



Optical and structural properties of Ge–Sb–Se thin films fabricated by sputtering and thermal evaporation

Yu Chen^a, Xiang Shen^{a,*}, Rongping Wang^b, Guoxiang Wang^a, Shixun Dai^a, Tiefeng Xu^{a,*}, Qiuhua Nie^a

^a Laboratory of Infrared Materials and Devices, Ningbo University, Ningbo 315211, China

^b Laser Physics Centre, Research School of Physics and Engineering, Australian National University, Canberra, ACT 0200, Australia

ARTICLE INFO

Article history:

Received 31 May 2012

Received in revised form 4 September 2012

Accepted 10 September 2012

Available online 18 September 2012

Keywords:

Chalcogenide glass

Thin films

Radio-frequency magnetron sputtering

Thermal evaporation

Local structure

ABSTRACT

We deposited $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ chalcogenide films using either thermal evaporation or radio-frequency magnetron sputtering techniques, and then measured their structural and optical properties using various diagnosis tools. The refractive indices of the films were obtained from the transmission spectra based on Swanepoel method, and the optical band gaps were derived from optical absorption spectra using the Tauc plot. Raman and X-ray photoelectron spectra (XPS) were measured and decomposed into several peaks that correspond to the different structural units, and then the evolution of the relative concentrations of the structural units was investigated in order to build up the correlation between the structure and optical properties of the films. It was found that, the films generally possess a large number of $\text{Ge}_2\text{Se}_6/2$, $\text{Sb}_2\text{Se}_4/2$ units and Se–Se bonds, and therefore are relatively higher defective compared with their bulk counterpart. This together with the modification of the chemical compositions results in a higher refractive index as well as a smaller optical band gap in the films. Thermal annealing of the deposited films could convert the optical and structure properties of the films close to those of bulk glass.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Chalcogenide glasses have been studied for decades owing to their unique photosensitivity, wide transparency window, high linear refractive index, and tunable material properties through compositional tailoring [1–3]. Being photonics materials, chalcogenide glasses are also very promising due to their striking ultrafast response and large third-order nonlinearity. Whilst the optical properties of some binary chalcogenide compositions such as $\text{As}_x\text{S}_{1-x}$ and $\text{As}_x\text{Se}_{1-x}$ have been well studied [4–6] and improved processing methods have been applied to As_2S_3 films to produce waveguide devices with high performance [7–9], recent results have shown that the ternary or quaternary compounds could have better properties for the application in photonics [10]. This has been demonstrated in Ge–As–Se-based waveguide devices [11,12]. However, elemental arsenic is toxic and this makes it environmentally unacceptable as a constituent both during manufacturing and for photonic devices that are likely to be discarded after use [13], such as sensor chips. As a result alternative network formers are essential.

One interesting opportunity is to substitute antimony for arsenic. Compared with As, Sb has a larger polarizability and this should lead to large linear and nonlinear refractive indices parameters that are important for photonics. Whilst the glass forming re-

gion of Ge–Sb–Se glasses has been studied, in general, the ternary glasses such as Ge–Sb–Se have attracted much less attention than the binary compositions and, therefore, few of their optical properties are known especially in the Ge–Sb–Se films. Understanding structure and optical properties in the films is essential since most of the devices need to be integrated in the formation of the films.

In principle, thin chalcogenide films can be created by either thermal evaporation (TE) [14], RF-sputtering (RF) [4], pulsed laser deposition (PLD) [15], sol–gel process (SC) [16], or chemical vapor deposition (CVD) [17]. While some of the recent works [18,19] investigated the effect of the composition and heat treatment conditions on the optical and electrical properties of the glasses, few attention were paid to the different structure and optical properties of Ge–Sb–Se films created by different deposition methods. Certainly this is important to improve the film deposition technique and is prerequisite to fabricate optical waveguide with excellent performance. We therefore deposited $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ thin films deposited by TE and RF techniques and investigated their structure and optical properties. The reasons we choose these two deposition methods are due to their relative simplicity, easy control and ability to deposit high quality films over large areas.

2. Experiments

Homogeneous $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ glasses were obtained by conventional melt-quenching technique using high-purity Ge, Sb, Se (all of 5 N) as raw materials. All the elements were weighted in appropriate amounts, placed in quartz ampoules,

* Corresponding authors.

E-mail addresses: shenxiang@nbu.edu.cn (X. Shen), xutiefeng@nbu.edu.cn (T. Xu).

evacuated to 10^{-3} Pa and finally sealed. The quartz ampoules containing the mixtures were heated at 900 °C for 12 h in rocking furnaces to ensure the homogenization. Then, the ampoules were quenched in water, swiftly moved to a preheated furnace to anneal at 10 °C below T_g for 4 h to minimize inner tension induced by a quenching step. The bulk sputtering target was obtained from glass rods in the form of cylinders with 50 mm in diameter and 3 mm in thickness.

The $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ films were deposited onto glass slide substrates. Before the substrates were loaded into the chambers, they were cleaned in an ultrasonic bath, rinsed in alcohol, dried with dry air. The chamber was evacuated down to approximately 1×10^{-4} Pa. Prior to the deposition, the rotated substrates were irradiated by an Ar^+ beam with an energy of 20 eV for 5 min to improve adhesion of the films to the substrates. During thermal evaporation deposition, the current on a tantalum boat containing the powdered target glass was monitored, until the evaporation rate reached 2 nm/s. The RF sputtering films were deposited at an operating argon pressure of 0.2–3 Pa and a RF power of 20 W. Thermal annealing was performed at 290 °C (below the glass transition temperature) for 2 h at a base pressure of 2×10^{-4} Pa.

The atomic ratios of the target and films were analyzed by electron dispersive spectrometry (EDS) equipped in a Tescan VEGA 3SBH scanning electron microscope (SEM). The thickness of the film was examined by a surface profiler (Veeco Dektak 150). The transmission spectra of the studied films were measured using the spectrophotometer (Perkin Elmer Lambda 950), and then the refractive indices were calculated using Swanepoel method. The refractive index of the bulk glass was measured by a prism coupler (SAIRON SPA4000). XPS spectra of these bulk glasses were collected using an AXIS ULTRADLD system under a vacuum of 10^{-7} Pa, using monochromatic Al K_{α} X-rays (1486.6 eV) at a power of 450 W as the excitation source. An energy increment of 0.05 eV was used for recording the core level spectra. Carbon was selected as the internal reference and the binding energies of the C 1s line were referenced at 284.8 eV. Raman spectra of the bulk glass and films were recorded using a confocal microscopic Raman spectrometer (Renishaw inVia) with a 785 nm exciting source at 0.25 mW. In order to avoid any damage induced by laser irradiation, the measurements were performed within 10 s at 10 accumulations.

3. Results

The SEM images of cross-sectioned Ge–Sb–Se sputtered and TE films are shown in Fig. 1. The thicknesses of the as-deposited TE and RF film derived from cross-sectioned images is 2.04 and 1.12 μm , respectively, which is in excellent agreement with the surface profiler measurements that show a respective thickness of 2.0198 μm and 1.1079 μm . It is also noted that both the prepared layers are smooth without any defects and pores. Moreover, the presence of column-like structure that is typical for sputtering process was almost completely depressed by the selection of appropriate experimental conditions [20]. On the other hand, the chemical composition of the bulk glass, TE and RF-sputtered films was measured and the results were summarized in Table 1. Compared with the bulk glass, the composition of the TE film showed a slight variation in the Ge/Sb ratio while the RF sputtered film presented a composition identical to that of the parent bulk glass.

The UV–Vis–NIR transmission spectra of the as-deposited and annealed films are presented in Fig. 2. A periodic variation as a function of wavelength in the transmission spectra is observed, which is due to the interference between multiple reflections at the two surfaces of the film, indicating that all the films are homogeneous in terms of the thickness. On the other hand, it is evident from Fig. 2 that the position of the absorption edge of films shifts to shorter wavelength due to thermal annealing.

The refractive index (RI) and thickness of films was extracted from their transmission spectra, as was suggested by Swanepoel [21]. According to Swanepoel's method of creating the upper and lower envelopes of the transmission spectrum with interference fringes, the refractive index was calculated by the following equation.

$$n = \sqrt{N + \sqrt{(N^2 - n_s^2)}} \quad (1)$$

where

$$N = 2n_s \times (T_M - T_m)/(T_M T_m) + (n_s^2 + 1)/2 \quad (2)$$

Here T_M and T_m are the transmission maximum and the corresponding minimum at a certain wavelength. The necessary value of the refractive index of the substrate, n_s , obtained from the transmission of substrate at the wavelengths (T_s), using the equation:

$$n_s = 1/T_s + (1/T_s^2 - 1)^{1/2} \quad (3)$$

In order to compare the results of the films with that of bulk glass, the dispersion curve of refractive index for the bulk glass was measured using a prism coupler, and the refractive indices value of films and bulk glass was further fitted using the Cauchy dispersion relationship of $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$, where n is refractive index, A , B and C are the fitting constants, and λ is wavelength. All the result was shown in Fig. 3, from which it is clear that the index of both films is higher than that of the bulk glass and that the index of the TE film is higher than that of the RF film. On the other hand, compared with that of as-grown films, there is a decrease in refractive indices of the annealed films. Considering the stoichiometric and thickness modifications of the films were not apparent during annealing process, the slight decrease of refractive index (RI) during thermal annealing processes could be due to the rearrangement of the chemical bonds that has been demonstrated by Kincl and Tichý [22].

The band gap of the films was derived from the Tauc plot as shown in Fig. 4, the optical gap can be derived from the intersection of linear fitting line with the energy axis. The obtained optical gap of RF film is lower than that of the TE film. However, both of them are very close to the bandgap of the bulk glass at 1.62 eV [23]. It is also noted that thermal annealing can blue-shift the bandgap in both films.

For Se-rich Ge–Sb–Se ternary system, a well-accepted structural model involves tetrahedral $\text{GeSe}_{4/2}$ and pyramidal $\text{SbSe}_{3/2}$ units cross-linked by Se-chain fragments in a stochastic fashion. However, Se-chain fragments could be consumed out in Se-poor glasses, and this could induce homopolar Ge–Ge, Sb–Sb or Ge–Sb bonds. In order to unravel the structural origins of the change of the physical properties, we measured Raman spectra of the bulk glass and films as shown in main panel of Fig. 5. A dominant feature, centered around 200 cm^{-1} , is formed evidently by overlapping of other three bands at 190, 202 and 218 cm^{-1} , which correspond to the E_1 mode of $\text{SbSe}_{3/2}$ pyramids (PYR), A_1 vibrations of the corner-sharing (CS) $\text{GeSe}_{4/2}$ tetrahedra and A_1^0 breathing vibration of edge-sharing (ES) $\text{Ge}_2\text{Se}_2\text{Se}_{4/2}$ bi-tetrahedral respectively [24–26]. Another band located in the high wavenumber region of 250–300 cm^{-1} with low-intensity may be attributed to several vibration modes, including the A_1 modes of vibration of the homopolar Se–Se bond (in dimers) and the Ge–Ge bonds in modified $\text{Ge–Ge}_m\text{Se}_{4-m}$ ($m = 1, 2, 3, 4$) structural unit [27,28]. In addition, an obvious shoulder at 170 cm^{-1} is due to the stretching vibration modes of the Ge–Ge and Sb–Sb bonds in ethane-like (ETH) structure [24,27]. The assignments and their origins are summarized in Table 2 and a typical deconvolution of Raman spectrum based on these assignments is presented in an inset of Fig. 5. The ratio of the integrated area of each peak to that of total spectrum is shown in Fig. 6.

Furthermore, in order to clarify the discrepancies between the structure of bulk glass and that of thin films, we measured core-level XPS spectra and investigated the local chemical surroundings. Figs. 7 and 8 show Ge 3d, Sb 4d and Se 3d spectra for the bulk glass, fresh and annealed films, and their deconvolution, respectively. Ge 3d spectra can be well fitted using two pairs of the peaks that correspond to two different environments [29]. The major pair positioned on the high-energy side is associated with $\text{GeSe}_{4/2}$ tetrahedra, while the minor pair at lower energy could be assigned to the deformed tetrahedral where one or two of the chalcogen atoms could be substituted by Ge or Sb atoms [30]. On the other

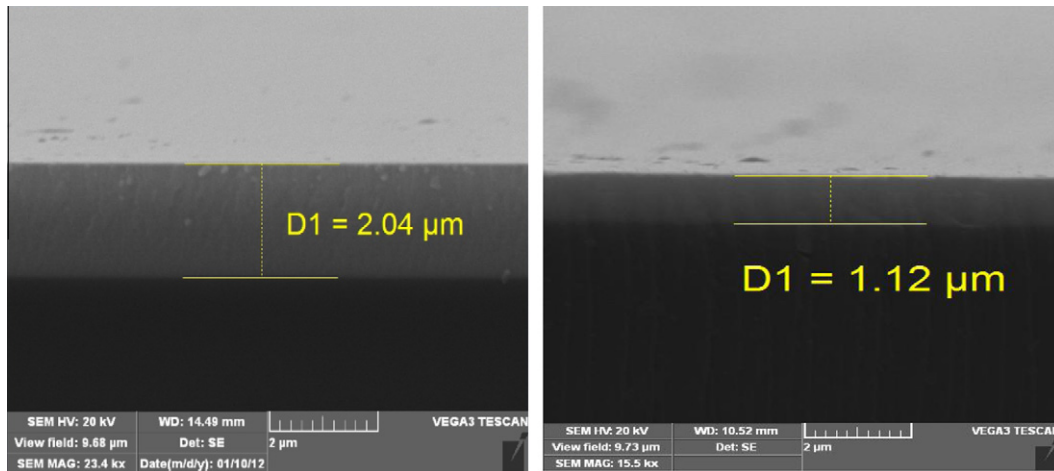


Fig. 1. Scanning electron microscopic images of cross-sectioned Ge-Sb-Se TE (left) and RF-sputtered (right) films.

Table 1

Chemical composition (± 1 at.%) of Ge-Sb-Se Bulk, TE and RF-sputtered films.

Elements	Bulk (at.%)	TE films (at.%)	RF-Sputtered films (at.%)
Ge	28.67	25.86	27.55
Sb	12.77	15.49	12.91
Se	58.56	58.65	59.54

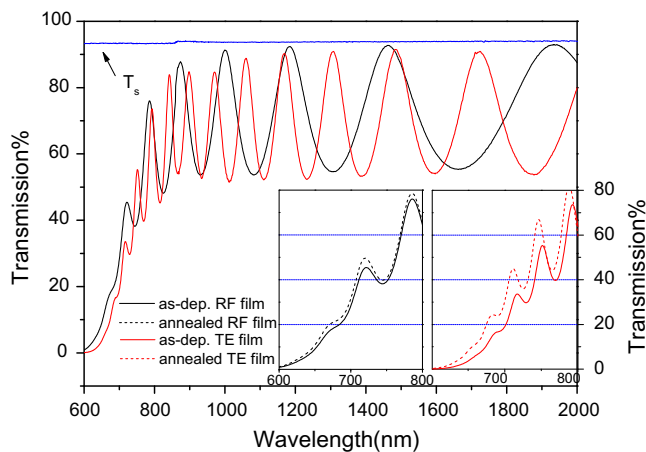


Fig. 2. Optical transmission spectra of the as-grown TE and RF-sputtered films. The insert figures are the enlarged transmission edges of as-deposited (solid line) and annealed (dot lines) RF-sputtered and TE films, respectively.

hand, the primary component ($4d_{5/2}$) at $33.45(\pm 0.05)$ eV in Sb 4d spectra is due to Se-Sb-(Se)₂ pyramidal structure, while another doublet at lower energy is ascribed to the deformed pyramidal that one Se atom is replaced by Ge or Sb. All the fitting parameters including the binding energy (BE), full width of half maximum (fwhm), and the ratio of the integrated area of the individual peak to that of the total spectrum (R) are summarized in Table 3.

4. Discussion

Let us start from the chemical compositions of the bulk and the films. As shown in Table 1, TE film has a 3% higher concentration of Sb and a 3% lower of Ge while the RF film keep a good stoichiometry compared with the bulk glasses. This could be an important factor to account for the difference in the physical properties be-

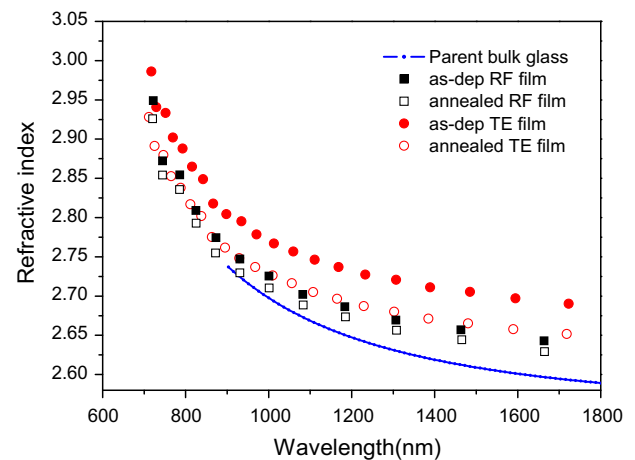


Fig. 3. Spectral dependences of refractive index of the bulk glass, TE and RF-sputtered films.

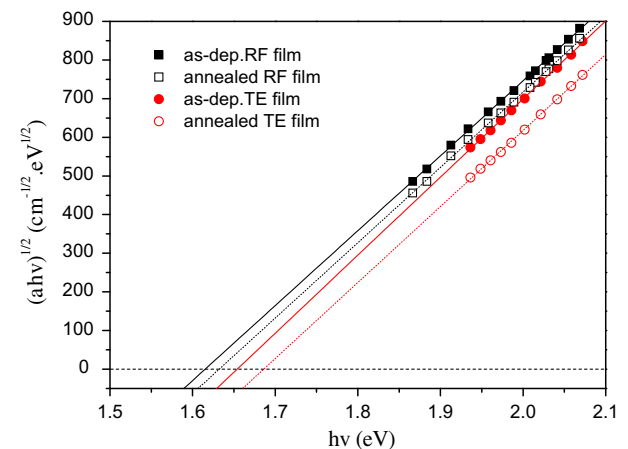


Fig. 4. The determination of the optical gaps using Tauc's plots of the strong absorption data for the TE and RF-sputtered films.

tween the films and bulk glass. Recent investigation has shown that the refractive index and density increases with increasing Sb and decreasing Ge concentrations in Ge-Sb-Se bulk glass [31]. This is in consistent with our present results where the TE film has a

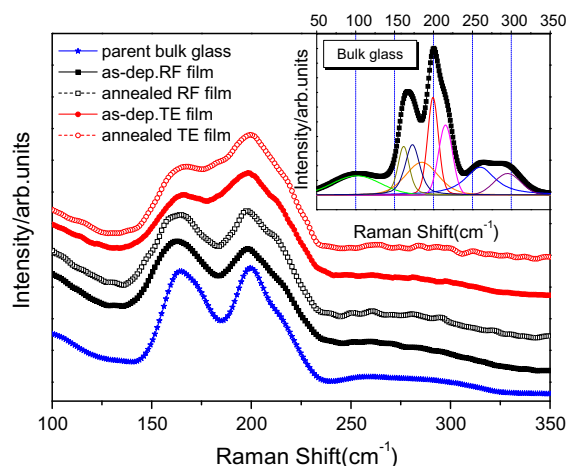


Fig. 5. Micro-Raman spectra of bulk glass and TE and RF films without the application of Bose-Einstein correction. The typical deconvolution of Raman spectrum is shown as an inset.

large refractive index compared with the bulk due to the difference in their chemical compositions. However, it should be noted that the different structure could also contribute to the difference in the physical properties between the films and the bulk, which will be discussed later.

While the composition in the RF film is almost identical to that in the bulk, it is ideal system to compare their bandgap and thermal annealing behaviors. The band gap in the fresh RF film is at 1.589 eV and shifts to 1.605 eV upon thermal annealing that becomes close to that in the bulk glasses (1.62 eV). This provides clear evidence that thermal annealing is an effective way to accelerate the structure relaxation into more stable bulk-like structure [5,14,32]. The bandgap in the TE film is slightly larger than that in the bulk, and this could be mostly due to the difference in their chemical compositions. Nevertheless, thermal annealing still can slightly blue shift the bandgap as shown in Fig. 4.

In accordance with previous studies [5,14], film deposited directly onto a cold substrate is formed in non-equilibrium conditions and therefore a highly disordered structure compared with the bulk glasses. Appropriate thermal treatment can then be used to convert the film into a more chemically or mechanically optimized structure. As a result, the annealing process leads to the variation in properties, which are more similar to those of the bulk glass, including a blue shift of the band gap in Fig. 4 and a reduction in the refractive index in Fig. 3. The structural origin could be due to the partial removal of homopolar bonds and a corresponding increase in the ES, CS and PYR units in the films [33], and this will be further confirmed from our Raman and XPS data.

Fig. 6 provides clear evidence that, the amount of the relative ratios of Sb–Sb and Ge–Ge in the films could have up to 1%

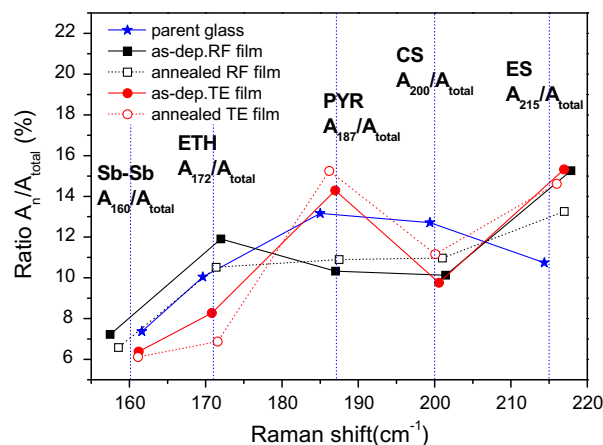


Fig. 6. Variations of mode normalized scattering strengths (A_n/A_{total}) of the different bands in the micro Raman fitted spectrum of bulk glass and films.

difference compared with that in the bulk glass, the concentrations of these structural units indeed decrease upon thermal annealing. However, the contents of PYR, CS and ES structural units are complicated: PYR contents in TE films are larger than that in bulk and RF films, mainly due to the large Sb concentration in the TE films. Most interestingly, CS concentrations in all the films are less while ES concentrations are higher than that in the bulk glass. This implies a direct conversion of the CS into ES species in the tetrahedral backbone of network upon thermal annealing. Such a conversion is reasonable since the formation of ES species is most economical way to consume Se atoms in Se-poor $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ glasses.

The deconvoluted results of XPS spectra in Table 3 gives additional evidence that the concentrations of the homopolar Ge–Ge and Sb–Sb bonds decrease upon thermal annealing. The relative ratio of Sb–Se₃ (PYR) structure is 62% and increases to 65% upon thermal annealing in the RF film, and this is 72% and increases to 74% in the TE film. Such a trend of the change is in excellent agreement with that in Fig. 6, in which however we should emphasize that the relative ratios in both Fig. 6 and Table 3 are not equal to the absolute concentrations, and therefore only reflect the relative change of each structural unit. The relative ratios of Ge–Se₄ structure in the TE films in Table 3 is 90% that is relatively larger compared with that in the RF films and bulk glasses. The reason could be due to the slight oxygen contamination in the TE film. However, Sb or Se related XPS spectra are not affected by the contamination since Ge has the strongest oxidation ability amongst these three elements. The oxidation behavior normally only appears in the surface of the films that happens to be the sensitive limit of XPS method (around 30 nm on the surface) [34], and cannot be observed in Raman spectra as well as physical properties measurements.

Finally, Se–Se bonds were found in all the films and bulk glasses which is in agreement with the previous works [33], and thermal

Table 2

Assignments of some vibrational modes seen in the Raman spectrum of $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$.

Raman shift (cm^{-1})	Assignment	Refs.
160 cm^{-1}	Sb–Sb bonds vibration modes of $[\text{Se}_2\text{Sb–SbSe}_2]$	[26]
170 cm^{-1}	Stretching vibration modes of the Ge–Ge bonds in $[\text{Ge}_2\text{Se}_{6/2}]$ structure	[23]
190 cm^{-1}	E_1 mode of $[\text{SbSe}_{3/2}]$ pyramids	[24,25]
200 cm^{-1}	ν_1 Symmetric stretching mode of $[\text{GeSe}_{4/2}]$ tetrahedra	[23]
215 cm^{-1}	A_1^0 Breathing vibration of edge-sharing (ES) $[\text{Ge}_2\text{Se}_2\text{Se}_{4/2}]$ bi-tetrahedral	[23]
250 cm^{-1}	Se–Se bond	[27]
270 cm^{-1}	Ge–Ge bonds vibration modes of $[\text{Ge–Ge}_m\text{Se}_{4-m}]$ ($m = 1,2,3,4$)	[26]
300 cm^{-1}	F_2 asymmetric vibration modes of $[\text{GeSe}_4]$ tetrahedra	[31]

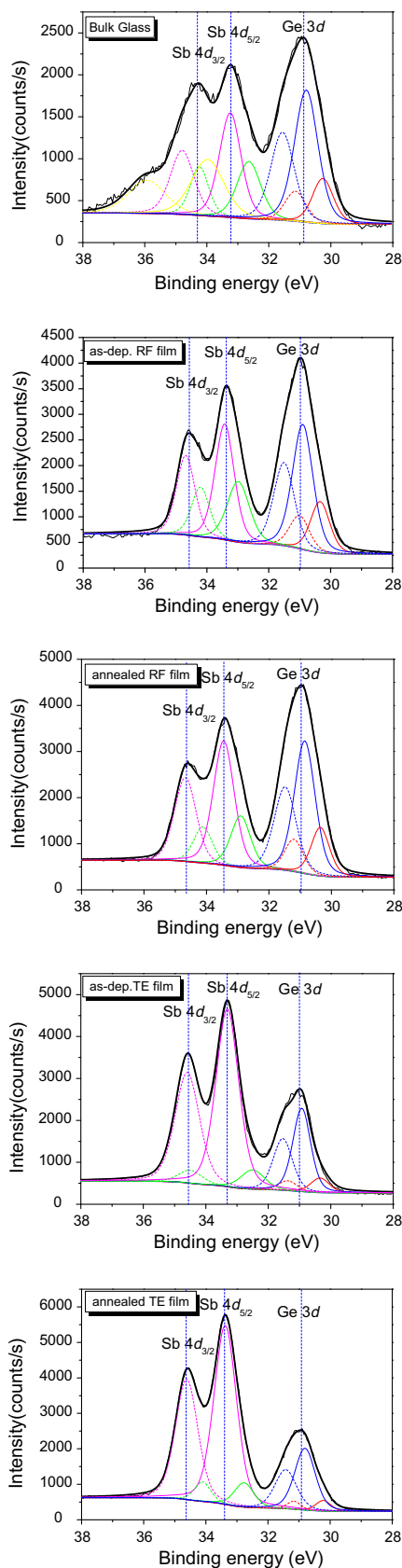


Fig. 7. Deconvolution of Ge 3d and Sb 4d core level spectra for $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ glass and films (thin-experimental spectra, bold-fitted spectra, dash-fitted components).

annealing can reduce the concentrations of Se–Se bonds in the films as shown in Table 3. This also is reflected by increasing

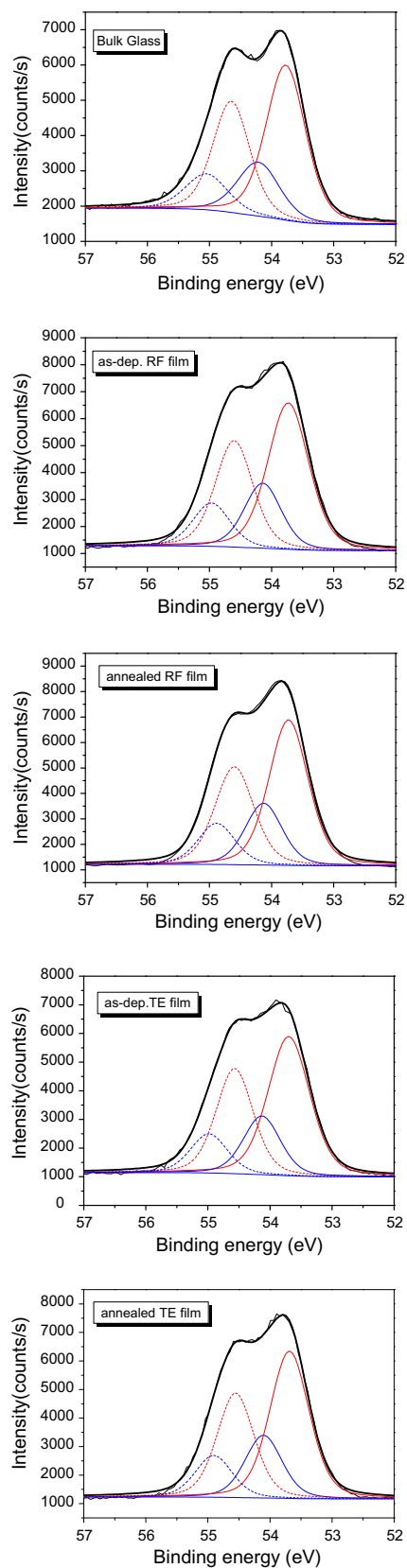


Fig. 8. Deconvolution of Se 3d core level spectra for $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ glass and films.

$\text{GeSe}_{4/2}$ concentrations in as well as Table 3, indicating that the broken Se–Se bonds can be reconnected with Ge, forming stable $\text{GeSe}_{4/2}$ structural units.

Table 3
The decomposed parameters for XPS Ge, Se $3d_{5/2}$ and Sb $4d_{5/2}$ spectra. BE/W/R represents the binding energy (eV), full width of half maximum (eV), and the ratio of the integrated area for different structural units, respectively.

	Ge–Se ₄ BE/W/R (%)	(Ge,Sb)–Ge–Se ₃ BE/W/R (%)	Sb–Se ₃ BE/W/R (%)	(Ge,Sb)–Sb–Se ₂ BE/W/R (%)	(Ge,Sb)–Se–Se BE/W/R (%)	(Ge,Sb)–Se–(Ge,Sb) BE/W/R (%)
Bulk glass	30.79/0.89/77	30.25/0.80/23	33.24/0.83/68	32.64/0.89/32	54.21/0.80/27	53.77/0.79/73
As-dep. RF film	30.90/0.79/73	30.33/0.74/27	33.42/0.73/62	32.98/0.85/38	54.14/0.78/30	53.73/0.78/70
Annealed RF film	30.85/0.79/75	30.35/0.71/25	33.46/0.79/65	32.90/0.81/35	54.13/0.76/28	53.72/0.77/72
As-dep. TE film	30.80/0.78/89	30.22/0.70/11	33.43/0.80/72	32.99/0.89/28	54.13/0.79/28	53.69/0.79/72
Annealed TE film	30.95/0.71/90	30.34/0.70/10	33.38/0.78/74	33.00/0.9/26	54.14/0.78/26	53.68/0.78/74

5. Conclusion

Chalcogenide Ge₂₈Sb₁₂Se₆₀ films with composition close to the glassy target were successfully deposited on glass slides at room temperature by TE and RF-sputtering methods. The deposited layers were further characterized by analyzing their morphology, chemical composition, optical functions, and structure. While the difference in chemical compositions between the bulk glass and the films induces the different physical properties, our detailed structural analysis through Raman and XPS spectra indicated that thermal annealing is indeed an effective way to modify the film structure through a conversion of a pair of corner-shared GeSe_{4/2} tetrahedra into an edge-sharing configuration via bond switching, as well as a reduction in the density of homopolar bonds.

Acknowledgments

This work was financially supported by International Science & Technology Cooperation Program of China (Grant No. 2011DFA12040), the Natural Program on Key Basic Research Project (973 Program) (Grant No. 2012CB722703), the Natural Science Foundation of China (Grant Nos. 61008041 and 60978058), the Natural Science Foundation of Zhejiang Province, China (Grant No. Y1090996), the Research Foundation of Education Department of Zhejiang Province, China (Y200803996), Natural Science Foundation of Ningbo City, China (Grant No. 2011A610092), the program for Innovative Research Team of Ningbo city (Grant No. 2009B21007), Students Science and Technology Innovation Program of Zhejiang Province (No. 2001R405055), the outstanding Dissertation Engagement Foundation of Graduate School of Ningbo University and sponsored by K. C. Wong Magna Fund in Ningbo university.

References

- [1] A. Zakery, S.R. Elliott, Journal of Non-Crystalline Solids 330 (2003) 1.
- [2] B.J. Eggleton, B. Luther-Davies, K. Richardson, Nature Photonics 5 (2011) 141.
- [3] A.B. Seddon, Journal of Non-Crystalline Solids 184 (1995) 44.
- [4] W.C. Tan, M.E. Solmaz, J. Gardner, R. Atkins, C. Madsen, Journal of Applied Physics 107 (2010) 033524.
- [5] R.P. Wang, S.J. Madden, C.J. Zha, A.V. Rode, B. Luther-Davies, Journal of Applied Physics 100 (2006) 063524.

- [6] P. Němec, J. Jedelský, M. Frumar, M. Štábl, Z. Černošek, Thin Solid Films 484 (2005) 140.
- [7] E. Nicoletti, D. Bulla, B. Luther-Davies, M. Gu, Nano Letters 11 (2011) 4218.
- [8] D.Y. Choi, S. Madden, D. Bulla, R. Wang, A. Rode, B. Luther-Davies, Journal of Applied Physics 107 (2010) 053106.
- [9] S.J. Madden, D.Y. Choi, D.A. Bulla, A.V. Rode, B. Luther-Davies, V.G. Ta'eed, M.D. Pelusi, B.J. Eggleton, Optics Express 15 (2007) 14414.
- [10] A. Prasad, C.J. Zha, R.P. Wang, A. Smith, S. Madden, B. Luther-Davies, Optics Express 16 (2008) 2804.
- [11] X. Gai, T. Han, A. Prasad, S. Madden, D.Y. Choi, R. Wang, D. Bulla, B. Luther-Davies, Optics Express 18 (2010) 26635.
- [12] D.Y. Choi, S. Madden, A. Rode, R. Wang, B. Luther-Davies, Applied Physics Letters 91 (2007) 011115.
- [13] T. Gebel, Chemico-Biological Interactions 107 (1997) 131.
- [14] D.A.P. Bulla, R.P. Wang, A. Prasad, A.V. Rode, S.J. Madden, B. Luther-Davies, Applied Physics A: Materials Science and Processing 96 (2009) 615.
- [15] R.K. Pan, H.Z. Tao, H.C. Zang, C.G. Lin, T.J. Zhang, X.J. Zhao, Journal of Non-Crystalline Solids 357 (2011) 2358.
- [16] M. Krbal, T. Wagner, T. Kohoutek, P. Nemec, J. Orava, M. Frumar, Journal of Physics and Chemistry of Solids 68 (2007) 953.
- [17] C.C. Huang, D.W. Hewak, J.V. Badding, Optics Express 12 (2004) 2501.
- [18] E.R. Shaaban, M.A. Kaid, E.S. Moustafa, A. Adel, Journal of Physics D: Applied Physics 41 (2008) 125301.
- [19] K.A. Aly, M.A. Osman, A.M. Abousehly, A.A. Othman, Journal of Physics and Chemistry of Solids 69 (2008) 2514.
- [20] V. Balan, C. Vigreux, A. Pradel, Journal of Optoelectronics and Advanced Materials 6 (2004) 875.
- [21] R. Swanepoel, Journal of Physics E: Scientific Instruments 16 (1983) 1214.
- [22] M. Kincl, L. Tichý, Materials Chemistry and Physics 110 (2008) 322.
- [23] G. Lenz, J. Zimmermann, T. Katsufuji, M.E. Lines, H.Y. Hwang, S. Spälter, R.E. Slusher, S.W. Cheong, J.S. Sanghera, I.D. Aggarwal, Optics Letters 25 (2000) 254.
- [24] K. Jackson, A. Briley, S. Grossman, D.V. Porezag, M.R. Pederson, Physical Review B: Condensed Matter and Materials Physics 60 (1999) R14985.
- [25] V. Nazabal, F. Charpentier, J.L. Adam, P. Nemec, H. Lhermite, M.L. Brandily-Anne, J. Charrier, J.P. Guin, A. Moréac, International Journal of Applied Ceramic Technology 8 (2011) 990.
- [26] J.H. Baek, T.H. Kim, H.J. Choi, K.H. Jeong, M.H. Cho, Journal of Physical Chemistry C 115 (2011) 13462.
- [27] Z.G. Ivanova, V. Pamukchieva, M. Vlek, Journal of Non-Crystalline Solids 293–295 (2001) 580.
- [28] D.R. Goyal, A.S. Maan, Journal of Non-Crystalline Solids 183 (1995) 182.
- [29] A. Kovalskiy, A.C. Miller, H. Jain, M. Mitkova, Journal of the American Ceramic Society 91 (2008) 760.
- [30] D.C. Sati, A. Kovalskiy, R. Golovchak, H. Jain, Journal of Non-Crystalline Solids 358 (2012) 163.
- [31] L. Petit, N. Carlie, H. Chen, S. Gaylord, J. Massera, G. Boudebs, J. Hu, A. Agarwal, L. Kimerling, K. Richardson, Journal of Solid State Chemistry 182 (2009) 2756.
- [32] R.A. Jarvis, R.P. Wang, A.V. Rode, C. Zha, B. Luther-Davies, Journal of Non-Crystalline Solids 353 (2007) 947.
- [33] R.P. Wang, D.Y. Choi, A.V. Rode, S.J. Madden, B. Luther-Davies, Journal of Applied Physics 101 (2007) 113517.
- [34] R.P. Wang, A. Rode, D.Y. Choi, B. Luther-Davies, Journal of the American Ceramic Society 91 (2008) 2371.