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LETTER TO THE EDITOR

EFFECT OF AGING ON SOME PHYSICAL PROPERTIES OF SELENIUM THIN FILMS

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Thin films of selenium were prepared by vacuum evaporation. The crystallization of the films is dependent upon temperature and time of aging. The consequence of crystallization is investigated by electron microscopy and X-ray diffraction. I. R. and U. V. spectra are elucidated. The optical gap energies calculated for different allotropes of selenium are: 1.65 eV for black Se, 1.8 eV for monoclinic and 2.05 eV for amorphous Se. The change of resistivity with temperature is examined for monoclinic and black Se.

Selenium is one of those materials which was first categorized as a semiconductor due to its small electronic conductivity compared with metals. The amorphous to crystalline transition as well as other physical properties of Se depend markedly on the preparation condition[1−3], moreover the conservation of the material characteristics is very important for the technological applications. Grenet et al.[4] determined the crystallization energy (about 1 eV), which increases slightly with the age of the sample. The crystallization behaviour of Se is strongly temperature dependent even at ordinary temperatures. Vitreous amorphous Se undergoes a slow transformation to the trigonal form which is the most stable modification. Yamamori[5] noted that vitreous and red amorphous selenium tended to crystallize imperfectly at room temperature after 2 to 3 weeks. The crystallization at this temperature was mainly due to the transformation to the trigonal Se and not to the monoclinic form.

X-ray diffraction studies gave a barely perceptible indication of monoclinic Se. These observations have been corroborated by other investigators[6]. In case of

Se samples heated near to the melting point, the coexistence of monoclinic and trigonal[5] phases was noted.

An earlier work suggests that some crystallinity was present in red amorphous Se on the basis of X-ray diffraction studies but it is conceivable that this crystallinity was in fact induced by the long exposure time (70 to 80 h) employed[7].

It was found[8] that the absorption edge in amorphous Se is not steep enough to deduce accurately the activation energy which is approximately between 1.9 to 2.1 eV. The conductivity is small at room temperature and it is difficult to determine the activation energy electrically. But Henkels[9] has determined activation energy by electrical measurements as $E = 2.3$ eV at $T = 0$.

This paper deals with the influence of aging on some physical properties of amorphous Se on transition to crystalline forms.

High purity Se powder was used for deposition of thin film in a vacuum of 10^{-5} Pa by evaporation from tungsten boat on quartz substrates. Such films were investigated by transmission electron microscope (TEM) (10-Zeiss). The structure of the thin film was examined using (Siemens D-500) X-ray diffractometer. The optical absorption in UV was measured for films deposited on quartz by a Beckman double-beam spectrophotometer (5260). Electrical conductivity measurements were carried out using specially designed holder. A high impedance electrometer (VA-J52 Dresden) was used through conventional electrical circuit.

The crystallization behaviour of amorphous Se is of considerable importance in the electrical and photoelectrical applications of the element. The morphology and growth of trigonal Se crystals reflect the polymeric nature of Se melts and bears a definite analogy to the behaviour of organic polymer. In the crystallization process, the complex ring-chain equilibrium in vitreous amorphous Se undergoes transformation to the orderly array of Se chains in the displaced screw plane structure of trigonal Se.

Numerous studies have shown that light, electron and nuclear irradiation have a definite effect on the crystallization behaviour of Se.

The action of light is believed to result in the creation of electron and hole pairs in vitreous selenium with the growth rate of Se crystallites controlled by the movement of holes to the crystal boundary, the crystallites acting as a sink for the holes[10].

Apparently only light with an energy in excess 2.2 eV (dissociation energy of the Se-Se bond) is effective in bringing about the crystallization of Se. Fitton and Griggiths[11] noted that the crystallization of amorphous Se films can be induced by electron beam irradiation and trigonal Se was obtained.

A series of electron micrographs show the crystallization of evaporated thin films of Se. Firstly, the investigated film appeared amorphous at low beam intensity. On increasing the electron beam intensity the crystallization proceeded very rapidly that it is not easy to be followed by successive micrographs. This is an indication that the technique used to study the amorphous allotropes of selenium might be influencing by the result obtained. The intermediate stage of crystallization was the hexagonal structure as shown in Fig. 1a while Fig. 1b ilustrates the final stage of crystallization which is the trigonal form. The transmission micrographs (Figs. 2a and 2b) show change in morphology of the film due to electron irradiation.

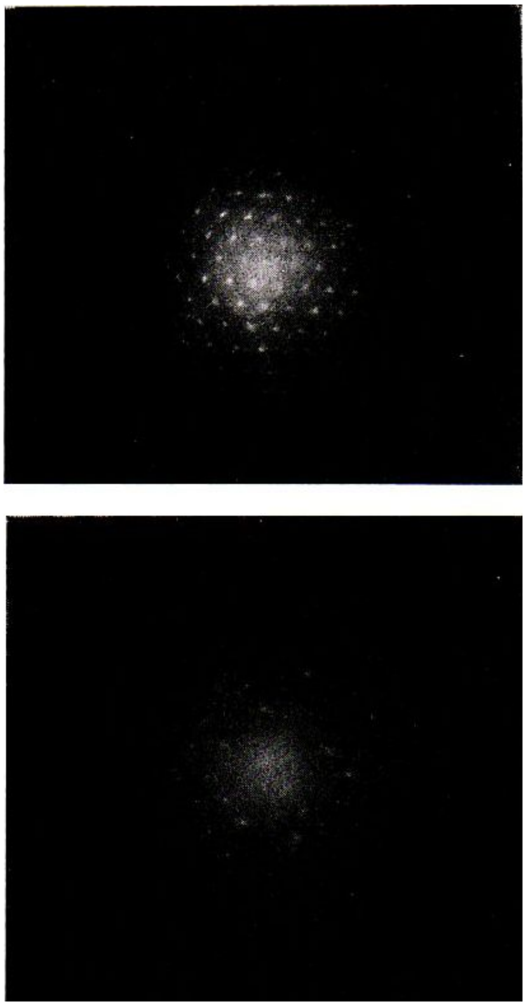

Fig. 1. Successive electron diffraction for Se*: (a) After a short period of irradiation; (b) After a long period of irradiation.*

The effect of aging has been followed by X-ray diffraction for evaporated film of Se on quartz substrate. Firstly the film was amorphous but for aging time of one month, X-ray diffraction Fig. 3a shows that the crystalline phase inferred was α-monoclinic and hexagonal phase. For aging time of one year at temperature 298 K the film crystallized to the stable black crystalline phase which shows a strong plane ($d = 5.1217$) while (211) and (400) planes correspond to β-monoclinic

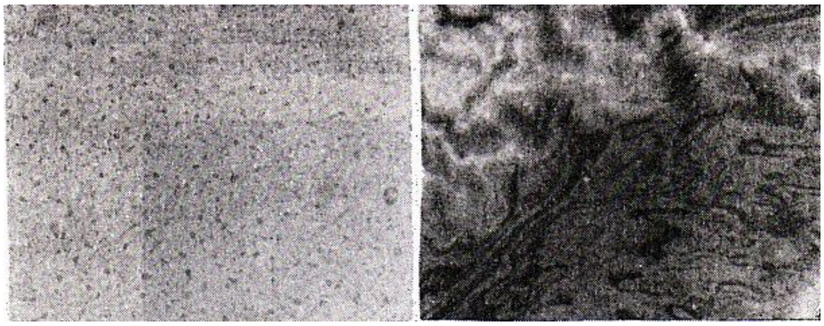

Fig. 2. Successive transmission micro-graphs for Se *thin film: (a) After a short period of irradiation; (b) After a long period of irradiation.*

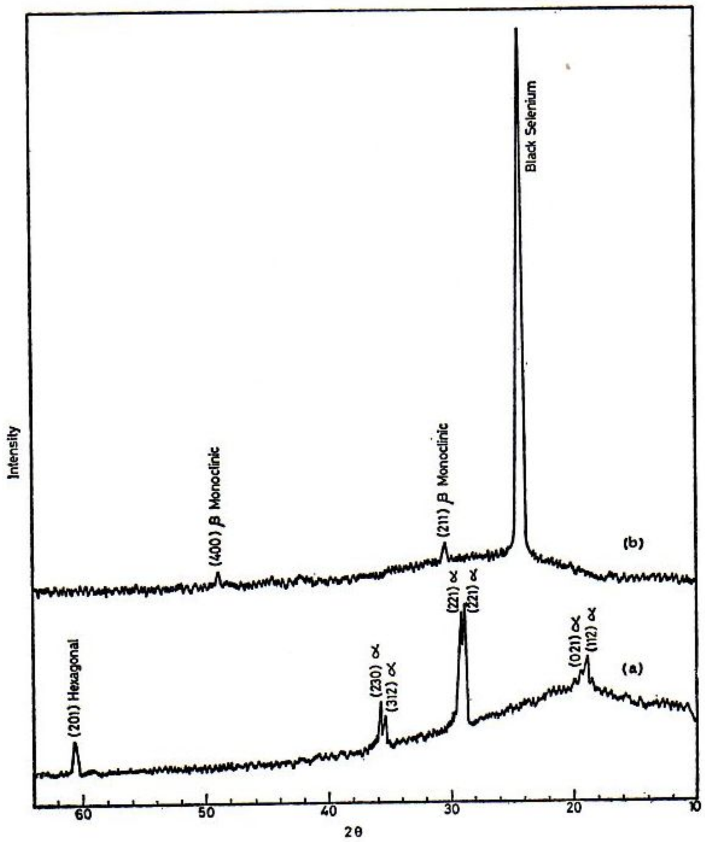

Fig. 3. X-ray diffraction of selenium after aging: (a) For aging time of one month; (b) For aging time of one year.

(Fig. 3b). This result contradicts with Grenet et al., who elucidate that sample aged one year is always amorphous; this point does not hold as far as the glass transition temperature[12] is concerned. It is therefore possible to use α-Se sample at temperatures lower than T_g (glass transition temp.) unless the age of the material influences its properties.

There is a little evidence available concerning the structure of black Se and the situation would appear to require considerable further work.

Since the kinetics of selenium crystallization is related to the rate of formation of nuclei on folded Se chains and the rate of transport of Se atoms to the growth face, consideration must be given to these two processes to obtain a better understanding of the crystallization behaviour and kinetics.

Amorphous Se absorbs strongly in the UV and short wavelength part of the visible spectrum, but becomes almost perfectly transparent at the red end of the visible region.

Near absorption edge, at energies higher than the band gap, no interference effects were observed. The absorption coefficient $\alpha(\omega)$ may be calculated from

$$\alpha(\omega) = \frac{1}{d} \ln \frac{[1 - R(\omega)]}{T(\omega)}$$

where $R(\omega)$ is reflectivity and $T(\omega)$ is transmittance. The analysis of $\alpha(\omega)$ shows that the rise of $\alpha(\omega)$ is due to an allowed transition described by[13]

$$\alpha^2 \sim (h\nu - E_g)$$

where E_g is the optical gap energy for direct transition.

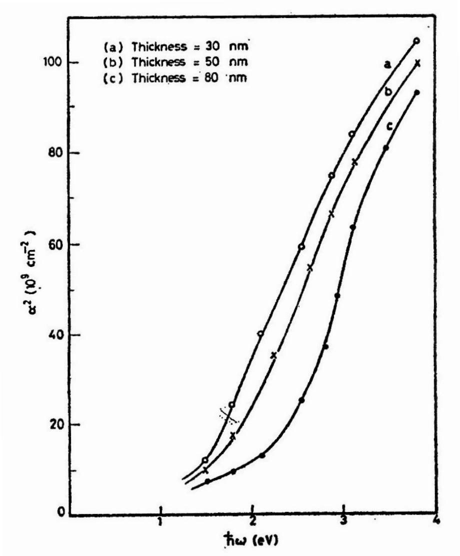

Fig. 4. The relation between the square of absorption coefficient against energy ($\hbar\omega$) for different thicknesses: (a) Thickness 30 nm*; (b) Thickness 50* nm*; (c) Thickness 80* nm.

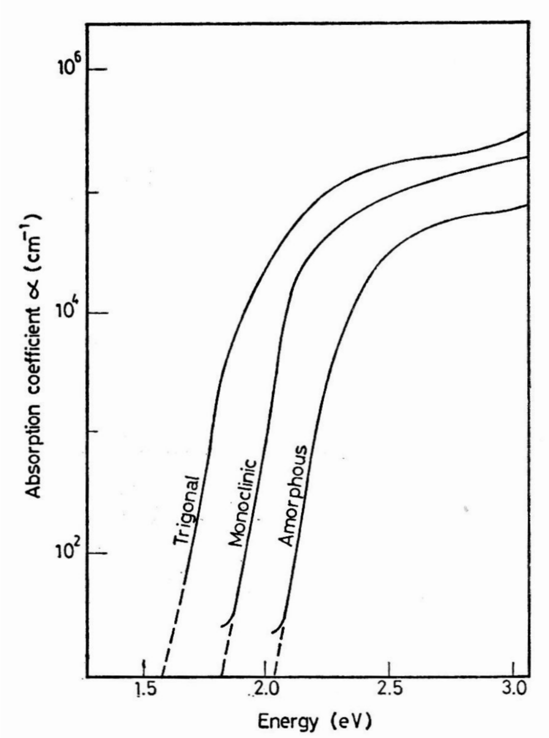

Fig. 5. Relation between absorption coefficient and energy for different allotropes.

The curves α^2 for different thicknesses are represented in Fig. 4. The experimental gap energy is changed from 1.5 eV up to 2.2 eV as the thickness ranges from 30 nm to 80 nm. Such change was attributed to the presence of more free carriers and small amounts of crystalline phase due to the slow rate of deposition.

Since Se exists in various allotropic forms, it is very interesting to investigate the effect of aging on optical absorption and electrical resistivity.

Figure 5 indicates the optical absorption versus energy. We obtained an energy gap $E_g = 2.05$ eV for amorphous Se, $E_g = 1.8$ eV for monoclinic form while for metallic Se $E_g = 1.65$ eV.

Figure 6 shows the IR transmission spectrum for two thicknesses of Se thin films in wavelenght range from 2.5 μm to 25 μm. The transmission is high and constant in the range from 2.5 μm up to 4.35 μm and then it drops sharply, with a well defined peak observed at 13.33 μm. This peak may be attributed to Se_2 molecule by analogy with similar bands in the spectrum of plastic sulfur observed by Taylor and Rideal[14)]. The 28.6 μm sample (a) shows a broad peak but sample (b) showed a sharp incerease in transmission, second peak may be due to Se_8.

Figs. 7a and 7b show the relation between $\ln P$, (where P is the resistivity of the thin film) against $1/T$ for monoclinic form and metallic form, which shows the decrease of resistivity from 10^{10} Ωcm to 10^5 Ωcm.

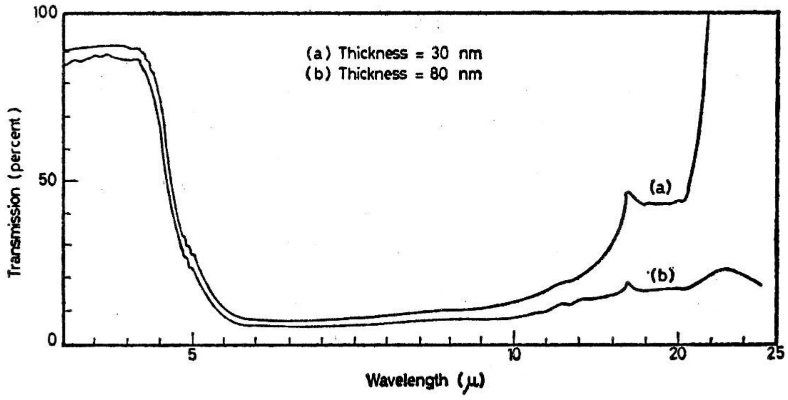

Fig. 6. I. R. transmission spectrum for Se *thin films: (a) For thin film of thickness 30* nm*; (b) For thin film of thickness 80* nm*.*

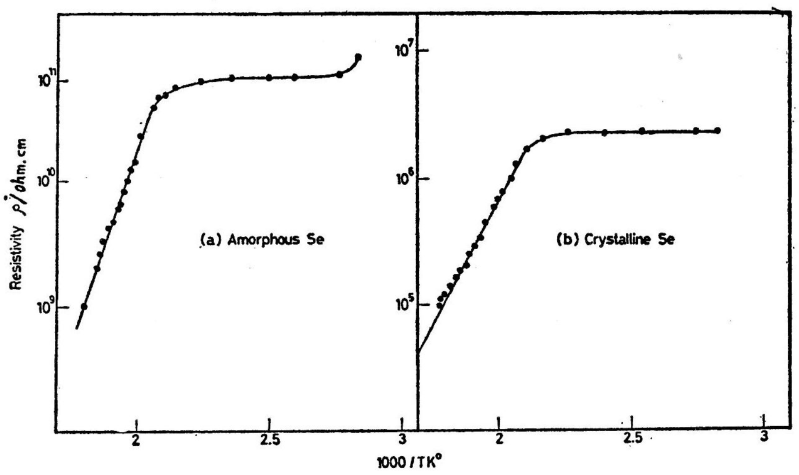

Fig. 7. Temperature dependence of resistivity: (a) For amorphous Se*; (b) For crystalline* Se*.*

Such curve follows Arrhenius relation

$$\sigma = \sigma_0 \exp(-E/kT)$$

σ is the conductivity corresponding to temperature T, σ_0 is const, and E is the activation energy for conduction. The main difference between both forms (α and β monoclinic) is due to the different packing of ring molecules in the lattices. The unit cell of both modifications is rather complicated, since it contains in each case 4 molecules each consisting of 8 atoms. The high number of 32 atoms per unit cell is the reason that band structure calculations for monoclinic selenium have not yet been performed.

The experimental results on monoclinic form are relatively low in number compared with the numerous investigations on the trigonal form[15].

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EFEKT STARENJA NA NEKA FIZIKALNA SVOJSTVA TANKIH SLOJEVA Se

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Tanki slojevi Se pripremljeni su naparivanjem u vakuumu. Kristalizacija filma ovisi o temperaturi i vremenu starenja. Posljedice kristalizacije istraživane su elektronskim mikroskopom i difrakcijom X-zraka. Napravljeni su također I.C. i U.V. spektri. Energije optičkog procijepa izračunate za različite alotrope Se su: 1,65 eV za crni Se, 1,8 eV za monoklinski i 2,05 eV za amorfni Se. Promjena otpora s temperaturom mjerena je za monoklinski i crni Se.