Rebonding of Se to As and Ge in $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films upon thermal annealing: Evidence from x-ray photoelectron spectra investigations

R. P. Wang,^{a)} D. Y. Choi, A. V. Rode, S. J. Madden, and B. Luther-Davies

Centre for Ultrahigh-bandwidth Devices for Optical Systems, Laser Physics Centre, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT0200, Australia

(Received 20 December 2006; accepted 2 April 2007; published online 7 June 2007)

We have measured and analyzed x-ray photoelectron spectra (XPS) of as-grown and annealed $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films compared with bulk material. We found that the as-grown film contains a large number of separated Se clusters which can coalesce with As and Ge after annealing at high temperatures. In addition, both the Ge and As 3*d* spectra show the presence of oxides. While the Ge oxidation increases with an increasing annealing temperature, As oxidation is almost unaffected by annealing. The difference could be due to their different electro-negativities. Our results suggest that, while thermal annealing is effective to move the film toward the bond structure of bulk glass, the simultaneous surface oxidation must be suppressed in order to achieve high quality films.

© 2007 American Institute of Physics. [DOI: [10.1063/1.2737785](https://doi.org/10.1063/1.2737785)]

I. INTRODUCTION

Chalcogenide glasses are promising candidates for fabricating nonlinear optical waveguide devices because they possess moderate third-order optical nonlinearity ($100-1000\times$ silica), which allows devices to operate with low switching energy; ultrafast broadband response, allowing fast switching speeds; and low linear and nonlinear loss.^{1,2} However, integrated waveguide devices are generally fabricated from films of chalcogenide glass deposited by physical vapor deposition and it has generally been found that such films, unlike the bulk glass, have unstable physical properties which usually degrade the device performance and reliability. These instabilities generally arise because the films are prepared in nonequilibrium conditions and this leads to different bond configurations from the bulk material.^{3,4} Although several methods, such as electron beam or x-ray irradiation,³ and thermal or optical annealing⁴ have been developed to release the excess internal energy stored in films that have been deposited in nonequilibrium conditions in an attempt to relax them back to the thermal equilibrium state, the evolution of the microstructure during these processes is still not well studied.

In this paper we focus on $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ glass (commercial as AMTIR-1, Amorphous Materials, Inc., Garland, Texas) which exhibits a high glass transition temperature, T_g of 362 °C, as well as a third-order nonlinearity that is several hundred times higher than that of silica at 1540 nm.⁵ High quality stoichiometric AMTIR-1 films were deposited at room temperature onto Si wafers using our ultrafast laser ablation system.⁶

In general, when short laser pulses are used to ablate a solid in vacuum, clusters, droplets, or sub-phases can condense from the vapor plume as it cools due to adiabatic expansion near the target surface.⁷ At the substrate, therefore, the plume consists of a mixture of atomized material and condensed clusters with quite different chemical bonds com-

pared with the original target. These become frozen into the film as the plume condenses onto the substrate at room temperature.⁸ Therefore, we expect that as-grown films will contain a large number of un-saturated chemical bonds or phase-separated clusters. We have tried to demonstrate this by Raman spectroscopy, unfortunately, it is difficult to assign the broad Raman bands that appear to any specific chemical bonds most likely because the system is highly disordered. In contrast, x-ray photoelectron spectroscopy (XPS) is very sensitive to the chemical environments of the elements in the compound. In this paper, therefore, we have used XPS to investigate the evolution of the chemical environments as a function of annealing temperature for AMTIR-1 films. Our results confirm that a large number of Se clusters are present in the as-grown films, but these clusters can be broken and re-bond with Ge and As upon thermal annealing, moving the film toward bulk glass properties.

II. EXPERIMENTS

Chemically stoichiometric AMTIR-1 bulk glass was used as an ablation target. The chamber was evacuated to 3×10^{-7} Torr, and the material ablated by scanning the focused beam from a high average power (10–15 W) mode-locked, frequency doubled Nd:YVO₄ laser over the target surface. A detailed description of the laser ablation system and deposition parameters can be found in our previous paper.⁶ A 2.0 μm thick film deposited onto a 100 mm diameter silicon wafer was cut into smaller pieces, and then annealed in a vacuum oven at approximately 20 mTorr. All samples were annealed for 15 h at various temperatures. XPS spectra of as-grown and annealed films as well as the bulk glass were collected using an Escalab 220-IXL system under a vacuum of $\sim 10^{-10}$ Torr, where a monochromatic Al *K α* x-ray ($h\nu=1486.6$ eV) at a power of 250 W was used as the exciting source. All high-resolution spectra were recorded using a pass energy of 20 eV and a step of 0.05 eV. The adsorbed hydrocarbon was used as the internal reference and the binding energies of C 1*s* line was referenced at 285.0

^{a)}FAX: 02-6125-0029; electronic mail: rpw111@rsphysse.anu.edu.au

FIG. 1. The valence band spectra of the as-grown, annealed film and bulk.

eV. XPSpeak 4.1 software was used to decompose each spectrum by removing the Shirley baseline. The doublet separation was fixed and then the spectra were fitted with as few peaks as possible until the χ^2 value, which measures the goodness of the fit, reached a minimum. Through self-consistency of all fitting results and our understanding of the material, we assigned the peaks to different chemical environments.

III. RESULTS AND DISCUSSION

Figure 1 shows valence band spectra for as-grown and annealed films as well as the bulk glass. At first glance all spectra contain two broadbands, one below 7 eV which could be ascribed to the bonding and anti-bonding p -bands, and another is located at 7–15 eV corresponding to the lone pair bonding s -band.^{9–11} Compared with the valence band spectra of pure Ge, As, and Se elements and their peak assignments listed in Table I, the basic spectral shape from all the films is similar and consists of split main s - and p -states located at 8–15 eV and 1–7 eV, respectively, although the peak positions vary slightly between samples. An obvious difference can be found in the p -state between the as-grown, the annealed films and the bulk. The band around 5.5 eV in the spectra of annealed films and bulk is featureless. However, the peak in this region in the spectra of the as-grown film is characteristic of elemental selenium,^{9,10,16,17} indicating that the as-grown film contains Se clusters.

TABLE I. Some previous results of the valence peak position and the assignment for Ge-As-Se.

	Position (eV)	Assignment	References
Ge	2.5	p	8–11
	7.5	s	8–11
	10	s	8–11
As	1	p	8,12–14
	4	p	8,12–14
	8.5	s	8,12–14
	12.5	s	8,9,12–14
Se	1	p	8,9,11–16
	5	p	8,9,11–16
	11	s	8,9,11–16
	15	s	8,9,11–16

(a)

(b)

(c)

FIG. 2. (a) Se 3d spectra of the as-grown, annealed film and bulk, the square dots are experimental data and the dot lines are simulation results, (b) peak position, and (c) the relative area ratio of three doublets in (a).

Considering the s -band spectra, it is expected that as the three elements coalesce into Ge-As-Se glass, strong repulsion between Se and Ge/As produces splitting of the s -band,¹⁵ downshifting the Se s -state peak from 11 to 9.3 eV and upshifting the As s -state from 12.5 to 14.3 eV. From the spectra in Fig. 1, it is clear that the splitting of the Se and As s -states increases with annealing and this suggests that annealing causes the Se clusters to break down and coalesce with Ge/As. This enhances the repulsion leading to an increase in the splitting between these two peaks as can be observed in the data.

Se 3d spectra of as-grown and annealed films and the bulk are shown in Fig. 2(a). To quantitatively understand the evolution of Se clusters in the film, we decomposed the Se 3d spectra by fixing the d -orbital separation at 0.85 eV.^{9,16} In principal, selenium in AMTIR-1 glass has many kinds of

possible chemical environments such as different coordination number and different neighboring elements. It has been claimed that for Ge-As-Se bulk glass, the As atoms are surrounded by Ge atoms and the Ge atoms are linked only to Se atoms and hence no direct As-Se bonds exist.¹ However, this is not true for the film since some $\text{AsSe}_{3/2}$ -related Raman peaks have been reported. This difference may be due to the fact that the film has been created in nonequilibrium conditions.^{19,20} We found that we could decompose the XPS spectra very well using three doublets to fit all the spectra. Roughly we sorted them into three types: Se-related, partly Ge(As)-related and full Ge(As)-related. The high energy wing in Fig. 2(a) is associated with the Se clusters. With decreasing binding energy, the decomposed peaks were assigned to partly and fully Ge(As)-related in sequence due to the different electronegativity.¹⁷ The decomposed 3d spectra are also shown in Fig. 2(a) as dotted lines, and the decomposed peak positions and the integrated areas for the three doublets as a function of the annealing temperature are plotted in Fig. 2(b) and 2(c), respectively. Figures 2(a) and 2(b), show that the overall trend is of a decreasing binding energy with an increasing annealing temperature although there is some deviation from this trend for the samples annealed at 150 and 200 °C. The binding energies for the film in fact decrease to that of the bulk after annealing at 300 °C. This decrease in binding energy after annealing provides support for the existence of a large number of Se clusters in the as-grown film due to the fact that the negative shift of the binding energy increases with the decrease of neighboring atom electro-negativity from Se(2.48) to As(2.18), and Ge(2.01).^{1,18} When the as-grown film was progressively annealed, the Se rebonded with elements with lower electro-negativity, leading to the decrease of the average binding energy.

The most likely explanation for the deviations about this general trend, particularly for the samples annealed at 150 and 200 °C, is related to the different glass transition temperatures of most probable clusters in the film. Thus, for example, Se-Se clusters would be expected to melt between 40 and 60 °C; GeSe_4 around 163 °C; AsSe around 164 °C; As_2Se_3 around 173 °C; GeSe_3 around 214 °C; Ge_2Se_3 around 322.5 °C; and GeSe_2 around 394 °C.¹ Thus below 150 °C only Se rings or chains can be broken and rebond with existing unsaturated Ge or As bonds. At higher temperatures, however, other clusters can melt and further rearrangement of the bonds would be expected. While we cannot definitively identify this evolution from the XPS data we believe it is most likely to explain the deviations observed in Fig. 2 about the general trend as the films evolve toward the state of the bulk glass.

As and Ge 3d spectra of as-grown and annealed films and the bulk glass are shown in Figs. 3(a) and 3(b), respectively. The spectra of the films both contain two distinctive features. On the basis of the standard XPS database,⁹ we assigned the lower energy bands to the Ge- or As-related chemical environments in AMTIR-1, and the higher energy bands to the oxidized states of Ge or As. Considering oxygen's electro-negativity of 3.44, the positive or negative shift of these two bands in Fig. 3 can be again explained by the

FIG. 3. XPS 3d spectra of as-grown, annealed films and bulk for As (a) and Ge (b).

different electro-negativities of these elements. Compared with the Se 3d spectra which have negligible oxide peaks, Ge and As show a different oxidized behavior. The intensity of the Ge oxide peak increased with an increasing annealing temperature while that of the As oxide peak is almost annealing temperature independent. Consequently instead of decomposing the low energy band into several separated doublets as before, we plotted the area ratio of the oxide band to the lower energy band versus the annealing temperature in Fig. 4 to compare their different oxidized behavior. Since XPS is only surface sensitive, we measured the depth profile of Ge and As 3d spectra (not shown here). The oxygen can only be found at the very surface (within 20 to 30 nm) for as-grown film, but diffuses deeply into the film upon thermal annealing. Figure 5 shows the typical depth profile of O 1s

FIG. 4. Relative area ratio of oxidized bands to 3d bands of Ge and As in Fig. 3.

FIG. 5. The depth profile of O 1s spectra for the as-grown film. The etching rate is 6 nm/s.

spectra in the as-grown film. The strong O 1s peak at approximately 531 eV can be found on the surface but disappear after 5 s *in situ* etching with a rate of 6 nm/s. There are a great deal of dangling bonds in the fresh film that are easy to saturate when the film was exposed to air and reacted with oxygen. When annealing, the residual oxygen in the oven could diffuse along the grain boundary since the amorphous film generally is not dense, leading to the deep distribution of oxygen. The oxide content in AMTIR-1 may modify the network of the glass and subsequently deteriorate the optical properties of the film in the infrared region,²¹ therefore, *in-situ* annealing at high vacuum is desired to achieve high quality film.

IV. CONCLUSIONS

In summary, we have measured the XPS valence band and 3d spectra of as-grown and annealed films and bulk of AMTIR-1. We found that a large number of Se clusters could be formed in the as-grown film. With an increasing annealing temperature, some of the clusters break down and coalesce with Ge or As, forming different structural units in the glass network while others serve as the link between these different structural units. On the other hand, both Ge and As-3d spectra show that oxidation occurred during laser ablation and thermal annealing: Ge oxidation increases with increasing annealing temperature while As oxidation is almost in-

sensitive to the annealing temperature. The difference could be due to their different electronegativities. Our results suggest that, while thermal-annealing is effective to move the film toward the bind structure of bulk glass, the simultaneous surface oxidation must be suppressed in order to get high quality films.

ACKNOWLEDGMENT

This research was supported by Australian Research Council through its Centers of Excellence, Discovery and Federation Fellow Programs.

- ¹M. A. Popescu, *Non-Crystalline Chalcogenides* (Kluwer, Dordrecht, 2001).
- ²A. Schulte, C. Rivero, K. Richardson, K. Turcotte, V. Hamel, A. Villeneuve, T. Galstian, and R. Vallee, *Opt. Commun.* **198**, 125 (2001).
- ³O. Nordman, N. Nordman, and N. Peyghambarian, *J. Appl. Phys.* **84**, 6055 (1998).
- ⁴R. P. Wang, S. J. Madden, C. J. Zha, A. V. Rode, and B. Luther-Davies, *J. Appl. Phys.* **100**, 063524 (2006).
- ⁵J. T. Gopinath, M. Solja, and E. P. Ippen, *J. Appl. Phys.* **96**, 6931 (2004).
- ⁶A. V. Rode, A. Zakery, M. Samoc, E. G. Gamaly, and B. Luther-Davies, *Appl. Surf. Sci.* **197–198**, 481 (2002).
- ⁷E. G. Gamaly *et al.*, *J. Appl. Phys.* **95**, 2250 (2004).
- ⁸D. B. Chrisey, *Pulsed Laser Deposition of Thin Films* (Wiley, New York, 1994).
- ⁹http://srdata.nist.gov/xps/main_search_menu.htm
- ¹⁰M. Kastner, *Phys. Rev. Lett.* **28**, 355 (1972).
- ¹¹R. G. Cavell, S. P. K. Lowalczyk, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, *Phys. Rev. B* **7**, 5313 (1973).
- ¹²E. Bergignat, G. Hollinger, H. Chermette, P. Pertosa, D. Lohez, M. Lannoo, and M. Bensoussan, *Phys. Rev. B* **37**, 4506 (1988).
- ¹³H. Jain, S. Krishnaswami, A. C. Miller, P. Krecmer, S. R. Elliott, and M. Vlcek, *J. Non-Cryst. Solids* **274**, 115 (2000).
- ¹⁴K. Antoine, J. Li, D. A. Drabold, H. Jain, M. Vlcek, and A. C. Miller, *J. Non-Cryst. Solids* **326–327**, 248 (2003).
- ¹⁵S. G. Bishop and N. J. Shevchik, *Phys. Rev. B* **12**, 1567 (1975).
- ¹⁶W. Y. Li, S. Seal, C. Rivero, C. Lopez, K. Richardson, A. Pope, A. Schulte, S. Myneni, H. Jain, K. Antoine, and A. C. Miller, *J. Appl. Phys.* **98**, 053503 (2005).
- ¹⁷N. J. Shevchik, *Phys. Rev. Lett.* **33**, 1572 (1974).
- ¹⁸V. I. Nefedov, *X-ray Photoelectron Spectroscopy of Solid Surfaces* (VSP, Utrecht, 1988).
- ¹⁹V. G. Nguyen, J. S. Sanghera, J. A. Freitas, I. D. Aggarwal, and I. K. Lloyd, *J. Non-Cryst. Solids* **248**, 103 (1999).
- ²⁰R. P. Wang, A. V. Rode, S. J. Madden, C. J. Zha, R. A. Jarvis, and B. Luther-Davies, *J. Non-Cryst. Solids* **353**, 950 (2007).
- ²¹S. Seal, K. A. Richardson, W. Li, C. Lopez, A. Schulte, A. Graham, and C. Rivero, *Corrosion* (Houston) **59**, 139 (2003).