

## RAMAN SPECTROSCOPY OF GeSe AND AgGeSe THIN FILMS\*

J.M. CONDE GARRIDO<sup>a</sup>, A. PIARRISTEGUY<sup>b</sup>, R. LE PARC<sup>c</sup>, M.A. UREÑA<sup>a</sup>,  
M. FONTANA<sup>a</sup>, B. ARCONDO<sup>a\*</sup>, A. PRADEL<sup>b</sup>

<sup>a</sup>Laboratorio de Sólidos Amorfos, INTECIN, Facultad de Ingeniería, Universidad de Buenos Aires – CONICET. Paseo Colón 850, (1063) Buenos Aires, Argentina.

<sup>b</sup>Institut Charles Gerhardt, UMR 5253 CNRS, CC1503, Université Montpellier 2, Pl.E. Bataillon, F-34095 Montpellier cedex 5, France.

<sup>c</sup>Laboratoire Charles Coulomb, UMR 5587, Université Montpellier 2, F-34095 Montpellier Cedex 5, France

The structural properties of  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  thin films ( $y=0, 0.07, 0.10, 0.15, 0.20$  and  $0.25$  at. fraction) were studied. The films were prepared by pulsed laser deposition using bulk glass targets of the studied ternary system and deposited onto microscope slides. Their amorphous structures were confirmed by XRD (X-ray Diffraction). The effect of silver content on films structures was analysed by Raman spectroscopy. Typical Raman vibration modes were observed in the  $\text{Ge}_{0.25}\text{Se}_{0.75}$  binary film: Ge-Se corner-sharing tetrahedra mode (CS) at  $199\text{ cm}^{-1}$ , edge sharing tetrahedra mode (ES) at  $217\text{ cm}^{-1}$ , and Se-Se rings and chains mode at  $255\text{-}265\text{ cm}^{-1}$  (CM). In the  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  ternary thin films, the same modes were observed but with a red shift and an intensity reduction in the ES and CM bands.

(Received October 8, 2013; Accepted November 11, 2013)

### 1. Introduction

Alloys of the AgGeSe system have been extensively studied because of their application in programmable metallization cell devices [1, 2]. These devices comprise a AgGeSe thin film placed between two electrodes: an inert one and an active Ag-rich electrode. Structural studies have shown that a covalent network of  $\text{GeSe}_{4/2}$  tetrahedra, as the elementary structural fundamental unit, constitutes the AgGeSe glass structure [3, 4]. Furthermore, Arcondo *et al.* [5, 6] reported, using Scanning Electron Microscopy, resistivity measurements and Mössbauer Spectroscopy, that AgGeSe bulk glasses are intrinsically separated into two amorphous phases (an Ag-rich and an Ag-poor phase).

The structure of  $\text{Ge}_x\text{Se}_{1-x}$  bulk glasses and films has been investigated by means of Raman scattering [1,2,7-11]. Bulk glasses of a wide composition range ( $x<0.40$ ) were investigated by different authors [7-9]. Three main bands were reported in these spectra and were associated to: the stretching mode of Se in  $\text{GeSe}_{4/2}$  corner-sharing tetrahedra (CS mode), the vibrations of Se atoms that form the edge-sharing Ge-Se tetrahedra (ES mode) and the stretching of the Se-Se bonds in the Se rings and chains (CM mode). These three modes also appear in Raman results for Se-rich AgGeSe glasses. A reduction of intensity is reported for the ES and CM modes with the addition of Ag [12-13].

In a previous work, Raman spectroscopy was performed in three kinds of thin films prepared by pulsed laser deposition (PLD): Ge-Se films before Ag doping, Ge-Se films after Ag doping and photodiffusion and films obtained using ternary targets [14]. A red shift of the different excited modes was observed for the ternary films spectra when compared to the spectra of the binary films. Morphology and optical properties of the  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  films has also been

---

\*Paper presented at 6<sup>th</sup> International Conference on Amorphous and Nanostructured Chalcogenides, Brasov, Romania, June 24-28, 2013

\* Corresponding author: barcond@fi.uba.ar

studied [15]. It was found that as the silver content in the films increased, the refractive index also increased and the optical band gap energy decreased. In this work,  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  thin films ( $y=0, 0.07, 0.10, 0.15, 0.20$  and  $0.25$  at. fraction) prepared by PLD were studied by Raman spectroscopy and the effect of silver content on the films structures was analysed.

## 2. Experimental

Amorphous  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  films (500 to 1100 nm thick) were prepared by PLD using targets of bulk chalcogenide glasses with a composition of  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  ( $y = 0, 0.07, 0.10, 0.15, 0.20$  and  $0.25$  at. fraction, named **Ag0**, **Ag7**, **Ag10**, **Ag15**, **Ag20** and **Ag25**, respectively). The glass targets were prepared by direct synthesis from pure elements (4N) in evacuated silica ampoules, followed by melt quenching [16]. After this process, bulk glasses were sliced and polished to obtain targets with parallel faces.

Thin films were deposited on static substrates (chemically cleaned microscope glass slides) held at room temperature, which were positioned parallel to the target surface, inside a vacuum chamber (about  $6 \times 10^{-8}$  Pa). PLD was performed using a pulsed Nd:YAG laser (Quanta-Ray Spectra-Physics), operating at a 355 nm wavelength, with a 5 ns pulse duration and a 10 Hz repetition rate. The laser beam with an angle of incidence of  $45^\circ$  was spanned horizontally by the movement of a mirror in order to get a uniform ablation of the target surface. The energy density of the laser was 1.4–1.7 J/cm<sup>2</sup>.

The film composition was analyzed using Energy-dispersive X-ray Spectroscopy (EDS) in a Carl Zeiss AG - SUPRA 40 electron microscope. The film thickness was measured using a Dektak 3 Veeco profilometer.

The amorphous structure of the thin films was confirmed by X-Ray Diffraction (XRD) using a Rigaku diffraction system in grazing incidence (incidence angle =  $2^\circ$ ) with monochromatized  $\text{Cu}(K_\alpha)$  radiation.

Raman spectra were recorded, at room temperature, with a Jobin-Yvon T64000 using a He-Ne laser (647 nm). An additional Raman spectrum of  $\text{Ge}_{0.25}\text{Se}_{0.75}$  bulk glass was also measured.

## 3. Results

The amorphous structure of the thin films was confirmed by X-ray diffraction as shown in Fig. 1. XRD patterns of the films present a prominent pre-peak at the diffraction angle  $2\Theta \approx 14^\circ$  ( $q = (4\pi/\lambda)\sin\Theta \approx 1 \text{ \AA}^{-1}$ ) as was previously observed in the bulk glasses used as targets [4, 17]. This pre-peak is characteristic of amorphous chalcogenide glasses and is associated with medium-range order. Pre-peak intensity decreases with increasing Ag content, as shown in Figure 1. This fact points out that silver addition to the binary glass decreases the medium-range order. This behavior is also observed in AgGeSe bulk glasses [3, 17] and thin films obtained by PLD [14].

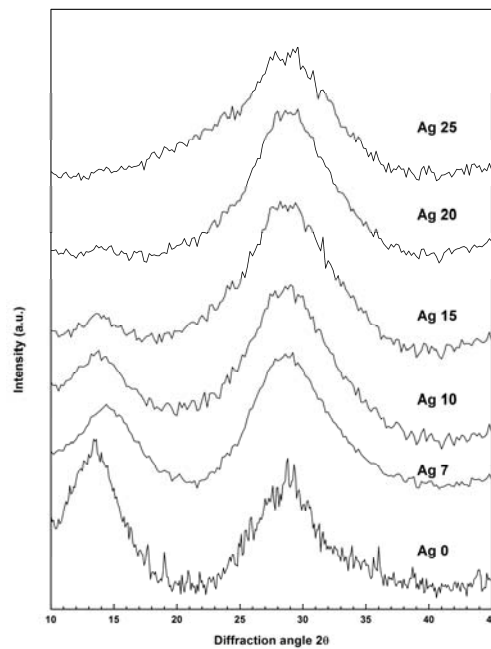


Fig. 1: X-ray diffraction patterns of  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  films.

Table 1 shows the composition of the  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  thin films. The measured relative composition between Ge and Se ( $x$ ) in the **Ag0** film exhibits an important difference with the nominal composition. Ternary films are mildly selenium-deficient and  $x$  differs from their target compositions in up to +0.04 atomic fraction. The selenium loss can be explained by the high volatility of selenium. It is worth mentioning that the measured silver composition ( $y$ ) has a higher experimental error due to the high mobility of  $\text{Ag}^+$  ions as was previously reported [5, 6].

Table 1:  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  films: identification, films nominal compositions and measured compositions using EDS.

$\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$ <b>Identification</b>	Nominal Composition (atomic fraction)		Measured Composition (atomic fraction)	
	<b>x</b>	<b>y</b>	<b>x</b> ( $\pm 0.03$ )	<b>y</b> ( $\pm 0.05$ )
Ag0	0.25	0	0.38	0
Ag7	0.25	0.07	0.26	0.08
Ag10	0.25	0.10	0.28	0.16
Ag15	0.25	0.15	0.29	0.24
Ag20	0.25	0.20	0.29	0.25
Ag25	0.25	0.25	0.29	0.31

Figure 2 shows the Raman spectra of the **Ag0** film and  $\text{Ge}_{0.25}\text{Se}_{0.75}$  bulk glass. Raman spectra of  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  films are depicted in Figure 3. All Raman spectra exhibit similar dominant features. A main band at  $194\text{-}200\text{ cm}^{-1}$ , with a shoulder at about  $178\text{-}180\text{ cm}^{-1}$  (very noticeable in the Ag0 film but almost absent in the  $\text{Ge}_{0.25}\text{Se}_{0.75}$  bulk glass and ternary films). A second band at  $210\text{-}217\text{ cm}^{-1}$  and a third broad band at  $255\text{-}265\text{ cm}^{-1}$ . The Raman results obtained in

this work are similar to those of Ge-Se and Ag-Ge-Se bulk glasses obtained in previous works [7-9, 13, 18-20]. For  $\text{Ge}_x\text{Se}_{1-x}$  bulk glasses, four main modes are observed (depending on the Ge content,  $x$ ): a band at  $192\text{-}201\text{ cm}^{-1}$  (CS mode), an accompanying side band near  $210\text{-}218\text{ cm}^{-1}$  (ES mode), a broad band near  $255\text{-}270\text{ cm}^{-1}$  (CM mode) and a band at  $178\text{ cm}^{-1}$  observed in glasses with high Ge content. This Raman peak is associated to Ge-Ge homopolar bonds mode in  $\text{Ge}_2(\text{Se}_{1/2})_6$  ethane-like units (Ge HB) [9, 18-19].

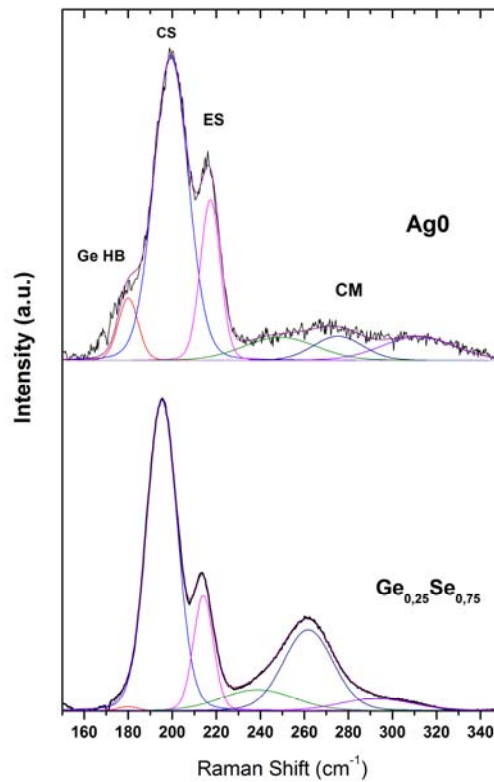


Fig. 2: Raman spectra of Ag<sub>0</sub> film and Ge<sub>0.25</sub>Se<sub>0.75</sub> bulk glass.

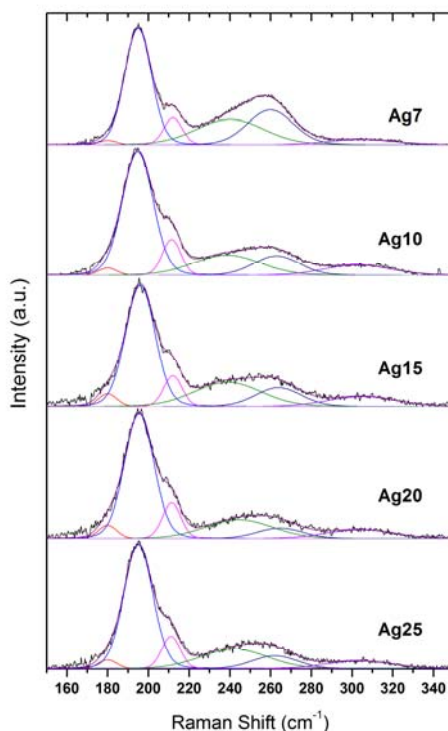


Fig. 3: Raman spectra of  $Ag_y(Ge_xSe_{1-x})_{1-y}$  films (Ag7, Ag10, Ag15, Ag20 and Ag25 films).

#### 4. Discussion

The Raman spectra of the thin films and the  $Ge_{0.25}Se_{0.75}$  bulk glass (Figures 2 and 3) show specific features closely matching those reported by other authors in bulk glasses [7-8, 18-20]: Ge-HB, CS, ES and CM modes.

The Raman spectra of the **Ag0** binary film and the  $Ge_{0.25}Se_{0.75}$  bulk glass (Figure 2) are similar to one another. However, some differences can be observed. The **Ag0** film has: a) a Ge-HB mode with higher intensity, b) a blue shift (towards higher wavenumbers) of the CS and the ES modes, and c) a CM mode with lower intensity. These changes can be explained by a difference in the measured composition of the two types of samples (as measured by EDS) (see Table 1, where the composition of the target is equal to the nominal composition).

Boochehand *et al.* [20] observed in  $Ge_xSe_{1-x}$  bulk glasses that CS and ES modes shift to higher wavenumbers (blue shift) with increasing Ge concentration. They found three different Ge content dependences of these modes' wavenumbers: a) a floppy regime for  $0.08 < x < 0.20$  (lineal dependence), b) a transition region for  $0.21 < x < 0.25$ , c) a rigid regime for  $0.26 < x < 0.33$  (power-law dependence). The Ge-HB mode appears at high Ge concentrations ( $x > 0.30$  for bulk glasses [19, 20] and  $x = 0.22-0.28$  for PLD films [11]) and this is related to the increase in the amount of Ge-Ge bonds. As the Se concentration decreases, the amount of homopolar Se-Se bonds decreases and therefore the intensity of the CM mode also decreases. Summarizing for the **Ag0** film, the observed differences (higher intensity of the Ge-HB mode, blue shift of the CS and ES modes and lower intensity of the CM mode) are consistent with the film having a higher Ge concentration ( $x = 0.38$ , see Table 1) than the target. The measured composition of the **Ag0** film (shown in table 1) indicates that the film is selenium deficient and corroborates the previous idea. This is consistent with the fact that the Raman spectrum of the **Ag0** film is similar to the Raman spectrum of bulk glasses with  $x = 0.33$  reported in the literature [17].

The Raman spectra of the ternary thin films (Figure 3) shows similar Raman features to those reported by other authors in  $Ag_y(Ge_{0.25}Se_{0.75})_{1-y}$  bulk ternary glasses with  $0 \leq y \leq 0.25$  [12, 13] and thin films of compositions  $Ag_y(Ge_{0.25}Se_{0.75})_{1-y}$  with  $y = 0.25$  [14] and  $Ag_y(Ge_{0.20}Se_{0.80})_{1-y}$  with  $y = 0.06, 0.11, 0.23$  [21]. Comparing with the GeSe binary sample, the  $Ag_y(Ge_{0.25}Se_{0.75})_{1-y}$  ternary

thin films show a red shift in CS and ES modes and an intensity reduction of the ES and CM bands. On the other hand, the spectra of **Ag10**, **Ag15**, **Ag 20** and **Ag25** are very similar to one another and there are no clear differences among them (as was observed by Mitkova *et al.* for bulk glasses with  $y \geq 0.10$  [13]). This fact suggests that the Ge-Se and Se-Se bonds are not significantly influenced by the silver content in the films with  $y \geq 0.10$ . The spectrum of the **Ag7** film is similar to the others but with two differences, i.e., higher intensity of the ES and CM modes (this fact was also observed by Mitkova *et al.* in bulk glasses [13]).

In a previous work [15], optical properties of AgGeSe thin films in the UV-visible-NIR region were studied. Some important changes in the optical properties of  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  thin films were observed: a decrease in the energy of the optical band gap (from 2.06 to 1.55 eV) and an increase in the refractive index (from 2.33 to 2.82) when the silver content was increased from  $y=0$  to 0.25. In this work, Raman parameters remained almost unchanged, especially in the region of ionic conduction ( $y \geq 0.10$ ). It was therefore concluded that the observed changes in the optical properties were not caused by a change in the vibration modes of the Ge-Ge, Se-Se or Ge-Se bonds.

## 5. Conclusions

It was found that the main features of the Raman spectra of both binary and ternary thin films are similar to those of Ge-Se and Ag-Ge-Se bulk and film glasses obtained in previous works [7-9, 11, 13-14, 18-21]. Comparing the  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  ternary thin films with the binary film, the former show a red shift in the CS and ES modes and an intensity reduction in the ES and CM modes. The  $\text{GeSe}_4/2$  tetrahedra remain the basic structural element even in Ag-Ge-Se amorphous films with high Ag content.

The Raman spectra of the ternary thin films with  $y \geq 0.10$  show no clear differences among them and they all have lower intensities in the ES and CM modes than the thin films with  $y=0.07$ .

Raman results from this work do not seem to correlate with the significant changes of the optical properties measured by UV-visible-NIR (in Ref. 15), which indicates that the observed optical behavior was not due to a change in the studied vibration modes.

## References

- [1] M. Mitkova, M.N. Kozicki, J. Non-Cryst. Solids **299-302**, 1023 (2002).
- [2] M. Mitkova, M.N. Kozicki, H.C. Kim, T.L. Alford, J. Non-Cryst. Solids **338-340**, 552 (2004)
- [3] R. Dejus, S. Susman, K. Volin, D. Montague, D. Price, J. Non-Cryst. Solids **143**, 162 (1992).
- [4] A. Piarristeguy, M. Mirandou, M. Fontana, B. Arcondo, J. Non-Cryst. Solids **273**, 30 (2000).
- [5] B. Arcondo, M.A. Ureña, A. Piarristeguy, A. Pradel, M. Fontana, Applied Surface Science **254**(1) 321 (2007).
- [6] B. Arcondo, M.A. Ureña, A. Piarristeguy, A. Pradel, M. Fontana, Physica B **389**(1), 77 (2007).
- [7] S. Sugai, Phys. Rev. B **35**(3), 1345 (1987).
- [8] Y. Wang, K. Tanaka, T. Nakaoka, K. Murase, Physica B **316-317**, 568 (2002).
- [9] X. Feng, W. J. Bresser, P. Boolchand, Phys. Rev. Lett. **78**(23) 4422 (1997).
- [10] E. Sleafckx, L. Tichy, P. Nagels, R. Callaerts, J. Non-Cryst. Solids **198-200**, 723 (1996).
- [11] P. Nemeč, J. Jedelsky, M. Frumar, M. Stabl, Z. Cernosek, M. Vlček, Philosophical Magazine **84**(9), 877 (2004).
- [12] R. Le Parc, A. Piarristeguy, N. Frolet, M. Ribes, A. Pradel, J. Raman Spectroscopy **44**, 1049 (2013).
- [13] M. Mitkova, Yu Wang, P. Boolchand, Phys. Rev. Lett. **83**(19) 3848 (1999).
- [14] M. Erazú, J. Rocca, M. Fontana, A. Ureña, B. Arcondo, A. Pradel, J. Alloys and Compounds **495**, 642 (2010).
- [15] J.M. Conde Garrido, A. Piarristeguy, M.A. Ureña, M. Fontana, B. Arcondo, A. Pradel, J. Non-Cryst. Solids **377**, 186 (2013).

- [16] M.A. Ureña, M. Fontana, B. Arcondo and M.T. Clavaguera-Mora, *J. Non-Cryst. Solids* **320**, 151 (2003).
- [17] A. Piarristeguy, M. Fontana, B. Arcondo, *J. Non-Cryst. Solids* **332**, 1 (2003).
- [18] T. Edwards, S. Sen, E. Gjersing, *J. Non-Cryst. Solids* **358**, 609 (2012).
- [19] P. Boolchand, W.J.Bresser, *Phil. Mag. B* **80**(10) 1757 (2000).
- [20] P. Boolchand, X.Feng, W.J.Bresser, *J. Non-Cryst. Solids* **293-295**, 348 (2001).
- [21] J. Orava, T. Kohoutek, T. Wagner, Z. Cerna, Mil. Vlcek, L. Benes, B. Frumarova, M. Frumar, *J. Non-Cryst. Solids* **355**, 1951 (2009).