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Co-thermal evaporation: a new method to deposit telluride films

E. BARTHÉLÉMY, C. VIGREUX-BERCOVICI*, P. YOT, A. PRADEL
Equipe Physicochimie des Matériaux Désordonnés et Poreux, Institut Charles Gerhardt, UMR 5253, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

Te-rich films of the Te-Ge-Ga ternary system were deposited by two techniques: the thermal evaporation from glass powder placed in a single source and co-thermal evaporation from the pure elements Te, Ge and Ga placed in three different sources. The last technique was used for the first time to produce chalcogenide films. The composition of the films obtained by thermal evaporation from a single source varied from experiment to experiment indicating the non reproducibility of the procedure. Preliminary results were obtained with the second procedure: Co-thermal evaporation indeed allowed depositing films of the Te-Ge-Ga ternary system with different compositions. Their refractive index and optical band gap were estimated using the transmission spectra recorded in the 400-2500 nm range. Refractive index at 2 μm was situated between 3.5 and 4 and the optical band gap was about 1 eV.

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1. Introduction

Chalcogenide glasses are widely investigated materials due to their unique property of transmission in the infrared. The Te-rich Te-Ge-Ga glasses are particularly attractive for far infrared applications since their transparency can lay up to 28 μm [1]. Among them, the $Te_{75}Ge_{15}Ga_{10}$ glassy composition was highlighted as a very promising material for the fabrication of optical fibres since it is also thermally stable [1].

Such materials could be very interesting for the fabrication of components for integrated optics. In such a case thin films need to be produced. The thermal evaporation, an easy method to implement, has been widely used for the deposition of binary or ternary chalcogenide thin films [2-10]. Two papers indeed report on the deposition of Te-Ge-Ga ternary films using thermal evaporation of glass powders of appropriate composition [2; 3]. In these reports very thin films, i.e. less than 500 nm in thickness, were produced and their optical characteristics studied.

The present work deals with the deposition of thicker Te-Ge-Ga films (1 μm thick or more and therefore more suitable for further development in IR integrated optics). A first series of films was produced by the thermal evaporation of $Te_{80}Ge_{15}Ga_5$, $Te_{75}Ge_{15}Ga_{10}$ and $Te_{75}Ge_{20}Ga_5$ glassy powders on a substrate. A second method of deposition, used for the first time for preparing telluride films, i.e. the co-thermal evaporation of the pure elements Te, Ge and Ga, has been investigated. The preliminary results obtained with this technique are described in the paper.

2. Experimental procedures

$Te_{80}Ge_{15}Ga_5$, $Te_{75}Ge_{15}Ga_{10}$ and $Te_{75}Ge_{20}Ga_5$ bulk glasses were prepared by the melt-quenching technique. Appropriate quantities of high-purity (99.999%) constituent elements were introduced in a quartz ampoule in an Ar-filled glove box (H_2O < 5 ppm). The ampoule was sealed under high vacuum conditions (P # 10^{-3} Pa), heated in a vertical furnace at a 10 °C.h^{-1} rate and kept at 750 °C for 24 h. $Te_{80}Ge_{15}Ga_5$, $Te_{75}Ge_{15}Ga_{10}$ and $Te_{75}Ge_{20}Ga_5$ bulk glasses were obtained after quenching the ampoule in a mixture of water, salt and ice. XRD analysis confirmed the amorphous state of the three samples.

Thermal evaporated (TE) films were deposited from the $Te_{80}Ge_{15}Ga_5$, $Te_{75}Ge_{15}Ga_{10}$ and $Te_{75}Ge_{20}Ga_5$ glasses using an ALCATEL Dion 300 device. The microscope slides used as substrates were cleaned with a commercial DECON detergent, rinsed in alcohol and dried with dry air. The substrate holder was placed at 11 cm above the evaporation tungsten crucible. Glass powder weight was optimised in order to obtain films of 1 μm in thickness. Before deposition, the chamber was evacuated down to approximately 10^{-4} Pa to avoid ambient contamination. Current intensity was progressively increased until total evaporation of the glass powder. Rate of deposition and film thickness were not controlled. During the process, the substrate holder was neither rotated nor heated, but cooled down by water circulation.

Co-thermal evaporated (CTE) films of the ternary system Te-Ge-Ga were deposited from the pure elements Te, Ge and Ga, using a PLASSYS MEB 500 device, equipped with two Joule effect sources and an electron beam. The Joule effect sources were used to evaporate tellurium and germanium, whereas the electron beam was used to evaporate gallium. The three sources were placed in a specific configuration allowing deposition of homogeneous ternary films. Tellurium and germanium grains were placed in two similar homemade carbon crucibles inserted in molybdenum nacelles. Gallium was placed in the electron beam copper crucible. The

microscope slides used as substrates were cleaned with the same procedure as the one used for thermal evaporation. The substrate holder was placed at 25 cm above the evaporation sources. Before the deposition, the chamber was evacuated down to approximately 10^{-5} Pa. The deposition rate and thickness of each element were controlled with a precalibrated quartz cristal monitor. During the process, the substrate holder was rotated and cooled down by water circulation.

Table 1. Theoretical and experimental compositions of bulk glasses and TE films.

Bulk composition		TE film composition (± 0.3)	
theoretical	experimental (± 0.1)	distance 11 cm	
$Te_{80}Ge_{15}Ga_5$	$Te_{81.9}Ge_{13.8}Ga_{4.2}$	$Te_{80.3}Ge_{19.5}Ga_{0.2}$	$Te_{76.5}Ge_{19.8}Ga_{3.7}$
$Te_{75}Ge_{15}Ga_{10}$	$Te_{77.0}Ge_{14.5}Ga_{8.5}$	$Te_{81.7}Ge_{17.4}Ga_{0.9}$	$Te_{75.4}Ge_{18.0}Ga_{6.6}$
$Te_{75}Ge_{20}Ga_5$	$Te_{76.9}Ge_{19.6}Ga_{3.5}$	$Te_{78.8}Ge_{21.0}Ga_{0.2}$	$Te_{81.3}Ge_{18.4}Ga_{0.3}$

Film thickness was calculated by profilometry using a DEKTAK 3 Veeco instrument. The chemical compositions of both bulk glasses and films were estimated using a CAMECA SX100 Electron Probe MicroAnalyser (EPMA). The optical transmittance of the films in the range 400-2500 nm was recorded with an UV-visible spectrophotometer (CARY 5000 from VARIAN). The transmittance spectra were used to measure the band gap energy (E_g) of the films and to evaluate their refractive index at 2 µm.

3. Results

Thicknesses at the centre of the TE films were comprised between 1 and 1.2 µm as expected taking into account the quantity of glass powder which was evaporated. Thickness decreased as the measured area moved away from the centre of the film, following the cosinusoidal law (Eq. 1):

$$d/d_0 = 1/(1+(l/h)^2)^2 \quad (1)$$

where d is the thickness of the film at the measured point, d_0 is the thickness at the film centre, l the distance between the evaporation crucible and the substrate (i.e. 9 or 11 cm depending on the sample) and h the distance between the centre of the layer and the measured area. On the contrary the thicknesses of the CTE films were homogenous all over the film.

The compositions of both bulk glasses and TE films measured by electron microprobe are reported in Table 1 and compared to the theoretical compositions. Several series of TE films were prepared in similar conditions in order to check the reproducibility of the procedure. The results of two of them are shown in Table 1.

As shown in Table 1, the compositions of the TE films were very different from those of the evaporated powders. Moreover two films deposited in similar conditions have different compositions indicating the non-reproducibility of the procedure.

CTE films with different compositions were obtained by varying the rates of deposition of each pure element.

To date, the rate of deposition could only be controlled manually and therefore some fluctuations during the deposition process could not be avoided. The compositions of the CTE films as measured by electron microprobe are given in Table 2.

The transmission spectra of the CTE films were recorded in the range 400-2500 nm. The absorption coefficient α can be calculated from the transmission data T using Eq.2, where d is the film thickness.

$$\alpha = \ln(100/\%T)/d \quad (2)$$

Such data can be used to evaluate the band gap energy E_g by two methods: from the spectral distribution of absorption coefficient α and using Tauc relations [11]. The first method consists in defining the optical band gap $E_g(04)$ as the energy when α equals 10^4 cm^{-1} [12]. The second method consists in estimating the optical band gap energy E_g(Tauc) using Eq.3, considering the high absorption (absorption coefficient $\alpha > 10^4$ cm^{-1}) part of the transmission spectra. In this region:

$$\alpha(\omega) = \beta(\hbar\omega - E_g)^2/\hbar\omega \quad (3)$$

where β is a constant which depends on the transition probability. E_g(Tauc) can thus be obtained by plotting $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ and extending the band-to-band transition region up to a point where $(\alpha\hbar\omega)^{1/2}$ is equal to zero.

Fig. 1 presents a typical transmission spectrum (Fig. 1a), the corresponding spectral dependence of optical absorption coefficient (Fig. 1b) which is allowed to calculate $E_g(04)$ and the Tauc's plot (Fig. 1c) which is allowed to determine E_g(Tauc). The values of $E_g(04)$ and E_g(Tauc) for CTE films are given in Table 2.

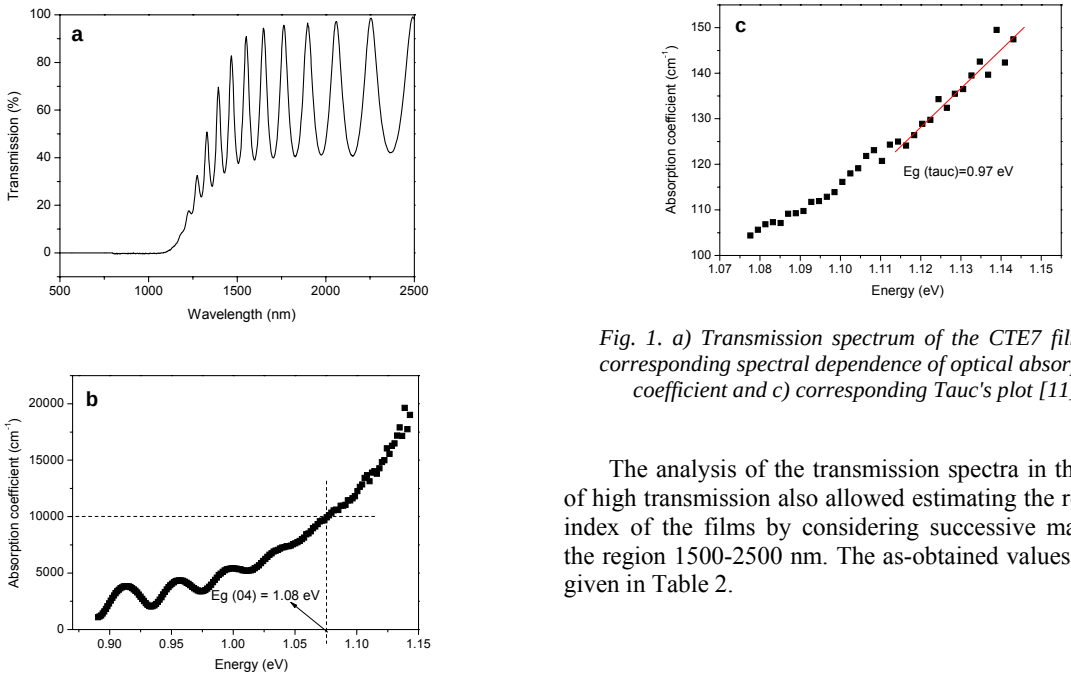

Fig. 1. a) Transmission spectrum of the CTE7 film; b) corresponding spectral dependence of optical absorption coefficient and c) corresponding Tauc's plot [11].

The analysis of the transmission spectra in the region of high transmission also allowed estimating the refractive index of the films by considering successive maxima in the region 1500-2500 nm. The as-obtained values of n are given in Table 2.

Table 2. Composition, thickness, optical band gaps $E_g(04)$ and $E_g(Tauc)$ and refractive index of the CTE films.

Ref	Composition ± 0.1	d (µm) ± 0.05	E_g(04) (eV) ± 0.01	E_g(Tauc) (eV) ± 0.05	n ± 0.03
CTE1	$Te_{74}Ga_{26}$	2.13	1.02	1.03	3.54
CTE2	$Te_{79}Ga_{21}$	2.73	0.98	0.97	3.75
CTE3	$Te_{81}Ga_{19}$	2.10	0.98	0.96	3.79
CTE4	$Te_{84}Ga_{16}$	2.07	0.93	0.90	3.96
CTE5	$Te_{69.0}Ge_{16.3}Ga_{14.7}$	3.32	1.10	0.98	3.56
CTE6	$Te_{72.8}Ge_{14.0}Ga_{13.2}$	2.94	1.08	1.04	3.56
CTE7	$Te_{73.1}Ge_{12.2}Ga_{14.7}$	3.33	1.08	0.97	3.66
CTE8	$Te_{75.8}Ge_{15.4}Ga_{8.8}$	4.51	1.06	1.02	3.65
CTE9	$Te_{75.9}Ge_{13.3}Ga_{10.8}$	2.76	1.06	1.05	3.59

4. Discussion

The deposition of films from the Te-Ge-Ga ternary system was studied. Two methods were used: thermal evaporation from glassy powder of appropriate composition and co-thermal evaporation from the three pure elements Te, Ge and Ga.

The first method had already been used to deposit films from the Te-Ge-Ga ternary system [2;3]. The authors indicated that no significant difference between the composition of the obtained film and that of the evaporated glassy powder could be observed. A different result was obtained in the present work, with an important difference (up to 40 %) between the film and the initial glass compositions as shown in Table 1. Moreover, the thermal evaporation procedure led to non reproducible results for the deposition of Te-Ge-Ga films. Such a finding is different from that obtained in the case of Te-As-Se films. In the last case the same evaporation set-up allowed obtaining films with reproducible compositions close to that of the bulk glass [13]. Such a different behaviour can be explained by the fact that Te, As and Se have close vapor pressures, which is not the case of Te, Ge and Ga

A second deposition method, i. e. the co-thermal evaporation of the elements, was investigated. The obtained films had their thickness comprised between 2 and 4.5 µm. The thickness was homogeneous all over the film, thanks to a rotation of the substrate during deposition. It was possible to obtain films with different compositions, by varying the deposition rates of the three different elements. Note that this new method to deposit chalcogenide films is very convenient to study films of very different compositions of a ternary system, without any synthesis of bulk glass.

The optical band gap and refractive index of the co-thermal evaporated films were measured. The results are given in Table 2. As expected for the Te-Ge binary films, i.e. CTE1, CTE2, CTE3 and CTE4 films, the optical band gap decreases and the refractive index increases when the tellurium content increases. The data obtained for the ternary films are preliminary ones. They only aim at demonstrating the feasibility of ternary telluride films by co-thermal evaporation. Therefore no systematic trend in the composition of the films was looked for to date. However it appears that the optical band gap of the CTE films is in the same order of magnitude than that of the TE films of similar composition ($Ge_{14}Te_{71}Ga_{15}$: $E_g(04)$ = 1.01 eV, $Ge_{18}Te_{72}Ga_{10}$: $E_g(04)$ = 1.07 eV, for example [2]).

5. Conclusions

Two methods were used to deposit Te-rich films of the Te-Ge-Ga ternary system: the thermal evaporation from glassy powder and co-thermal evaporation from the pure Te, Ge and Ga elements. The first method did not allow obtaining reproducible films with composition close to that of the evaporated powder. The second method, used for the first time for chalcogenide films, allowed obtaining films in a wide range of compositions and with similar band gap energies than those of films of same composition obtained by thermal evaporation.

The first results obtained by this new method of deposition of chalcogenide films are very encouraging. Investigation to produce in the future reproducible films with controlled thickness, composition and refractive index is currently in progress. Such a work opens the door to the realisation of integrated optics components based on Te-Ge-Ga thick films able to work in the range [4-20 µm].

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*Corresponding author: cvigreux@lpmc.univ-montp2.fr