

Te-Ge-Ga thin films deposited by co-thermal evaporation

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Thin films of the Te-Ge-Ga ternary system have been deposited by co-thermal evaporation: tellurium and germanium were evaporated by current induced heating and gallium was evaporated by electron beam bombardment. Co-thermal evaporation allowed depositing films with very different compositions. A large amorphous region was defined and compared to that obtained for the bulk materials. Films were proved to be adhesive to the substrate, dense and characterised by a low roughness. The thickness and composition of the films were shown to be homogeneous all over the substrate. The refractive indexes and optical band gap of the co-thermally evaporated films were estimated using the transmission spectra recorded in the region 800-2500 nm.

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1. Introduction

Films of chalcogenide materials can be deposited by different methods: RF-sputtering, thermal evaporation, pulsed laser deposition, chemical vapour deposition, etc, as testified by literature [1-7]. The very first results concerning a new deposition method for chalcogenide glasses, the co-thermal evaporation, were published recently [8]. The deposition of films with an atomic percentage in tellurium comprised between 70 and 85 was reported. The co-thermal evaporation was shown to be a very promising method to obtain films with a high density, a very good adhesion to the substrate and a good homogeneity [8]. It was shown that the method allows varying the compositions of the films very easily by selectively adjusting the evaporation rates of each deposited elements. In order to further validate the method, the investigation has been extended to a much larger region of the Te-Ge-Ga ternary system. The paper reports on the deposition and characterization of the films. The characterization aimed (i) at probing the quality of the films obtained by co-evaporation; (ii) at probing the ability of the method to provide amorphous layers over a wide composition range. Finally preliminary optical characterization was carried out since the layers, being transparent in the IR, could be used to develop waveguides for IR integrated optics [8-10].

2. Experimental

The layers were deposited by co-thermal evaporation of pure elements Te, Ge and Ga (ALDRICH, 99.999%), using a PLASSYS MEB 500 device. Tellurium and germanium were evaporated by current heating whereas gallium was evaporated by electron beam bombardment. Powders of the three elements were placed in different crucibles. A homemade carbon crucible inserted in a

molybdenum vessel was used for germanium. A similar system was used for tellurium but a molybdenum perforated lid was added, in order to ensure a stable evaporation rate. Gallium was placed in a copper crucible previously coated with an aluminium layer in order to avoid the formation of alloys between copper and gallium. Microscope slides with dimensions 5 x 2.5 cm² were used as substrates. They were placed on a cooled and rotating substrate holder which was located at about 25 cm above the evaporation sources. Before the deposition, the chamber was evacuated down to approximately 10⁻⁷ mbar to avoid ambient contamination. The evaporation rates of each element were measured thanks to pre-calibrated quartz crystal monitors. They were typically comprised between 0.5 and 3 nm.s⁻¹.

The film thickness was measured using a DEKTAK 3 Veeco profilometer. The film adhesion was verified by the classical adhesive tape test. The film morphology and roughness were examined by scanning electron microscopy (SEM) using a JEOL JSM-6300F microscope and atomic force microscopy (AFM) using a Digital Instruments D3100 equipment, respectively. The amorphous or crystalline state of the films was studied by X-ray diffraction using a PANalytical XPERT diffractometer. A monochromatised Cu (K α) radiation ($\lambda=1.5406$ Å) was used for the excitation. An operating voltage of 40 kV and a beam current of 30 – 40 mA were applied. The film composition was estimated by Electron Probe Micro-Analysis using a CAMECA SX-100 instrument with an acceleration voltage of 20 kV and probe current of 1 nA. The optical transmittance spectra in the range 800-2500 nm were recorded using a VARIAN CARY 50 UV-vis-NIR spectrophotometer. The area, probed through a mask of 1 x 1 cm², was the central part of the films. The variation of the refractive index of the films with the measurement wavelength was obtained from the transmission spectra, using a procedure described by Swanepoel [11].

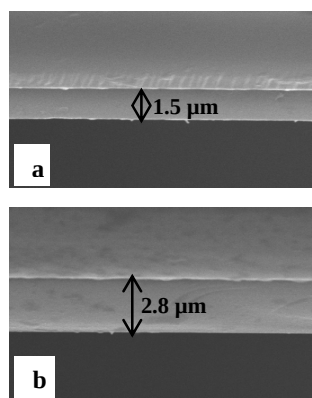


Fig. 1. SEM pictures of the cross-sections of: (a) a $\text{Te}_{80.4}\text{Ge}_{19.6}$ and (b) a $\text{Te}_{63.8}\text{Ge}_{28.0}\text{Ga}_{8.2}$ co-thermally evaporated films.

3. Results and discussion

The film thickness, in the range of 1-2 μm , was measured at different points of the $5 \times 2.5 \text{ cm}^2$ film surface. In all case, the thickness was similar all over the film. As an example, the results obtained for a film of Te-Ge-Ga typical composition are reported in Table 1. The thickness variation from one point to another is of the same order of magnitude than the uncertainty on the measurements.

Table 1. Thickness of a typical Te-Ge-Ga film, depending on the distance between the measured point and the edge of the substrate (in cm.).

Dist. (cm)	0.5	1.5	2.5	3.5	4.5
Thick. (μm) ± 0.05	2.22	2.26	2.28	2.29	2.23

The chemical composition was measured at different points of the surface of the films. These measurements confirmed the excellent homogeneity in the film composition all over the surface. A typical example is presented in Table 2 where the atomic percentages in Te, Ge, Ga for a film of Te-Ge-Ga typical composition are given.

Table 2. Atomic percentages in tellurium, germanium and gallium for a typical Te-Ge-Ga film, depending on the distance between the analysed point and the edge of the substrate (in cm.).

Dist. (cm)	Te (at.) ± 0.1	Ge (at.) ± 0.1	Ga (at.) ± 0.1
0.7	72.3	13.3	14.4
1.4	73.7	12.9	13.4
2.1	74.0	12.7	13.3
2.8	73.9	12.8	13.3
3.5	73.9	12.7	13.4
4.2	73.7	12.8	13.5
4.9	73.7	12.9	13.4

The films were shown to be very adhesive to the microscope slide substrates. Moreover, the SEM pictures of the film cross-sections revealed that the films were very dense, as illustrated in Fig. 1.

The film roughness was estimated by scanning a $5 \times 5 \mu\text{m}^2$ surface by atomic force microscopy. Several films with very different compositions and thicknesses comprised between 1 and 2.5 μm were analysed. Whatever the film composition and thickness, the roughness lays between 0.5 and 3 nm. Note that these values are of the same order of magnitude than that of the microscope slide used as a substrate. A typical AFM picture of a Te-Ge-Ga film surface is shown in Fig. 2.

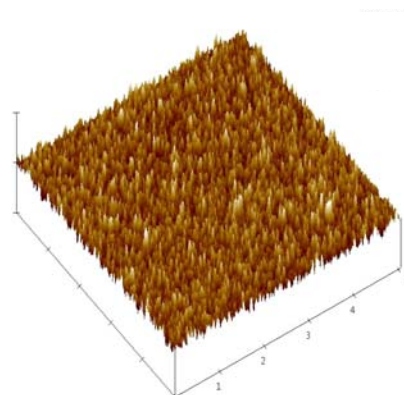


Fig. 2. AFM picture of the surface of a 1.58 μm thick $\text{Te}_{70.0}\text{Ge}_{19.0}\text{Ga}_{11.0}$ film.

The amorphous or crystalline character of the films was analysed depending upon their composition. Figure 3 shows a truncated Te-Ge-Ga ternary diagram limited to atomic percentages in tellurium higher than 50 %. Squares stand for amorphous compositions and triangles for crystalline ones. As it can be seen, most of the films are amorphous. It allowed defining an amorphous region, represented by the dashed zone in Figure 3. This result is to be compared with that obtained for the corresponding bulk materials, where the amorphous region is limited to a very small area around the composition $\text{Te}_{75}\text{Ge}_{15}\text{Ga}_{10}$ [12].

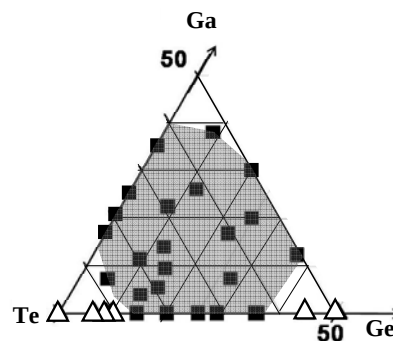


Fig. 3. Part of the Te-Ge-Ga ternary diagram. Squares correspond to amorphous films and triangles to partially or totally crystallised films. The grey zone delimits the amorphous region.

The refractive index of some of the films was plotted versus the wavelength, using the transmission spectra $T(\lambda)$ according to the procedure described by Swanepoel [11]. Note that the use of this method implies to have films uniform in thickness. It is the case for the co-thermally evaporated Te-Ge-Ga films. The transmission spectra are delimited by two curves $T_M(\lambda)$ and $T_m(\lambda)$ which are determined using an interpolation function of the maximum and minimum values, T_M and T_m of the interference pattern. After having determined $T_M(\lambda)$ and $T_m(\lambda)$, the refractive index is calculated using equation 1:

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

where s is the refractive index of the substrate and N is calculated using eq. 2:

$$N = \frac{2s(T_M - T_m)}{T_M T_m} + \frac{1}{2}(1 + s^2) \quad (2)$$

As an approximation, the refractive index of the substrate s was considered constant and equal to 1.51. The variation of the refractive index n versus the wavelength λ is given for a selection of films with typical compositions in Figs. 4a, 4b, 4c and 5. A large degree of scattering is observed, especially at low wavelengths. This can be explained by the fact that the model is less accurate in this region. The variations of the refractive index of two typical films of the binary Te-Ge system are compared in Figure 4a. One can see that the refractive index of the film containing the larger amount of tellurium is higher than that of the film containing less tellurium. This result was expected and accounts for the fact that tellurium is more polarisable than germanium. The variations of the refractive index of two typical films of the binary Te-Ga system are compared in Figure 4b. Here also a large amount of tellurium is responsible for a high refractive index. The variations of the refractive index of $\text{Te}_{64.1}\text{Ge}_{35.9}$ and $\text{Te}_{64.5}\text{Ga}_{35.5}$ films are compared in Figure 4c. In this case, one can conclude that the replacement of germanium by gallium is responsible for a decrease in the refractive index.

The variation of the refractive index of several films in the Te-Ge-Ga system are compared in Figure 5. The values obtained for the films deposited by co-thermal evaporation are of the same order of magnitude than those already reported in literature for Te-Ge-Ga films deposited by other deposition techniques. For example, Te-Ge-Ga films were deposited by classical thermal evaporation by Sripathi et al. [13]. According to this work, the refractive index of a $\text{Te}_{50}\text{Ge}_{30}\text{Ga}_{20}$ film is about 3.6 at $\lambda = 1.3 \mu\text{m}$. This value is lower than those reported in Figure 5 for a similar wavelength. It can be explained either by a lower amount in tellurium in the film or by a larger amount in Ga when the tellurium content is similar.

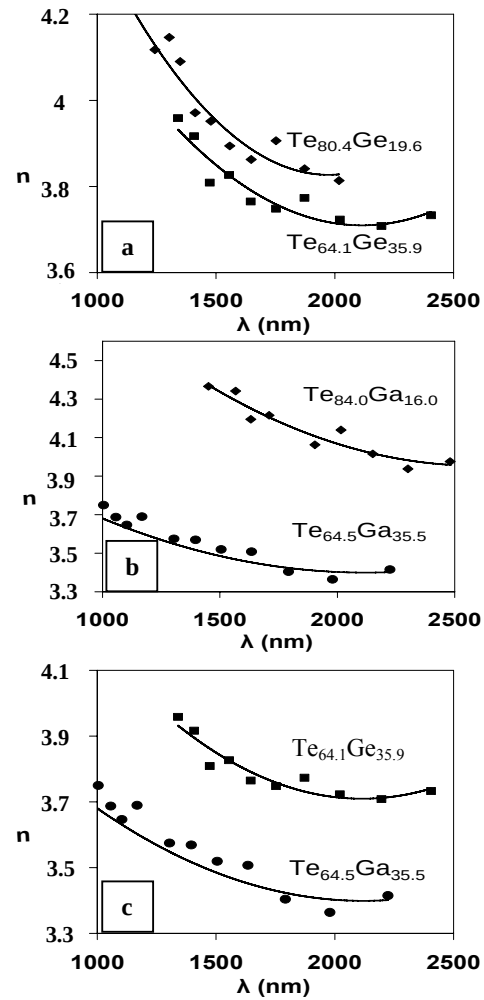


Fig. 4. Variations of the refractive index versus the wavelength for different films: a) two Te-Ge films; b) two Te-Ga films and c) $\text{Te}_{64.1}\text{Ge}_{35.9}$ and $\text{Te}_{64.5}\text{Ga}_{35.5}$ films. The lines are guides for the eyes.

Note that, in order to validate the accuracy of the results, the thickness of the films which refractive indices are shown in Fig. 5, was calculated using the graphical method described by Swanepoel [11] and compared to the experimental values measured by profilometry. The results are given in table 3, along with the optical band gaps E_g estimated by considering the high absorption part of the transmission spectra and using equation 3:

$$\alpha(\omega) = \frac{\beta(\hbar\omega - E_g)^2}{\hbar\omega} \quad (3)$$

where β is a constant which depends on the transition probability. Owing to the precision in the measurements and calculations (refer to Table 3) and due to the difference in the film compositions, it is difficult to derive the trend of the optical gap versus composition.

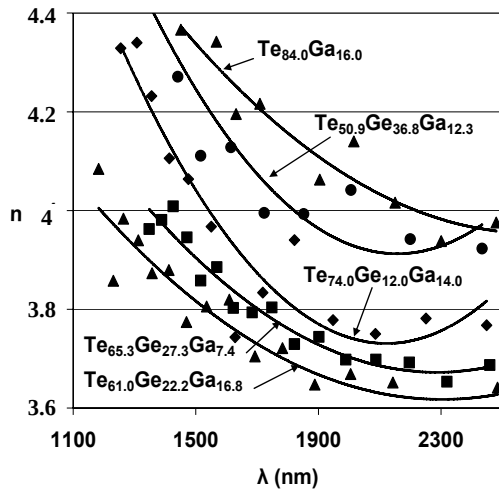


Fig. 5. Variations of the refractive index versus the wavelength for different Te-Ge-Ga co-thermally evaporated films.

Table 3. Film experimental and calculated thicknesses and optical band gaps.

Film	d (μm) exp. (±20nm)	d (μm) calc. (±2%)	Eg (eV) (±0.05eV)
Te _{61.0} Ge _{22.2} Ga _{16.8}	2.27	2.09	0.92
Te _{65.3} Ge _{27.3} Ga _{7.4}	2.88	2.71	0.88
Te _{74.0} Ge _{12.0} Ga _{14.0}	1.98	1.93	0.91
Te _{50.9} Ge _{36.8} Ga _{12.3}	1.56	1.24	0.84
Te _{84.0} Ga _{16.0}	2.07	1.89	0.78

Nevertheless, the obtained values can be compared with those already reported in the literature. For example, P. Petkov et al. reported on the optical properties of (GeTe₄)_{1-x}Ga_x and (GeTe₅)_{1-x}Ga_x films deposited by thermal evaporation [14]. The addition of gallium in the GeTe₄ and GeTe₅ structures was said to lead to a decrease in the optical band gap. The values reported for the optical band gap are of the same order of magnitude than those obtained in the present study for the co-thermally evaporated films. For example, the optical band gap of the Te₇₁Ge₁₄Ga₁₅ film is 1.01 eV [14].

The main result of this study on the optical characteristics of the deposited films is the fact that films with very different refractive indexes (from 3.8 to 4.4 at $\lambda = 1500$ nm for example) can be obtained by varying the film composition. It is particularly interesting since these Te-Ge-Ga films are expected to be transparent in the IR, in the same way as the corresponding bulk glasses. Therefore they are potential candidates for applications requiring IR integrated optics components. The ability to prepare films with a large choice in refractive index opens the door to the realisation of IR single-mode waveguides [8-10].

4. Conclusions

A study of co-thermally evaporated films of the Te-Ge-Ga ternary system is reported. Thanks to the co-thermal evaporation, a method which allows varying very easily the film composition, a large domain in composition in the Te-rich region (larger than 50 at.%) could be explored. The region where amorphous films could be obtained is very large compared to that reported for corresponding bulk materials [12]. In particular, the amorphous zone of the Te-Ge binary system is much extended. A more detailed study of this region is being published elsewhere [15].

The co-thermal evaporation technique allows preparing very thick chalcogenide films (> 10 microns) which are homogeneous in thickness and composition. They are adhesive to the substrates and have good optical quality. This method is thus particularly attractive and opens the door to the fabrication of mid- and far-infrared waveguides [16].

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References

- [1] J. M. Gonzales-Leal, R. Pietro-Alcon, J. A. Angel, E. Marquez, L. Non-Cryst. Solids **315**, 134 (2003).
- [2] D. A. Turnbull, J. S. Sanghera, V. Q. Nguyen, I. D. Aggarwal, Mater. Lett. **58**(1-2), 51 (2004).
- [3] E. Marquez, P. Nagels, J. M. Gonzales-Leal, A. M. Bernal-Oliva, E. Sleenckx, R. Callaerts, Vacuum **52**, 55 (1999).
- [4] C. Vigreux-Bercovici, L. Labadie, J. E. Broquin, P. Kern, A. Pradel, J. Optoelectron. Adv. Mater. **7**(5), 2625 (2005).
- [5] M. Frumar, B. Frumarova, P. Nemec, T. Wagner, J. Jedelsky, M. Hrdlicka, J. Non-Cryst. Solids **352**, 544 (2006).
- [6] M. Martino, A. P. Caricato, M. Fernandez, G. Leggieri, A. Jha, M. Ferrari, M. Mattarelli, Thin Solid Films **433**, 39 (2003).
- [7] V. Balan, C. Vigreux and A. Pradel, J. Optoelectron. Adv. Mater. **6**(3), 875 (2004).
- [8] E. Barthelemy, C. Vigreux-Bercovici, P. Yot, A. Pradel, Optoelectron. Adv. Mater.-Rapid Comm. **1**, 487 (2007).
- [9] M. Barillot, E. Barthélémy, J.-E. Broquin, J. Frayret, J. Grélin, G. Hawkins, V. Kirschner, G. Parent, A. Pradel, E. Rossi, C. Vigreux, S. Xiang, X. Zhang, Proc. SPIE, Astronomical Instrumentation: Optical and Infrared Interferometry **7013**, 1314 (2008).

- [10] L. Labadie, P. Kern, P. labeye, E. LeCoarer, C. Vigreux-Bercovici, A. Pradel, J.-E. Broquin, V. Kirschner, *Advances In Space Research* **41**, 1975 (2008).
- [11] R. Swanepoel, *J. Phys. E, Scientific Instruments* **16**, 1214 (1983).
- [12] S. Danto, P. Houizot, C. Boussard-Pledel, X. H. Zhang, F. Smektala, J. Lucas, *Adv. Funct. Mater.* **16**, 1847 (2006).
- [13] Y. Sripathi, L. K. Malhotra, G. B. Reddy, *Thin Solid Films* **270**, 60 (1995).
- [14] P. Petkov, M. Wuttig, P. Llechev, T. Petkova, J. Optoelectron. Adv. Mater. **5**(5), 1101 (2003).
- [15] A. A. Piarristeguy, E. Barthélémy, M. Krbal, J. Frayret, C. Vigreux, A. Pradel, *J. Non-Cryst. Solids*. Accepted (2009).
- [16] S. Albert, E. Barthélémy, C. Vigreux, A. Pradel, M. Barillot, *Proc. SPIE, Europe Optical Systems Designs: Advances in Optical Thin Films III* **7101**, 71011N (2008).

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