 1.907 eV, rise steeply near 2.07 and a shoulder in the absorption curve can be seen at about 2.48, 3.1, 3.26 and 3.44 eV.

The smallest energy gap is located at point H of the Brilloiun zone according to calculations of energy band scheme[28,29)]. The onset of the optical absorption as given by my measurements should thus involve transitions in the surroundings of this point in K-space. The following interpretation of the absorption curve (Fig. 2) is supported by measurements of other optical constants[11,30,31)] and by the selection rules at H[28)]. The absorption at 1.907 eV originates from an exciton which is composed of wave functions from the conduction band and the top valence band near H. At this energy a peak at 1.937 eV is found with previously published data on Se[13,21,31)]. The structure at 2.07 eV (was observed for $E \perp C$ at 2.08 eV[13,21)]) can be understood in the following way. The highest valence band is split into three bands by spin-orbit interaction[32)]:

$$H_3 \rightarrow H_4 + H_5 + H_6.$$

Dipole transitions from the H_6 valence band to the H_6 conduction band are allowed by group theory for both polarizations, but are relevant only in second order[33)]. Therefore only the doublet H_4, H_5 of valence bands is of interest in this connection. A doublet of lines in the electroreflectance spectrum have been explained according to such a spin-orbit splitting[31)]. This doublet of valence bands and the simple conduction band generate two exciton series. Arrow (b) would then mark the absorption by that exciton, which is associated with the deeper of the two valence bands. The broadness of this response — as well as that of exciton (a) — can be explained quite naturally, because this second exciton level coincides with the continuum states which produce the steeply rising background absorption. All the other shoulders in the absorption curve are also interpreted as being caused by an exciton absorption. The absorption responsible for the other shoulder is interpreted as occurring at a saddle point Z in the Brillouin zone.

Fig. 3 shows the spectral dependence of the transmission of Se films of different thicknesses deposited onto mica substrates in the infrared range. The important features of the room temperature transmission spectra are the pronounced dip in transmission at about 3.2 μ. The dip in transmission at 3.2 μ has been attributed[34)] to a gap in the valence band.

Fig. 4 I shows the final values of (k) obtained in the calculations and Fig. 4 II shows the values of (n) resulting from the transmission method at different thicknesses. As seen from Fig. 4 I, the extinction coefficient (k) increases with the increase of the wavelength and thickness, but, the refractive index (n) Fig. 4 II decreases with the increase of wavelength. The present results are significantly different in magnitude from those published by Caldwell[35)] and Gobrecht[36)] in the infrared region.

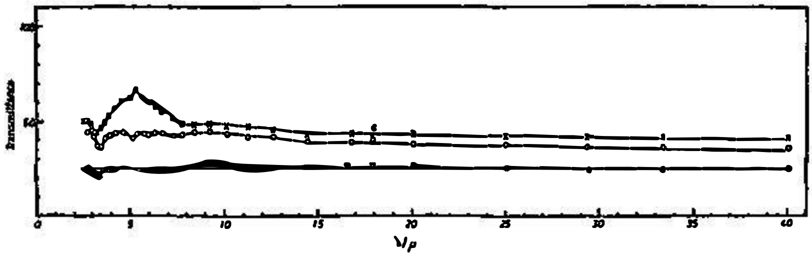

Fig. 3. Spectral dependence of the transmission of selenium films in the infrared range

(a) $d = 400$ nm; (b) $d = 300$ nm; (c) $d = 200$ nm.

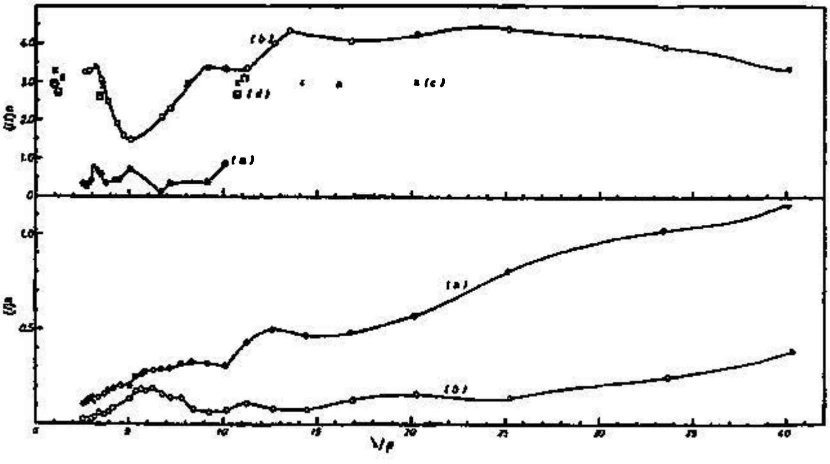

Fig. 4. (I, II) The dependence of the extinction coefficient (k) and refractive index (n) on wavelength

(a) $d = 400$ nm; (b) $d = 300$ nm; (c) From Ref. 36; (d) From Ref. 35.

From the value of k and n given in Fig. 4 (I, II), the imaginary part of the dielectric constant ε_2 can be calculated. Since the imaginary part of the dielectric constant ε_2 is directly related to the density of states in the band-to-band one-electron transitions, the ε_2 spectrum at 300 K in Fig. 5. deserves the most attention. The structure observed is tabulated in Table 1, which contains the peak position in eV.

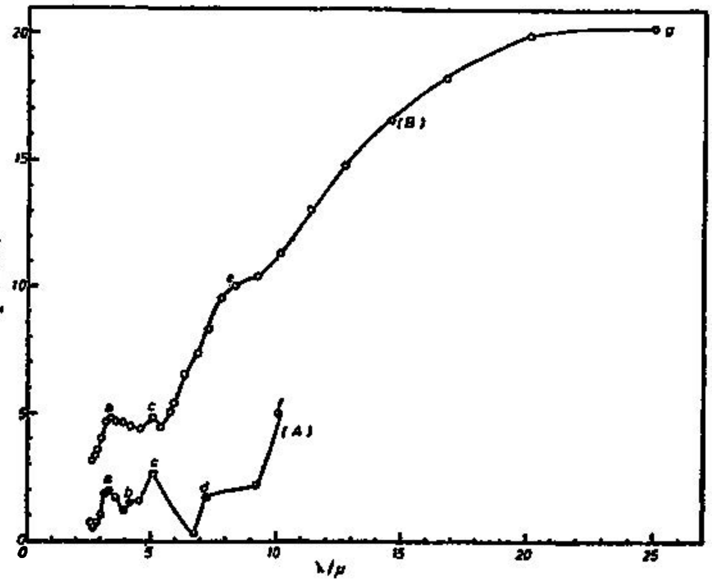

Fig. 5. Imaginary part of dielectric constant (ε_2) of selenium films at 300 K in the infrared range

(A) $d = 400$ nm; (B) $d = 300$ nm.

TABLE 1.

Peak	Peak energy (eV)	Thickness 400 nm	Thickness 300 nm
a	0.372	—	—
b	0.297	—	
c	0.248	—	—
d	0.174	—	
e	0.161		—
f	0.124	—	
g	0.05		—

Energies of observed peaks on different thicknesses.

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OPTIČKA SVOJSTVA VAKUUMSKI-DEPONIRANIH FILMOVA SELENA

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U radu je opisan transmisioni spektar filmova selena, mjeren na 300 K. Mjerenja su izvedena pomoću dvostrukog spektrometra Backman IR 4220 i diferencijalnog spektrometra UV-300, sa dvije zrake. Iz mjerenih transmisionih podataka određen je realni i imaginarni dio indeksa loma, kao i imaginarni dio kompleksne dielektričke konstante, te apsorpcioni koeficijent. Izbočenja transmisione krivulje interpretirana su u termima prijelaza na simetrijskim točkama u *K*-prostoru. Na osnovu dobivenih energija prijelaza, pretpostavljena je zonska struktura selenovih tankih filmova i uspoređena s publiciranim teorijskim proračunima.