J Mater Sci (2007) 42:1196–1201
DOI 10.1007/s10853-006-1456-y

Optical and electrical properties of obliquely deposited a-GeSe$_2$ films

Priyamvada Bhardwaj · P. K. Shishodia · R. M. Mehra

Received: 8 May 2003 / Accepted: 13 April 2006 / Published online: 24 January 2007

Abstract Oblique deposition and exposure to photons of energy greater than the bandgap have a marked effect on the structure and consequently on electrical and optical properties of amorphous chalcogenides. This paper presents a detailed study of photoinduced effect and oblique deposition effect on electrical and optical properties of a-GeSe$_2$ films deposited at different angles (0°–80°). The indirect-optical bandgap energy (2.18 eV) was found to be independent of angle of incidence. The spectral response of refractive index and extinction coefficient has been determined in the wavelength range of 0.6–1 μm using the transmission spectra. Refractive index decreases with the increase in angle of incidence. The value of refractive index was observed to be 2.28 for 0° and 2.00 for 80° films at 0.646 μm. An increase in bandgap was also observed on exposure to the UV light for ~120 min. The change in bandgap became more significant with the increase in angle of incidence (~ 2.3% for 0° and ~10.6% for 80°). The temperature dependence of conductivity along with time dependence and spectral response of photocurrent has also been investigated.

P. Bhardwaj (✉) · R. M. Mehra
Department of Electronic Science, University of Delhi
South Campus, Benito Juarez Road, New Delhi 110021,
India
e-mail: priyam75@yahoo.com

P. K. Shishodia
Department of Physics & Electronics, Zakir Hussain
College (University of Delhi), New Delhi 110002, India

Introduction

Chalcogenide glasses have attracted a great deal of interest since the past two decades. Due to the photoinduced transformations thin films of amorphous chalcogenide glasses have been a subject of intensive investigations. Detailed studies have been reported on photoinduced structural transformations in these films [1–4]. Besides it has also been shown that the columnar structure contributes to a great extent in changing the film properties with respect to those of the corresponding bulk material [5]. These differences are more pronounced in obliquely deposited films [6] which can be reasonably explained by an inclination of the columns and increasing of the void volume in samples prepared at high vapour incidence angles. The occurrence of photoinduced effects is facilitated by flexible or deformable structural network in amorphous semiconductors. Here, we report a systematic study of effect of oblique deposition and light induced changes in the optical and electrical properties of typical GeSe$_2$ films deposited at different angles by vacuum evaporation technique. A comprehensive study on the spectral dependence of optical parameters (Bandgap, Refractive index and Extinction coefficient) is essential to precisely model the spectral response of optoelectronic devices. The electrical properties have been measured to elucidate the conduction mechanism of the films.

Experimental

The normal and oblique films of GeSe$_2$ were prepared by vacuum evaporation of the source material. The oblique films were deposited at 20°, 40°, 60°and 80°, this being the angle between the normal to the substrate and direction of incidence of the evaporated atoms. Glass slides (Corning 7059) were used as the substrate for depositing the films. The evaporation was carried out on the substrates at room temperature in a vacuum of about $1*10^{-6}$ Torr from a molybdenum boat heater. A surface profiler (DekTek 3) was used to measure the thickness of the films. The films were having thickness of the order of 1 μm.

The optical transmission measurements were performed on thin films using UV–VIS spectrophotometer (Shimadzu 1240). The films were illuminated with 80 watt Mercury vapor lamp with quartz envelope (λ ~ 250 to 350 nm) for ~120 min.

Conductivity measurements were done on samples by depositing aluminium contacts on the films in a coplanar configuration with a gap spacing of ~1 mm.

Measurements were carried out under a vacuum of better than 10^{-3} Torr. The temperature dependence of conductivity was performed in the range of 300–500 K. The temperature of the films was varied by inserting heater into the cryostat and was measured using Chromel Alumel thermocouple. A constant dc voltage, from a highly stabilized power supply was applied across the sample and the current was measured by a Keithly 610C electrometer.

Photocurrent and light soaking measurements were performed using a tungsten halogen lamp (100 mW/cm^2). The cryostat has a window facing films to let the light fall on it. Different coloured filters were used to measure the spectral response of photocurrent.

Results and discussion

The X-ray diffractograms of the films were obtained using a Phillips–Holland diffractometer (model PW 1130/00) with Bragg-Brenton arrangement in which the samples were mounted in the centre of diffractometer. The absence of any sharp peak in the diffractograms confirmed the amorphous nature of the films.

The bandgap, of the films was estimated using Tauc's relation

$$\alpha = (B/\eta v)\ (\eta v - \mathrm{E}_{o\pi\tau})^n$$

where B is a constant which is a measure of disorder, E_{opt} is the optical bandgap energy, hv is the photon energy and n depends on electronic transitions in k-space and takes the value ½ for direct and 2 for indirect bandgap.

Optical parameters were calculated using the transmission spectra. Refractive index and extinction coefficients have been calculated using the method suggested by Swanepoel [7–9].

Optical properties

Effect of oblique deposition

Figure 1 shows a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$). The optical band gap can be estimated by extrapolating the linear portion of the curve to x-axis. E_{opt} is found to be 2.18 eV for normally and obliquely deposited films. Figures 2 and 3 show the spectral response of refractive index (n) and extinction coefficient (k) for the films deposited at normal and oblique incidence. The refractive index of the films is found to obey the normal dispersive law and it decreases with the increase in angle of incidence. Similar trend has been observed in case of extinction coefficient. This change in refractive index and extinction coefficient of normal and oblique films may be attributed to the incoherent volume scattering and residual scattering losses originating from the lower density columnar microstructure in oblique films. When the substrate is held at an angle to the direction of evaporation, the deposited atoms create a shadow (or a void) in their vicinity and the atoms get deposited in a columnar way. Due to presence of voids, the density of materials is less in obliquely deposited films as compared to the normally deposited films, which results in a decrease in refractive index and extinction coefficient. Various research groups have reported the existence of columnar

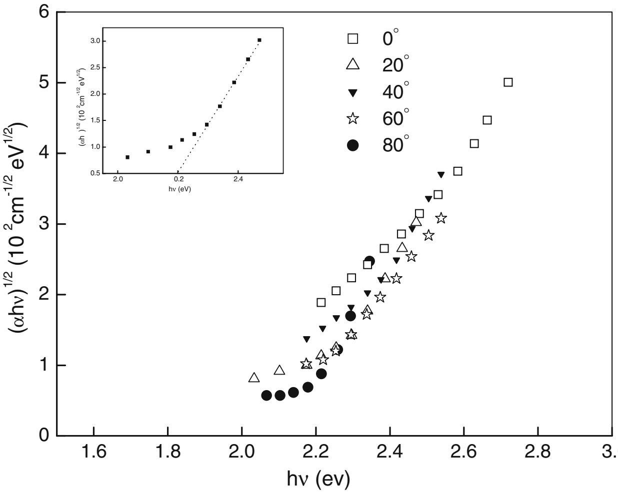

Fig. 1 The optical band gap of normal (0°) and oblique (20°, 40°, 60° and 80°) GeSe$_2$ films

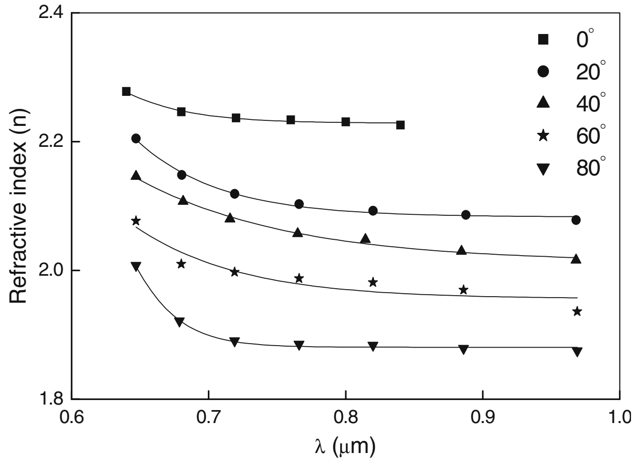

Fig. 2 Refractive index as a function of wavelength for normal (0°) and oblique (20°, 40° , 60° and 80°) $GeSe_2$ films

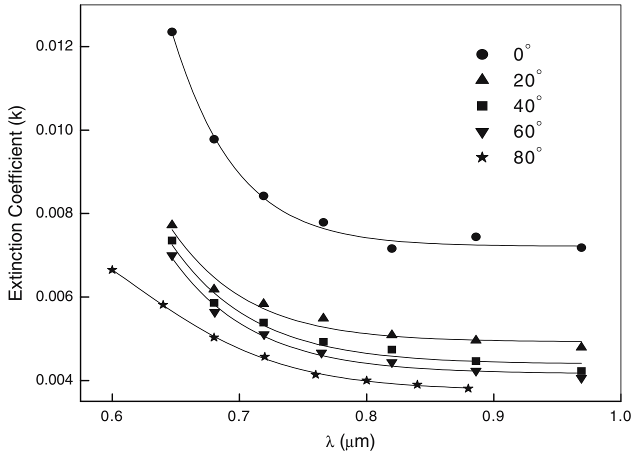

Fig. 3 Extinction Coefficient as a function of wavelength for normal (0°) and oblique (20°, 40°, 60° and 80°) $GeSe_2$ films

structure and low density of atoms with many voids in obliquely deposited films [10, 11]

Photoinduced effect

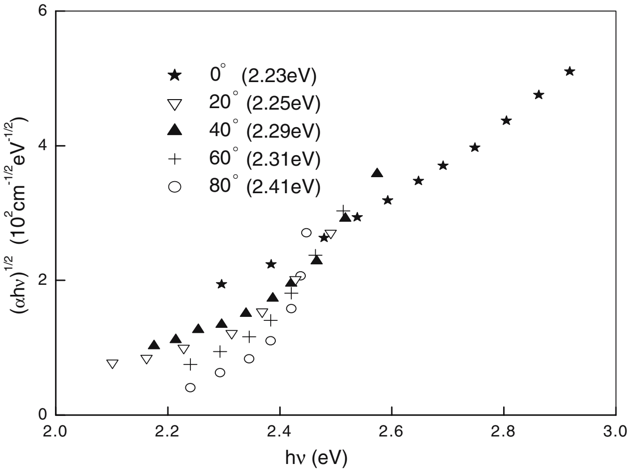

Fig. 4 The optical band gap of exposed normal (0°) and oblique (20°, 40°, 60° and 80°) $GeSe_2$ films

Figure 4 shows the change in the bandgap of the films on exposure to UV-light. The films were exposed to UV-light for 2 h. An increase in the bandgap (Photobleaching) and decrease in thickness (~8–9% in 80° films) i.e., Photo Volume contraction (PVC) has been observed. These changes are in agreement with the earlier reported results [4]. The structural changes, on the other hand, accompany the change in optical constants besides the change in bandgap and hence these effects can be useful for devices, such as optical memory applications. Exposure of $GeSe_2$ films (both normal and oblique films) results in a decrease in their refractive indices, the results of which are summarized in Fig. 5. The changes in extinction coefficient (Fig. 6) also indicate similar trends.

As is evident from the figures, the changes in the optical parameters like refractive index extinction coefficient and band gap in the obliquely deposited films are more significant as compared to those in normally deposited films and become more prominent as the angle of incidence is increased. Several models for the mechanism of photoinduced transformations have been proposed in literature. According to these models the factors responsible for these transformations are the changes in the atomic (chalcogen) positions due to prolonged illumination [12], bond breaking or bond alternation between the atoms [13] and a repulsion and slip motion of structural layers due to negative charging [14].

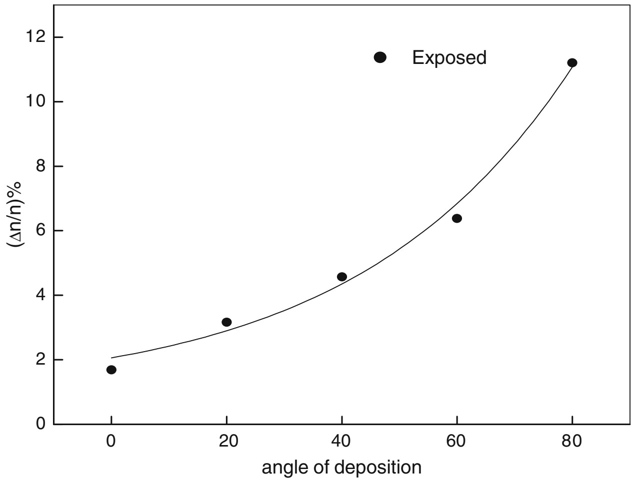

Fig. 5 % Change in refractive index with angle of deposition on illumination for $GeSe_2$ films

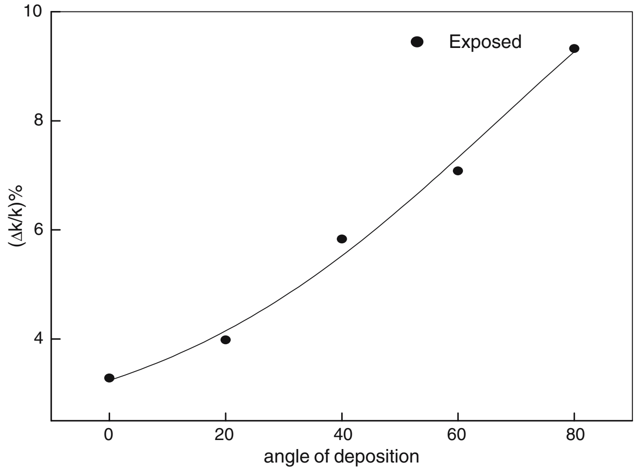

Fig. 6 % Change in extinction coefficient with angle of deposition on illumination for $GeSe_2$ films

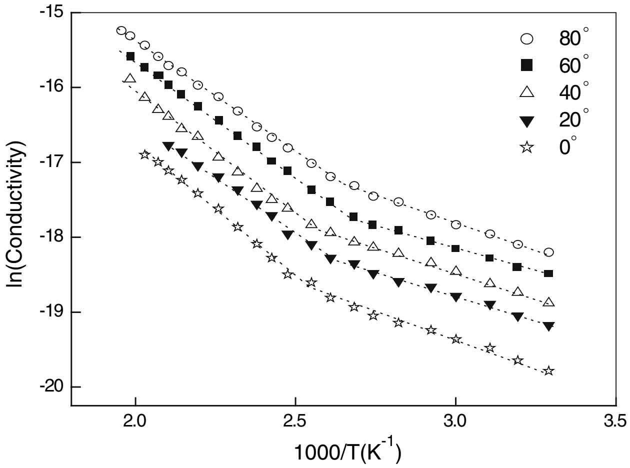

Fig. 7 Temperature dependence of dark conductivity (DC) for films deposited at different angles of incidence for $GeSe_2$ films

The observed photo-optical effects however can be explained in terms of the “repulsive layer model proposed by Shimakawa et al. [15]. This model can be applied to $As_2Se\ (S)_3$ systems, because these systems show Photo Volume Expansion (PVE) and Photodarkening (PD) with illumination. As the $GeSe_2$ system shows Photo Volume Contraction (PVC) and Photo bleaching (PB) with illumination in contrast with As-based systems, the model cannot be directly applied to Ge-based glasses. Shimakawa et al. have explained the changes in Ge-based films on the basis of the bond angle disorder. The value of B in the Tauc plot, is the measure of ‘‘disorder’’ (random in nature gives smaller value of B) [16]. The observed values of B in the present case ($B = 1.5 \times 10^3$ cm^{-1}eV^{-1} for 0° film, 1.04×10^3 cm^{-1}eV^{-1}for 20° film, 1.01×10^3 cm^{-1} eV^{-1} for 40° film, 9.27×10^2 cm^{-1}eV^{-1}for 60° film and 8.58×10^2 cm^{-1}eV^{-1}for 80° film) suggests that there is a large extent of bond angle disorder (short-range order) in these systems. Bond angle disorder increases particularly for obliquely deposited Ge-based chalcogenides, which can be due to large structural constraints of this system [17]. Unlike As-based chalcogenides, a change in bond angle disorder may dominate photo-structural changes and an interaction between layers may not be important.

Electrical properties

Effect of oblique deposition

Figure 7 shows the temperature dependence of the dc dark conductivity, for the samples of a-$GeSe_2$. The dc electrical conductivity can be expressed by the relation

$$\sigma_{DC} = \sigma_O \exp(\frac{-E_a}{kT})$$

where σ_0 is the pre exponential factor, E_a is the activation energy for electrical conduction, k is the Boltzmann constant and T is temperature. The plot of $\log\sigma$ vs $1{,}000/T$ is found to have a kink at temperatures greater than ≈370 K. The temperature (T_k) at which the kink in the conductivity occurs is between 370 K and 410 K for different angles of deposition. Table 1 shows the pre-exponential factor and activation energy in the two temperature regimes (above and below T_k). The calculated values of activation energy and pre-exponential factor in the high temperature region suggest that the conduction is due to thermally assisted tunneling of charge carriers in localized states present in the band tails [18]. Besides this there also exists a correlation between the activation energy and pre-exponential factor i.e., the pre-exponential factor decreases with the decrease in activation energy. This correlation is referred to as the Meyer–Neldel rule [19]. This type of variation in activation energy with pre-exponential factor indicates the movement of

Table 1 The activation energy (E_a) for dc conductivity in the two temperature regimes (above and below T_k) for $GeSe_2$ films deposited at different angles of incidence

Type of film	$T > T_k$		$T < T_k$	
	σ	E_a (eV)	σ	E_a (eV)
$GeSe_2$-0°	$9.4*10^{-5}$	0.33	$3.47*10^{-7}$	0.132
$GeSe_2$-20°	$4.1*10^{-5}$	0.29	$2.56*10^{-7}$	0.123
$GeSe_2$-40°	$3.15*10^{-5}$	0.276	$1.36*10^{-7}$	0.119
$GeSe_2$-60°	$2.19*10^{-5}$	0.249	$9.8*10^{-8}$	0.108
$GeSe_2$-80°	$2.1*10^{-5}$	0.248	$9.1*10^{-8}$	0.106

fermi-level through an exponential band tail density of states distribution as the temperature changes [20]. A decrease in activation energy with increase in angle of incidence in all the types of films indicates the movement of fermi level towards the valence band edge.

Photoinduced effect

Figure 8 shows the variation of I_P–I_C with time where I_P is photocurrent at any instant and I_C is the value of stable photocurrent after long exposure. In the present case the photocurrent becomes constant after ~1 h. This may be due to the creation of defects as a consequence of formation of self-trapped excitons in the form of an intimate valence alternation pair in the case of amorphous chalcogenides. Following this, bond switching results in the formation of well-separated metastable charged defects [21]. It is considered that these defects are responsible for the reported decay of the photocurrent under illumination.

A higher photocurrent degradation rate has been observed at an early stage of light soaking as defect generation rate is higher initially but as time increases the degradation rate becomes lower and finally photocurrent becomes constant. The decrease in the rate of degradation with light soaking could be understood in terms of the difference between light induced defect creation and annihilation. Since the annihilation component is directly dependent on the density of metastable defects, the density of defects increases more quickly initially.

Figure 9 shows the spectral response of photocurrent for films deposited at different angles. The photocurrent was found to increase with increase in deposition angle.

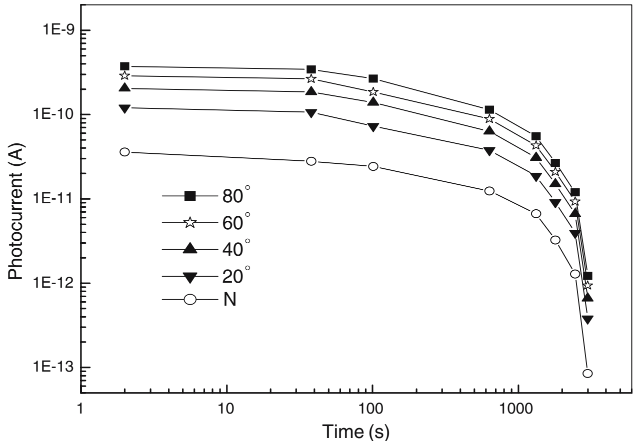

Fig. 8 Photocurrent in normal (0°) and oblique (20°, 40°, 60° and 80°) $GeSe_2$ films as a function of exposure time

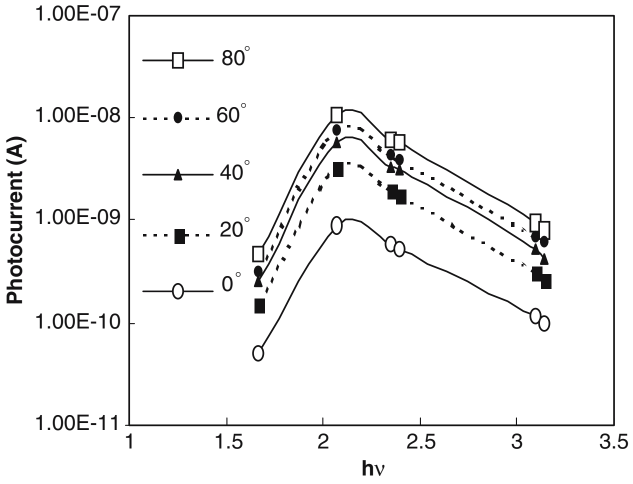

Fig. 9 Spectral dependence of photocurrent in normal (0°) and oblique (20°, 40°, 60° and 80°) $GeSe_2$ films (without light soaking)

Figure 10 shows the photocurrent spectra in a-$GeSe_2$ after light soaking for 1 h. At room temperature light soaking gives rise to decrease in the photocurrent over the entire spectral range investigated. The decay of photocurrent in chalcogenide glasses due to light soaking can be understood on the basis of charged defect model originally proposed by Mott [22]. According to the charged defect model, D^- centres can act as recombination (or trapping) centres for photoexcited holes due to Columbic attractive forces, and accordingly the photoconductivity decreases with light soaking at room temperature in a-$GeSe_2$ because new D^- centres (one of the Light Induced Metastable Defects (LIMD)) are created by illumination. Shimakawa et al. have also proposed a model of similar type [23]. The decrease in photocurrent

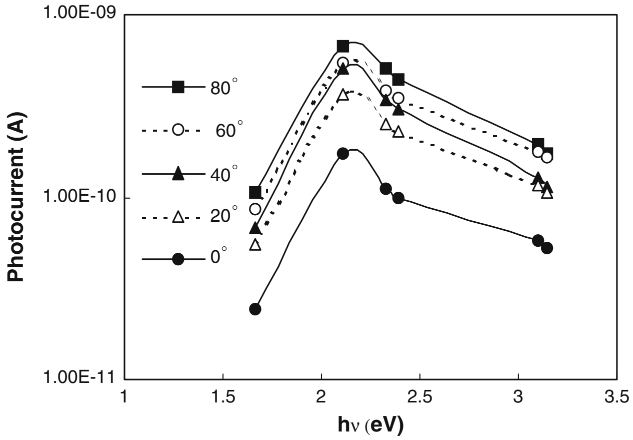

Fig. 10 Spectral dependence of photocurrent in normal (0°) and oblique (20°, 40°, 60° and 80°) $GeSe_2$ films (with light soaking)

is more in case of oblique films, which can be due to the photostructural changes induced by the absorbed light. The photobleaching may accompany the creation of new localized states that are close pairs of the charged D^+ and D^- centres. Thus the recombination of photoexcited holes will be more in oblique films then in normal incidence films, as photoinduced changes are significant in case of oblique films.

Conclusion

Detailed investigation of optical constants and electrical conductivity of $GeSe_2$ films deposited at normal and oblique incidence has been carried out. A study of photoinduced changes on the thickness, optical constants (Bandgap, refractive index, extinction coefficient) and electrical properties of a-$GeSe_2$ films deposited at different angles of incidence has also been performed. The results of the present study show that the obliquely deposited films have larger conductivity, lower refractive index and extinction coefficient as compared to normal films. This has been explained on the basis of changes in structure due to oblique deposition. It has been observed that the illumination with ultraviolet light is found to significantly increase the bandgap, refractive index and extinction coefficient and decrease the thickness of the films. However, these changes become more pronounced as the deposition angle is increased. The more prominent changes observed in obliquely deposited films have been explained on the basis of the existence of columnar structure and the presence of voids facilitating easier motion of layers in these films.

References

1. Shimakawa K, Kolobov A, Elliot SR (1995) Adv Phys 44:475
2. KTanaka (1998) Phys Rev B 57:5163
3. Shimakawa K, oshida NY, Ganjoo A, Kuzukawa Y, Singh J (1998) Philos Mag Lett 77:153
4. Kuzukawa Y, Ganjoo A, Shimakawa K (1998) J Non-Cryst Solids 227–230:715
5. Macleod HA (1986) J Vac Sci Technol A4:418
6. Leamy HL, Gilmer GH, Dirks AG (1980) Curr Top Mater Sci 6:1
7. Manifacier JC, Gassiot J, Fillard JP (1976) J Phys E 9:1002
8. Swanepoel R (1983) J Phys E 16:1214
9. Swanepoel R (1984) J Phys E 17:896
10. Rajagopalan S, Harshvardhan KS, Malhotra LK, Chopra KL (1982) J Non- Cryst Solids 50:29
11. Pandaya DK, Rastogi AC, Chopra KL (1975) J Appl Phys 46:2966
12. Ke Tanaka (1990) Rev Solid St Sci 4:641
13. Kolobov AV, Oyanagi H, Tanaka K (1997) Phys Rev B 55:726
14. Shimakawa K, Yoshida N, Ganjoo A, Kuzukawa Y, Singh J (1998) Philos Mag Lett 77:153
15. Shimakawa K, Yoshida N, Ashtosh Ganjoo, Kuzukawa Y, Singh J (1998) Philos Mag Lett 77:153
16. Mott NF, Davis EA (1979) Electronic processes in non-crystalline solids, 2nd edn. Claredon Press, Oxford, p 272
17. Phillips JC (1981) J Non-Cryst Solids 43:37
18. Mott NF, Davis EA (1971) Electronic processes in non-crystalline materials. Oxford Claredon Press
19. Meyer W, Neldel H (1937) Zh Tekh Fiz 12:588
20. Roberts GG, Apsley N, Munn RW (1980) Phys Rev 60:61
21. Shimakawa K, et al (1991) J Non-Cryst Solids 137–138:1017
22. Biegelsen DK, Street RA (1980) Phys Rev Lett 44:803
23. Shimakawa K (1986) Phys Rev B 34:8703