Optical properties of selenium thin films

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The optical properties of thin selenium films in the ultraviolet, visible and infrared regions ranging from 190 to 16800 nm in wavelength, have been studied using spectrophotometric technique. Changes in the transmission spectra of Se films with thickness variation, annealing and storage have been studied. Films were prepared by the thermal evaporation technique in vacuum and the substrates were KBr for the IR studies and quartz for the visible and UV studies. The film thickness ranged from 100 to 700 nm. Experimental curves of the transmission T with film thickness t at different wavelengths λ showed that T decreases as t/λ increases. It is also found that at certain wavelengths λ_c (cut-off wavelength), T tends to zero. λ_c is found to increase more rapidly with t for annealed films than for unannealed ones. Studies of the surface structure by electron microscopy and of the internal structure by X-ray diffraction of the Se film of $t = 250$ nm showed that the annealing gave an increase in the grain density and crystallized the film in a hexagonal lattice form. Changes of the film refractive index with thickness, annealing and storage, as well as changes of absorption coefficient of unannealed films with thickness have been calculated from the transmission data. Changes of optical constants of films are explained as a result of changes of the film structure arising from thickness variation, annealing and storage.

1. Introduction

A number of papers dealing with the physical properties of amorphous selenium (a–Se) have appeared in recent years [1]–[4].

Selenium rapidly cooled from its melting point (218°C) is amorphous, but crystallization begins if the solid is warmed to 60–70°C, and the material remains crystalline on cooling back to room temperature. Thus, selenium films, evaporated in vacuum on substrates remaining at room temperature, are amorphous.

. Film annealing, under certain conditions, results in its crystallization. Selenium can crystallize in different forms [5], [6].

Optical properties of thin films depend mainly on their volume and surface structures [7], [8]. Film structure is affected by its thickness, conditions of preparation, film material, substrate material and its treatment after preparation.

In this paper, we present experimental data on changes of optical parameters (transmission, refractive index, extinction and absorption coefficients) of selenium thin films, prepared by vacuum thermal evaporation, with film thickness, annealing and storage.

Optical properties of films are studied in the ultraviolet, visible and infrared ranges, using spectrophotometric methods.

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2. Experimental

a–Se films of different thickness (up to 700 nm) are obtained on suitable substrates (KBr for IR studies and quartz for VUV studies) by thermal evaporation technique in vacuum at a pressure of about 10^{-6} Torr in a Varian Coating unit model 3117 with evaporation rate of about 0.5 Å/s.

Thickness control is achieved by means of a quartz crystal monitor. Transmission curves of prepared films are studied using a pyeunicam spectrophotometer model SP–3100 in the spectral range 2500–16800 nm (IR range) and using pyeunicam spectrophotometer model SP–8 100 in the spectral range 190–800 nm (VUV range).

Changes of transmission curves with annealing and storage are also studied. Films have been annealed in a thermostated electric oven for 10 min at 85°C. Changes of surface structure of films with annealing have been checked using a Phillips 300 transmission electron microscope. For comparison purposes, two identical films are deposited on freshly-cleaved sodium chloride substrates under the same conditions. After annealing of one of the obtained films, electron microscopic investigation is achieved. Changes of volume structure of films with annealing have been studied using a Phillips X-ray diffractometer.

3. Results and discussion

From experimental transmission curves, we have plotted transmission T vs film thickness t at different wavelengths λ. It is found that T decreases with increase of radiation photon energy (decrease of λ). T also decreases as t/λ increases and tends to zero at a certain wavelength λ_c (cut-off wavelength). λ_c changes slightly with film thickness for amorphous films, while the change of λ_c with t for annealed films is more obvious as shown in Fig. 1. This can indicate that the band gap of annealed films increases with thickness decrease [9]. Analogous results are reported in [7] and [8] for silver films of 10 nm thickness.

In the case of small t/λ (in the IR range), films are considered as nonabsorbing (absorption $A = 0$) and the changes of film refractive index n_1 with t are calculated from the equation [10]

$$n_1 = \sqrt{\frac{n_0 n_2 (1 + \sqrt{R})}{1 - \sqrt{R}}} \tag{1}$$

where: n_0 — refractive index of substrate,
$\quad\quad n_2 = 1$ — refractive index of air,
$\quad\quad R = 1 - T$ — reflection from film surface.

Here, we neglect multiple reflections from film surfaces. Changes of n_0 with λ for KBr and quartz are considered in our calculations [11].

Figure 2 shows the calculated curves of changes of n_1 with t at different wavelengths for amorphous films (dashed curves) and for annealed films (solid curves). The curves show that n_1 increases linearly with t at a wavelength of
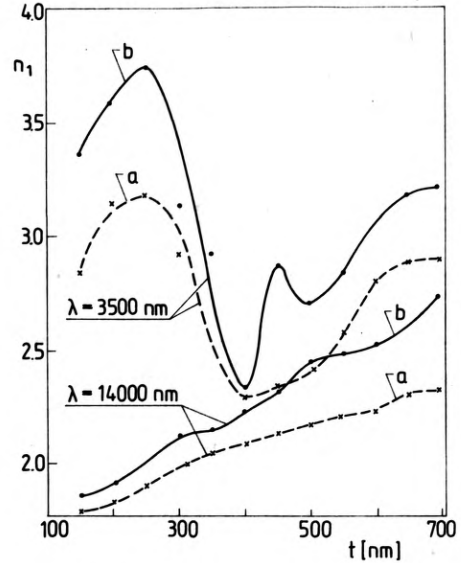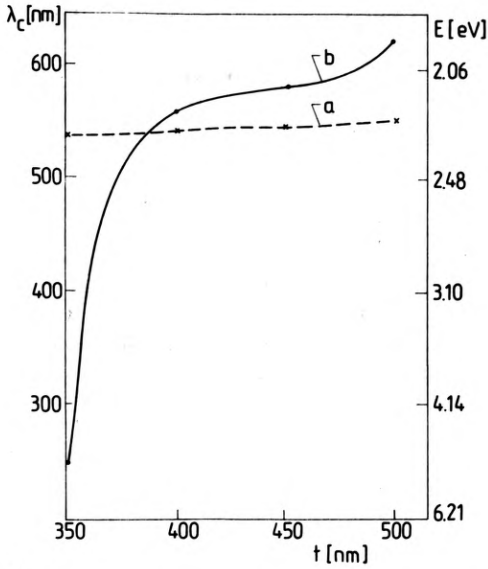
Fig. 1. Change of cut-off wavelength λ_c with film thickness t (E — energy of incident photons); **a** — amorphous films, **b** — annealed films)

Fig. 2. Change of film refractive index n_1 with its thickness t; **a** — amorphous films, **b** — annealed films

14000 nm for both types of films. At a wavelength of 3500 nm the change of n_1 with t is nonlinear. A minimum of n_1 is noticed for both types of films at a thickness of 400 nm, while maximums of n_1 are obtained at a thickness of 250 nm and 450 nm for annealed films and at a thickness of 250 nm for the amorphous ones.

Change of absorption coefficient α and extinction factor K_1 of a–Se film with its thickness

t [nm]	150	200	250	300	350
$\alpha \times 10^{-3}$ [nm^{-1}]	0.672	1.649	1.888	3.528	5.094
K_1	0.0299	0.0735	0.0842	0.1572	0.2270

$\lambda = 560$ nm, $n_1 = 4.2451$.

For large values of t/λ, T tends to zero at a certain λ_c as shown in Fig. 1, and the films are considered as absorbing. Using the results of KORSUNSKI [12] for the values of R from a–Se films, we calculate for such films the absorption coefficient α, extinction factor K_1 and refractive index n_1 from the equations [9], [12]:

$$\alpha = \ln[(1-R/T)]/t, \tag{2}$$

$$K_1 = \alpha\lambda/4\pi, \tag{3}$$

$$R = [(n_1-1)^2 + K_1^2]/[(n_1+1)^2 + K_1^2], \tag{4}$$

$$n_1 = (2\sqrt{R}+1)/(1-\sqrt{R}), \tag{5}$$

for $K_1^2 \ll (n_1 - 1)^2$. Here multiple reflections are neglected. Results of calculations are presented in the Table.

Analogous calculations for annealed films are not reported here since data for R of such films are not available.

Electron microscopic examinations of the surface structure of films for which $t = 250$ nm show that the average grain size increases with annealing.

X-ray patterns show an interplanar distance d of 0.3785 nm at an angle θ of 23.6° between the incident beam and the film surface, while $d = 0.3017$ nm at $\theta = 29.6°$. The patterns show that films crystallize in a hexagonal close-packed (hcp) structure.

Film storage leads to a decrease of its transmission. According to electron micrographs, the transmission change is due to the formation of crystallized areas in the films with storage and thus the films become more absorbing.

From the whole data reported above, it can be concluded that the changes of optical constants of films result from changes of film structure arising from thickness change, annealing and also from film crystallization with storage.

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Оптические свойства тонких слоёв селена

Исследованы оптические свойства термически кондиционируемых и некондиционируемых слоёв селена в пределах ультрафиолета, видимых и инфракрасной области спектра. Слои толщиной от 100 до 700 nm получены методом термического напаривания на основаниях из KBr для исследований в инфракрасной области спектра, а также на кварце для исследований в ультрафиолете и видимых пределах. Было экспериментально установлено, что проницаемость слоёв уменьшается вместе с повышением t/λ (t — толщина), доходя до ноля для определённых значений длины волн λ_c. Для термически кондиционируемых слоёв λ_c отчётливее повышается вместе с толщиной чем для некодиционируемых.