ELSEVIER

Journal of Non-Crystalline Solids 198–200 (1996) 723–727

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Thermally and photo-induced irreversible changes in the optical properties of amorphous Ge_xSe_{100-x} films

E. Sleeckx [a], L. Tichý [b], P. Nagels [a,*], R. Callaerts [a]

[a] *RUCA, University of Antwerp, B-2020 Antwerpen, Belgium*
[b] *Joint Laboratory of Solid State Chemistry, Czech Academy of Sciences and University of Pardubice, 53009 Pardubice, Czech Republic*

Abstract

Films of amorphous Ge_xSe_{100-x} were prepared by plasma-enhanced chemical vapour deposition (PECVD) using the hydrides GeH_4 and H_2Se as precursor gases and by standard thermal evaporation. The optical bandgap obtained from a Tauc plot showed a maximum ($E_g = 2.27$ eV) at the stoichiometric composition ($x = 33$) for the PECVD films. The bandgap values of the virgin evaporated films were much lower in the range $x = 40$ to 75, the difference being due to the incorporation of hydrogen in the PECVD films, detected in IR and Raman spectra. Thermal annealing and illumination by bandgap light of the evaporated films induced irreversible bleaching. The PECVD films showed a more complex behaviour of the optical shift upon annealing due to the loss of hydrogen. An IR and Raman investigation demonstrated that the changes in the optical transparency are accompanied by an increase of ordering in the local structure.

1. Introduction

Amorphous chalcogenide films, prepared by rapid quenching from the vapour phase, usually have a more or less disordered network, containing a substantial density of wrong chemical bonds. Upon thermal annealing or illumination with bandgap light, bond rearrangements can take place, leading to irreversible changes in many physical properties, e.g. optical absorption edge shifts. The relaxed state is usually the starting one for the study of reversible photo-induced changes, which have a different physical origin.

In this paper, we report on thermally and photo-induced irreversible changes in the optical transmission of amorphous Ge_xSe_{100-x} films prepared by plasma-enhanced chemical vapour deposition (PECVD) and by thermal evaporation. The main objective is to demonstrate and discuss the accompanying effects in the local structure of the alloys. We used IR and Raman spectroscopy, since these are powerful techniques for observing even subtle structural changes.

2. Experimental procedures

The method of film preparation of amorphous Ge_xSe_{100-x} by plasma-enhanced chemical vapour deposition was similar to that described by us in Ref.

---

[*] Corresponding author. Tel.: +32-3 218 0752; fax: +32-3 218 0652; e-mail: pnagels@ruca.ua.ac.be.

PII S0022-3093(96)00030-0

[1,2]. The precursor gases were GeH_4 and H_2Se diluted in hydrogen (15 vol% of the hydrides). Films of similar composition were also prepared by thermal evaporation of glasses obtained by a standard melting technique, with Ge atomic concentrations $x = 0$, 15, 25, 30, 33 and 40. Annealing of the as-deposited films was carried out in nitrogen atmosphere at ambient pressure for periods up to 2 h at temperatures below the glass-transition temperature T_g. The latter, determined by means of a thermal mechanical analyser, was found to increase linearly from ~ 50°C for Se to ~ 300°C for $Ge_{30}Se_{70}$, followed by a jump to ~ 400°C for stoichiometric $GeSe_2$.

3. Results

Measurements of optical transmission and reflection were analyzed in the standard way to yield the optical absorption coefficient α as a function of the photon energy $h\nu$. In the high-absorption range, the optical gap was evaluated from Tauc's equation $\alpha h\nu = B(h\nu - E_g)^2$, where E_g is the energy distance between the valence and conduction band mobility edges. The parameter B given by the slope of the plots is an interesting parameter, since it can be taken as a measure of the disorder. The characteristic optical parameters, E_g (eV) and $B^{1/2}$ ($cm^{-1/2}$ $eV^{-1/2}$) of PECVD and evaporated films are presented in Table 1. In Fig. 1 the compositional dependence of the optical gap is shown for as-deposited evaporated and PECVD films.

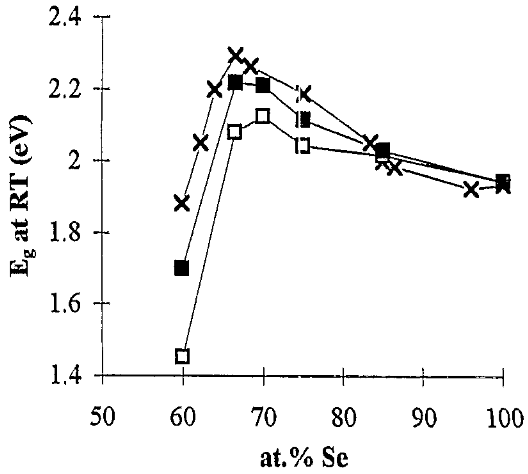

Fig. 1. Compositional dependence of the optical gap E_g for amorphous Ge_xSe_{100-x} films: (×) virgin PECVD, (□) virgin evaporated, (■) annealed evaporated. Lines are drawn as guides for the eye.

Table 1
Optical parameters E_g (eV) and $B^{1/2}$ ($cm^{-1/2}$ $eV^{-1/2}$) for Ge_xSe_{100-x} films prepared by PECVD and evaporation (EV), before and after annealing

		PECVD		EV	
		E_g	$B^{1/2}$	E_g	$B^{1/2}$
Se	(Virgin)	1.936	1280	1.945	1297
$Ge_{15}Se_{85}$	(Virgin)	2.000	1053	2.017	945
	(100°C)	2.003	1058	2.029	947
$Ge_{25}Se_{75}$	(Virgin)	2.090	816	2.044	827
	(175°C)	2.118	827		
	(250°C)	2.094	816	2.115	839
$GeSe_2$	(Virgin)	2.266	836	2.073	913
	(175°C)	2.326	891		
	(250°C)	2.269	854	2.233	1040
$Ge_{40}Se_{60}$	(Virgin)	1.881	621	1.452	552
	(125°C)	1.779	605		
	(300°C)	2.047	742	1.699	637

The evaporated films, subjected to thermal annealing for 2 h below the glass-transition temperature, displayed bleaching for all compositions, except a-Se. The blue shift of the optical absorption edge substantially increased for higher Ge concentrations. The E_g and $B^{1/2}$ values of the annealed materials are also summarized in Table 1. Annealing of PECVD films showed a more complex behaviour of the optical transmission change. Upon annealing to 175°C, the compositions $Ge_{25}Se_{75}$ and $Ge_{33}Se_{67}$ displayed gradual bleaching, similar to that observed in evaporated films, changing to darkening, however, above 175°C (see Table 1). On the contrary, annealing of a $Ge_{40}Se_{60}$ film at 125°C resulted in darkening, followed by a change to bleaching for $T_{ann} >$ 150°C (see Fig. 2).

Illumination by white light induced a blue shift of the optical gap in the evaporated films of composition $x = 25$, 30 and 33 but no effect was observed in the Se- and Ge-rich films ($x = 15$ and 40). The shift was maximum in the stoichiometric material ($\Delta E_g =$ 0.057 eV) but bleaching by illumination was less

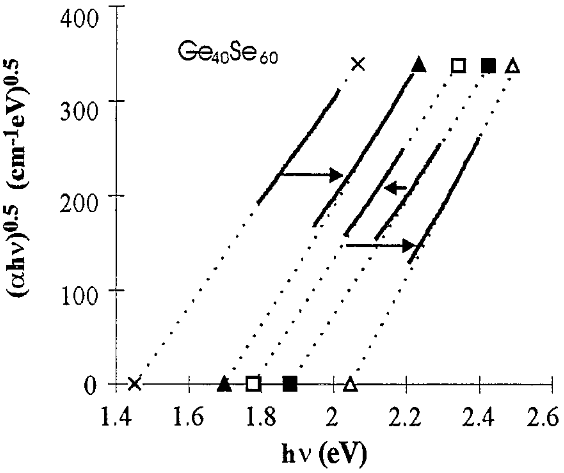

Fig. 2. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for $Ge_{40}Se_{60}$ films; evaporated: (×) virgin, (▲) annealed at 300°C; PECVD: (■) virgin, (□) annealed at 125°C, (△) annealed at 300°C.

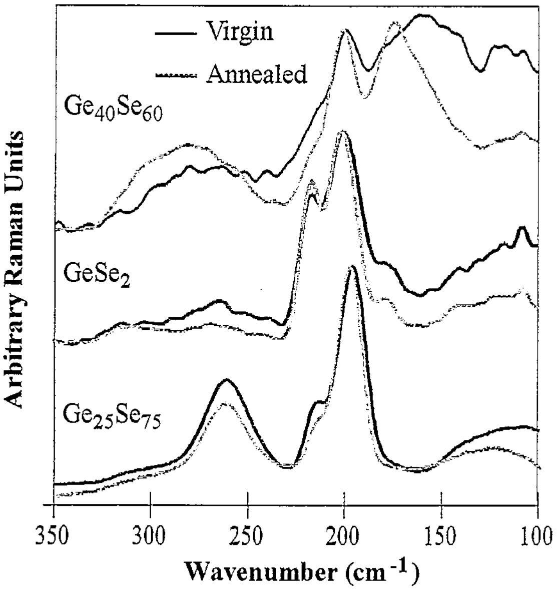

Fig. 4. Raman spectra of evaporated Ge_xSe_{100-x} films before and after annealing.

pronounced than the thermally-induced one. A $GeSe_2$ film kept at room temperature for several weeks was illuminated and exhibited, for up to 20 min of irradiation, a small photodarkening effect followed by photobleaching, remaining smaller (saturation value $\Delta E_g = 0.02$ eV), however, than that measured immediately after preparation. All compositions of PECVD films did not show any measurable shift of the optical absorption edge, indicating that these materials are closer to the ordered state than the evaporated ones. We also studied the shift of the optical absorption edge in the Ge_xSe_{100-x} system, when illuminated and measured at liquid nitrogen temperature. Whereas at room temperature prolonged illumination resulted in a blue shift of the gap, both virgin and well-annealed films prepared by PECVD or evaporation showed darkening, which remained small for compositions close to stoichiometry but markedly increased for higher Se contents. By heating to room temperature the darkening was reduced, especially for the Se-rich films. This process was completely reversible.

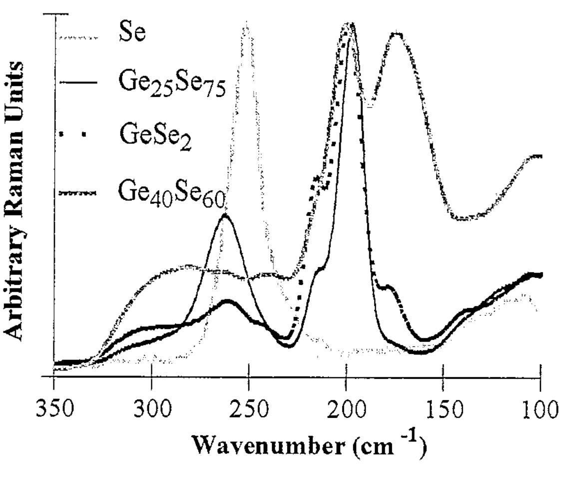

Fig. 3. Raman spectra of as-deposited PECVD Ge_xSe_{100-x} films.

The Raman spectra of as-prepared PECVD and evaporated films are represented in Figs. 3 and 4.

4. Discussion

From Fig. 1 it can be seen that the optical bandgap of the PECVD films exhibits a maximum ($E_g = 2.27$ eV) at the stoichiometric composition ($x = 33$) with a rapid decrease in the Ge-rich region and a slower one in the Se-rich region. The bandgap values of the virgin evaporated films were much lower in the range $x = 40$ to $x = 75$ and the maximum was slightly shifted to the Se-rich side. The difference can be explained by the incorporation of hydrogen in the PECVD films during the deposition in a hydrogen-rich plasma. This was evidenced by the presence of a Raman band at 2030 cm^{-1}, originating from Ge-H vibrations, in samples with an excess of Ge and a Raman band at 2240 cm^{-1}, arising from Se–H vibrations, in stoichiometric and Se-rich samples. Our data obtained on evaporated films agree well with those reported by other authors [3].

Fig. 1 also shows that the E_g values of the annealed evaporated films are still lower than those of the non-annealed PECVD films. After annealing, the maximum in the compositional dependence of the optical gap is shifted to the stoichiometric composition $Ge_{33}Se_{67}$. In Fig. 2 the Tauc plots of evaporated and PECVD $Ge_{40}Se_{60}$, before and after annealing for two hours, are shown. The striking difference between both films can be explained by the loss of hydrogen when PECVD films were subjected to heat treatment. Direct evidence came from Raman spectra, recorded on the three different compositions after annealing at increasing temperature. In $Ge_{40}Se_{60}$ a Raman band at 2030 cm^{-1}, due to Ge–H vibrations, completely disappeared in the temperature range 125 to 150°C. In $Ge_{33}Se_{67}$ and $Ge_{25}Se_{75}$ the hydrogen evolution occurred at higher temperature, as indicated by the gradual decrease of the intensity of a Raman band at 2240 cm^{-1}, associated with Se–H vibrations, between 150°C and 225°C. These observations indicated that darkening is a consequence of the disappearance of Se–H or Ge–H bonds with the formation of new Se–Se bonds in the Se-rich material and Ge–Ge bonds in the Ge-rich one.

The Raman spectra of as-prepared PECVD and evaporated films were very similar (see Figs. 3 and 4). The spectral features are: in Se, a strong band at 250 cm^{-1}, attributed by Lucovsky [4] to stretching vibrations of Se atoms in helical chain-like and ring-like arrangements ('meandering chain'); in Se-rich compositions ($x = 15$ and 25), a band near 260 cm^{-1} originating from Se–Se bonds and a strong band at 200 cm^{-1} accompanied by a side band near 215 cm^{-1}, assigned to the stretching mode of $GeSe_{4/2}$ corner-sharing tetrahedra (200 cm^{-1}) and to the vibrations of Se atoms in four-membered rings composed of two edge-sharing tetrahedra (215 cm^{-1}), respectively [5]; in $GeSe_2$, in addition to the typical 200 cm^{-1} band with its companion line, a small band at 175 cm^{-1}, originating from Ge–Ge bonds, and a band at 260 cm^{-1}, providing clear evidence for structures containing Ge–Ge and Se–Se bonds in stoichiometric material; in the Ge-rich composition ($x = 40$), PECVD films exhibited a well-resolved band at 175 cm^{-1} and a broad band around 280 cm^{-1}, both arising from Ge–Ge bonds, and in evaporated films, the band around 175 cm^{-1} was much broader and not as well-defined as in PECVD films.

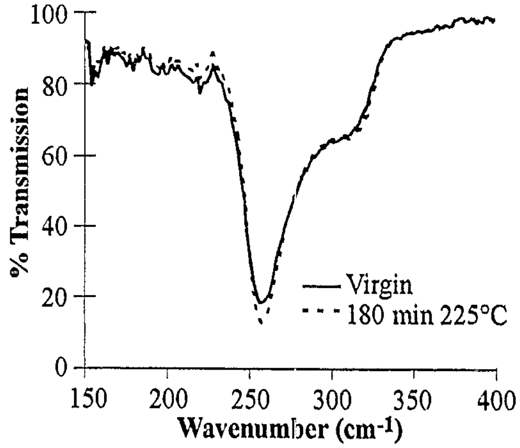

Fig. 5. IR transmission spectra of evaporated $Ge_{33}Se_{67}$ before and after annealing at 225°C.

The Raman spectra of annealed evaporated films are shown in Fig. 4. In $Ge_{25}Se_{75}$ the intensity of the vibration mode at 260 cm^{-1}, related to Se–Se bonds, decreased. The relative intensity of the companion peak at 215 cm^{-1} to the peak at 200 cm^{-1} slightly decreased, pointing to an increased number of corner-sharing tetrahedra. The spectra of stoichiometric $GeSe_2$ clearly indicated that annealing reduced the intensity of the bands at 260 cm^{-1} and 175 cm^{-1}, originating from Se–Se and Ge–Ge bonds. Hence, the density of homopolar bonds decreased, resulting in bond rearrangements with the formation of Ge–Se bonds. Further evidence for an increase in the density of heteropolar Ge–Se bonds was found in the slight increase in the intensity of the absorption band located at 260 cm^{-1} in the far-infrared spectrum of $GeSe_2$, annealed at 225°C for 180 min (see Fig. 5). In $Ge_{40}Se_{60}$ the Raman band at 175 cm^{-1} became sharper and better defined, reaching the shape of the same band observed in a PECVD sample. This is a sign of an increase in the short-range order.

5. Conclusions

From the Raman and IR measurements we can conclude that a certain degree of ordering in the local structure is the main cause of the irreversible blue shift of the optical gap in Ge_xSe_{100-x} films. In general, the films of different compositions prepared either by evaporation or by PECVD exhibit similar structural changes but the behaviour of the optical change is more complex in PECVD films than in evaporated ones, due to loss of hydrogen during heating.

References

[1] E. Sleeckx, P. Nagels, R. Callaerts and M. Van Roy, J. Phys. IV, C3, 3 (1993) 419; J. Non-Cryst. Solids 164–166 (1993) 1195.
[2] P. Nagels, E. Sleeckx, R. Callaerts and L. Tichý, Solid State Commun. 49 (1995) 49.
[3] M.F. Kotkata, K.M. Kandil and M.L. Theye, J. Non-Cryst. Solids 164–166 (1993) 1259.
[4] G. Lucovsky, in: The Physics of Selenium and Tellurium, ed. E. Gerlach and P. Grosse (Springer, Berlin, 1979) p. 210.
[5] S. Sugai, Phys. Rev. B35 (1987) 1345.