Characteristics of selenium films on different substrates under heat-treatment

S K Bhadra*, A K Maiti+ and K Goswami+

*Central Glass & Ceramic Research Institute, Jadavpur,
Calcutta-700 032, India

+Department of Physics, Jadavpur University, Jadavpur,
Calcutta-700 032, India

Abstract   : The structural changes on successive heat-treatment of vapour grown amorphous selenium films on different substrates, have been studied by observing scanning electron micrographs, X-ray diffractograms and Raman spectra Crystallization rate of a-Se films on aluminium substrate is found to be faster than glass or quartz and the films on quartz, heat treated at 50°C for 40 minutes, show characteristic metastable structure like dendritic growth with partial molecular hexagonal phases At this stage, the Raman active bands are not observed and on further high temperature annealing, the Raman spectrum shows more symmetric Se-molecular structure with disappearance of the dendritic features

Keywords   : Selenium film, substrates, structure

PACS Nos.   : 61.10.Nz, 78.66.Jg

1. Introduction

Chalcogenides have wide range of applications in material research. Several structural or photo-chemical changes have been observed in amorphous chalcogenide elements and compounds, *viz*, through ageing, photo-crystallizations *etc* [1,2]. Selenium is one such chalcogen which undergoes unstable morphological transitions from amorphous to crystalline phases. Generally, it is known that vapour-grown Se thin films crystallize to spherulitic patterns in hexagonal form composed of helical chains [3]. During transitions, the different phases of the a-Se films reveal that the structure, growth processes and other properties depend on the method of preparation, deposition conditions (vapour temperature, rate and angle of deposition), physical condition of the substrates and vacuum environment [4,5].

In early works [6–8], it has been observed that the deposition on a particular substrate is by no means absolute, rather the vapour conditions and the temperature of the substrates appear to be important. On critical assessment both for normal and heat-treated a-Se films, it has been ascertained that the substrate-film interface plays a dominant role during the transition phenomena [7]. In the present experiment, the treatment of a-Se specimens of similar film dimension on quartz and other substrates at lower thermal energy reveals a characteristic dendritic growth only on quartz substrate. The microstructures were analysed through Scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD).

2. Experimental procedure

Pure Se pellets (99.999%) obtained from Johnson Matthey & Co. are used for making thin films. Substrates of soda glass slides, Al foils and z-cut quartz crystals (obtained from a single block of synthetic quartz crystal-mirror polished) are used for depositing Se films and were cleaned using trichloroethylene, acetone and ethyl alcohol. All the substrates prepared, had been exposed to atmosphere before Se-coating were being taken place. Se pellets were melted slowly in a filament wound molybdenum boat under a vacuum of 2.5×10^{-3} Pa, when the substrate is placed 5 cm above the heating source (Polaron P-150 Vacuum Coating Unit). The temperature of the mass was gradually increased to 350°C and allowed to deposit with a rate of 5 nm/sec^{-1} for a desired time onto the substrates.

Several specimens of Se films grouped as G–I, A–I, Q–I for thickness 110 nm; G–II, A–II, Q–II, for thickness 220 nm and G–III, A–III, Q–III, for thickness 330 nm were prepared on glass, Al and quartz respectively, under identical environment of vacuum and vapour temperature, while the substrates were kept in room temperature. The deposition rate and thickness were recorded by Edward FTM5 thickness monitoring unit housed in the vacuum chamber, the thicknesses of the films were further verified by ellipsometric technique with a variation of ± 3 nm. All the films were heat-treated batch wise between 50°C and 105°C for 30 to 40 mins. and they were returned to room temperature by decreasing the temperature in steps of about 1°C min^{-1}. The SEM is performed (10–12 KV) using Cambridge ISI-60A instrument and XRD of the heat-treated Se film is obtained at room temperature using Philips diffractometer, model PW-1050 at CuK$_\alpha$ radiation (wavelength = 1.514 Å). The Raman spectra are recorded at room temperature using spectra physics spectrometer (Stabilite-2017) equipped with water cooled detector and 5145 Å radiation from an argon ion laser with power ~100 mW.

3. Results

The scanning electron micrographs (SEMs) which were taken in quick succession are shown in Figures 1(a–f). Most characteristic features for amorphous to crystalline transition of the films by isothermal annealing were observed for the thickness 110 nm.
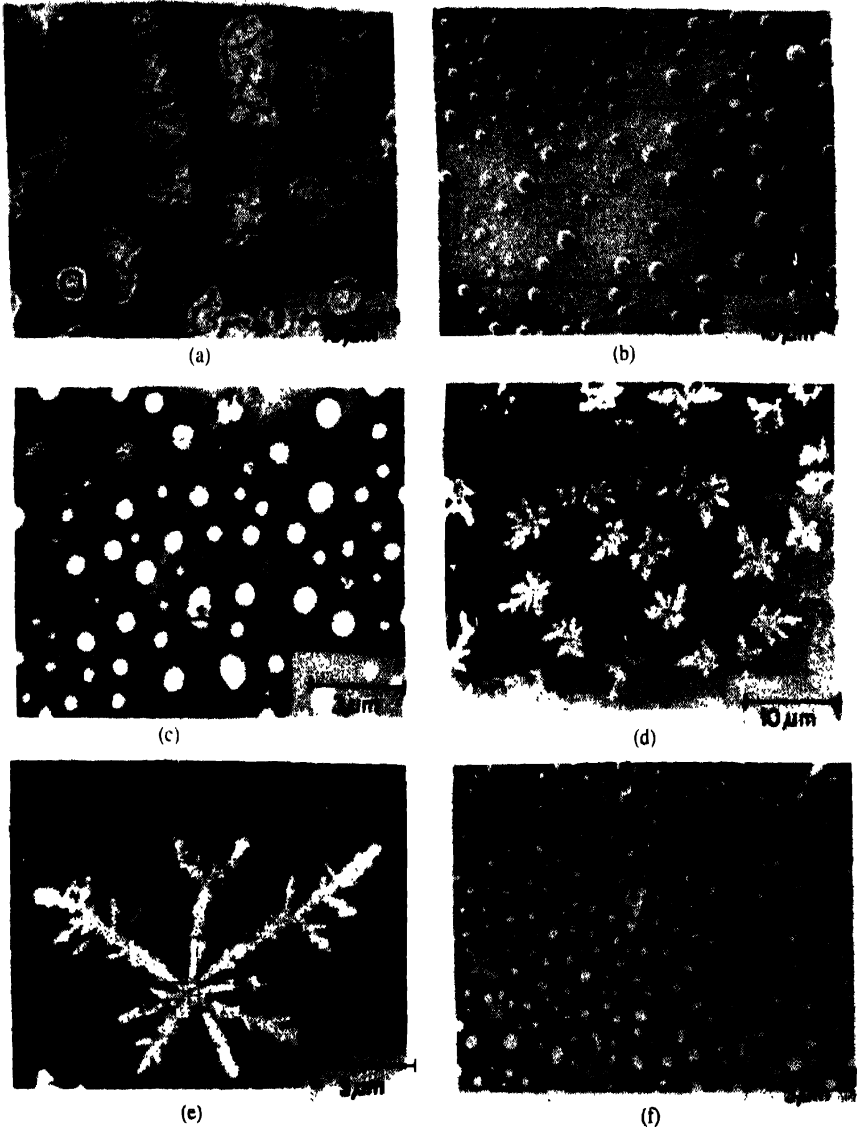
Plate 1

Figure 1. SEM showing : (a) G–I Se-films (110 nm) deposited on glass substrate after heat treatment for 30 minutes at 75°C, (b) after heat treatment of G–I for 30 mins at 90°C, (c) A–I films (110 nm) deposited on aluminium (Al) substrate after heat treatment for 30 mins at 75°C. (d) Q–I films (110 nm) deposited on Z-cut quartz substrate after heat treatment for 40 mins at 50°C, (e) magnified structure of (d) and (f) after heat treatment of Q–I for 40 mins at 90°C.

The specimen G–I when heat treated below 65°C, remains amorphous in nature; but at 75°C, the micro structures show presence of segregated worm loopings (Figure 1a) with few spherulites of circular front. The same specimen when heat treated above 90°C, shows sufficient distinct spherulites in the transparent zone, indicating completion of crystalline phase (Figure 1b). The XRD (Figure 2) shows that the structure is hexagonal one (100). Similar phenomena are delayed in case of specimens G–II and G–III.
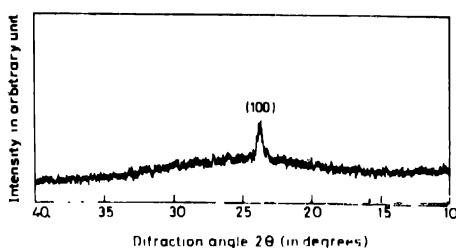

Figure 2. XRD showing G–I films after heat treatment for 30 mins at 90°C

Onset of crystallization has been observed in A–I specimens when heat treated at 65°C for 30 mins; at 75°C, decorated spherulites with few disjoined chains are observed (Figure 1c). When a virgin sample of the same lot is directly treated at 75°C, the microstructure is identical to that of stepwise heat treatment up to 75°C. For higher thicknesses (A–II and A–III specimens), the crystallization process starts at higher temperatures but the transition is very fast.

The Q–I films on quartz at the ambient have been found to be amorphous as in the case of glass and Al substrates when examined through XRDs (figures not shown). When the Q–I specimen was heat treated at 50°C for 40 mins, some distinct snowflake of ice like micro-structures are observed (Figure 1d). A magnified SEM of one such zone (Figure 1e) is identified clearly as dendritic in appearance. This pattern is characteristic and is absent when tried with other specimens including Q–II and Q–III samples. At 75°C, numerous tiny crystallites together with some smaller dendritic growths have been observed. On further heat treatment, the equilibrium condition for stable phase appears similar to that of other substrate films of same thickness but the sizes of crystallite are found to be smaller (Figure 1f).

The Bragg reflection peaks (Figure 3a) of Q–I heat treated at 50°C show high intense peak at $d = 3.68$ Å which indicates the monoclinic phase of Se with larger molecular separation. During stepwise heat treatment (15°C), the intensity of 3.68 Å peak starts decreasing and finally at 90°C, the Bragg peaks (Figure 3b) show phase transition towards stable state of Se which are identified as (100) and (101) crystal planes. Figure 3(c) shows (100) and (200) faces of the single crystal quartz substrate. The Raman spectra of Q–I films

at various stages were recorded but only the active bands are observed when the specimen was annealed at 90°C (Figure 4).
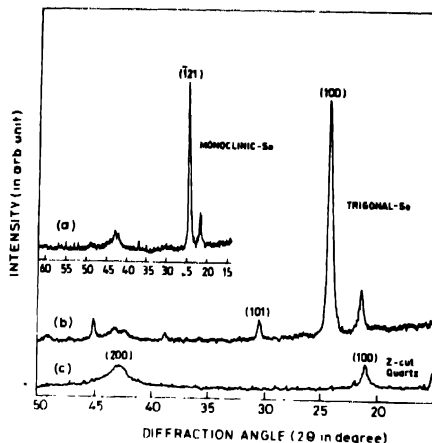

Figure 3. XRD showing   (a) Q-I films after heat treatment for 40 mins at 50°C, (b) Q-I films after stepwise heat treatment to 90°C for 40 mins and (c) blank Z-cut quartz substrate
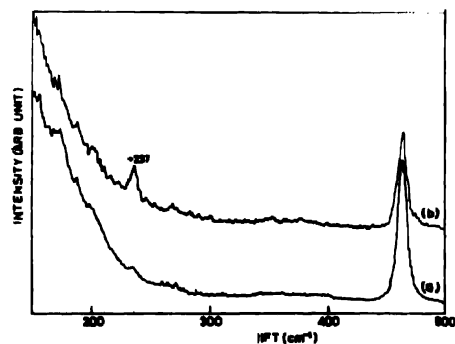

Figure 4. Raman spectra of Q-I films . (a) after heat treatment for 40 mins at 50°C and (b) after stepwise heat treatment to 90°C.

The dendritic feature did not occur in Q-II and Q-III specimens. A Q-III film on heat treatment at 65°C, shows swollen surfaces with clusters of indistinct pattern in SEM micrographs. Above 75°C, the microstructure of the same specimen (Figure 5) starts flattening with increase in sizes. Above 105°C, mixture of spherulites and swollen surfaces have been observed (figure not shown).

4. Discussion

Before the work of Audiere *et al* [9,10], it was believed that the amorphous Se_8 has a mixture of $Se_{n<8}$ and Se_8 whose proportion is the controlling factor in determining the
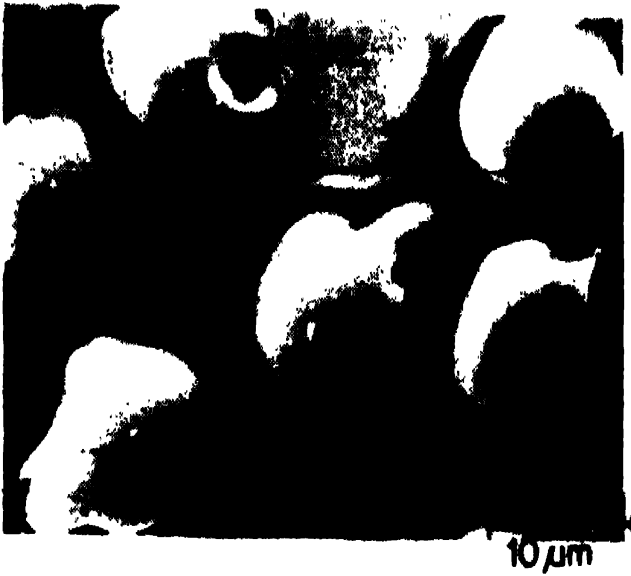
Plate II

Figure 5. SEM showing Q–III film (330 nm) after stepwise heat treatment to 75°C for 30 mins.

properties and they showed that Se vapour at the source temperature of 385°C quenches into long and short species in a manner to produce a mixed deposit of two amorphous materials. During annealing at a temperature greater than the glass transition temperature, nucleation commences only at the long species sites and crystallinity gradually develops by using up the relatively mobile short species. In the present case, an adequate mixture of long and short species are observed when the annealing is performed on G-1 (Figure 1a) where the source Se vapour temperature was maintained at 350°C, the results corroborate with Audiere *et al* [10]. It appears from Figure 1c that even under lower degree of heat treatment (65°C), the process of crystallization is accelerated by changing the substrate from glass to Al. Heavens and Griffiths [11] suggested that the substrate has a profound effect on crystal growth kinetics and morphology. According to Griffiths and Fitton [12], the spherulitic crystals of Se in contact with soda glass, grow faster than in the bulk with different microstructures. While studying the microstructures by considering the effect of recrystallization and grain growth under high electron beam irradiation, the present a-Se films deposited on various substrates show different morphological transitions.

The dendritic feature observed in Figures 1(d) and 1(e) arises from the differences in the solute content at a faster rate than the movement of the solidification isotherms [12]. The flow initially dispersed in many paths since the flowing warm material starts to dissolve the already solidified materials. The face growth rate lags and the corner growth increases to maintain the growth rate more or less steady. In order to attain the forced growth rate, the corner penetrates further while the faces grow slowly in depleted part of the material in the film [13]. When Se film heat-treated at 50°C and returned to room temperature, the warm Se cools on a highly polished substrate, the stem of the dendrite and the branches grow from its sides which are directed along the fast growing crystallographic axes. The symmetry of each flake may be due to haxagonal symmetry of Se and the substrate topology. Morphological instability occurs when the film subsequently heat treated at 75°C and further heat treatment coalesces the dendritic feature and the formation of the crystallites are similar in appearance to that of films on other substrates (Figure 1f).

The Raman shift at 237 cm^{-1} shown in Figure 4 corresponds to trigonal state of Se [14], other bands are characteristics of quartz crystal. But no active Raman bands have been found during the metastable transitions, it may be due to the presence of large asymmetry in the molecular structure. Since trigonal Se has highly active Raman bands along the *c*-axis and the incident laser polarised parallel to the plane of scattering, the Se-Se stretching vibrational modes at 250 cm^{-1} are observed to be absent. Dendritic nature of Se-film and bulk has been reported by several groups [15,16] and they explained the growth characteristics as metastable state of Se. While the typical nature of their growth pattern

observed on a quartz substrate is quite uncharacteristic, Griffiths *et al* [17] observed that Se film grown on (100) cleavage face of MgO has the structures which remain completely amorphous even exercising large temperature of heat treatment; the same is not true when the film is grown on different crystal planes of single crystal of KCl and KBr. They inferred that there is marked contrast with the structure of the film on different substrates and specially MgO has shown inhibitory effect on Se-crystallization. In a previous communication, Bhadra *et al* [7] emphasized that the sticking of Se-atoms on quartz is very high compared with glassy substrate, and the phenomena may attribute to peculiar orientation of the lamellae in the film-substrate interface as happened in the present case.

According to Kotkata [18], the crystallization time is shorter in case of thin films than those of bulk Se. It is evident from the results of Figures 1(a–f) that for isothermal annealing of a-Se films upto a particular thickness, quasi-homogeneous growth persists. As the thickness increases (Figure 5), the crystallization process becomes delayed and the mixed state prevails until a high activation energy be applied. Non-occurrence of dendritic growth for higher thicknesses on quartz is not clear; perhaps for a critical thickness of the a-Se film, the interfacial growth becomes relatively slower and the behaviour of amorphous to crystalline transition in this state is substrate dominant.

Acknowledgment

References

[1]   N F Mott and E A Davis *Electronic Processes in Non-crystalline Materials* (Oxford · Clarendon) p 518 (1979)

[2]   P Andonov, *J. Non-cryst. Solids* **47** 297 (1982)

[3]   M Kawarada and Y Nishina *Jpn. J. Appl. Phys.* **14** 1519 (1975)

[4]   K S Kim and D Turnbull *Appl. Phys.* **44** 5237 (1973)

[5]   G Gross, R B Stephens and D Turnbull *J. Appl. Phys.* **48** 1139 (1977)

[6]   S Choudhuri, S K Biswas, A Chowdhury and K Goswami *J. Non Cryst. Solids* **46** 171 (1982)

[7]   S K Bhadra, A K Maiti, R Bhar, D Talapatra and K Goswami *J. Mater. Sci. Lett.* **13** 525 (1994)

[8]   D C Campbell in *The Use of Thin Films in Physical Investigations* ed. J C Anderson (London : Academic) p 36 (1966)

[9]   J P Audiere, Ch Mazieres and J C Carballes *J. Non-Cryst Solids* **34** 37 (1979)

[10]   J P Audiere, Ch Mazieres and J C Carballes *J. Non-Cryst. Solids* **27** 411 (1978)

[11]   O S Heavens and C H Griffiths *Acta. Crysta.* **18** 532 (1965)

[12]   C H Griffiths and B Fitton in *Physics of Se and Te* ed. W C Cooper (Oxford : Pergamon) p 163 (1969)

[13]   B R Pamplin *Crystal Growth* (2nd edn.) (Oxford : Pergamon) p 485 (1980)

[14]· G Lucovsky, A Mooradian, W Taylor, G B Wright and R C Keezeer *Solid State Commun.* **5** 113 (1967)

[15]   M Ozenbas and H Kalebozen *J Cryst. Growth* **78** 523 (1986)

[16]   J C Brice *Crystal Growth Process* (London : Blackie) p 139 (1986)

[17]   C H Griffiths and H Sang in *Physics of Se and Te* ed W C Cooper (Oxford . Pergamon) p 135 (1969)

[18]   M F Kotkata *J. Mater Sci.* **27** p 4847, 4858 (1992)