Journal of Non-Crystalline Solids 442 (2016) 22–28

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Optical characterization of photosensitive AMTIR-1 chalcogenide thin layers deposited by electron beam deposition

Alexandre Joërg [a], Fabien Lemarchand [a], Mengxue Zhang [b], Michel Lequime [a], Julien Lumeau [a]

[a] Aix Marseille Université, CNRS, Centrale Marseille, Institut Fresnel UMR 7249, 13013 Marseille, France
[b] Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), F-75005 Paris, France

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form 4 March 2016
Accepted 10 March 2016
Available online 8 April 2016

Keywords:
Chalcogenide glass
Optical coating
Photosensitivity
Spectrophotometry

ABSTRACT

Amorphous $Ge_{33}As_{12}Se_{55}$ films have been deposited by electron beam physical vapor deposition and their optical properties have been studied using reverse engineering on spectrophotometric measurements. Definition of the different optical constants was made by Tauc-Lorentz model allowing simultaneous characterization in high and low absorption area. Moreover an investigation of the layer's photosensitivity with an exposure wavelength at ~808 nm has been carried out and reveals a photo-bleaching effect generating up to 0.04 refractive index variation at 1 μm. Finally the stability of the fabricated layers is studied.

1. Introduction

Chalcogenide glasses are now commonly used in different applications such as solar cells, infrared sensors [1] or phase-change memories [2,3]. These glasses consist of chalcogens elements from the sixteenth column of the periodic table (excepted oxygen) covalently bonded to heavy elements such as: As, Ge, Sb, Ga, Te, or Si. Due to their weak inter-atomic bonds, chalcogenide glasses are transparent in the near and the mid-infrared regions of spectrum. For example the sulfides transmit up to 11 μm, selenides up to 15 μm and tellurides up to 20 μm. In addition, chalcogenide glasses were already deposited in thin films to fabricate optoelectronic components [4–6] and ultra-narrow bandpass filters [7]. A striking property of chalcogenide glasses is their photosensitivity [8,9] i.e. the modification of the chemical bonds under an exposure light with wavelength included in the bandgap of the material. Actually, various photo-induced mechanisms were observed in chalcogenide layers such as photoionization [10], photoexpansion [11,12], photodensification [13], photocrystallization [14], amorphisation [15], photodarkening [16,17] or photobleaching [18]. These effects have been widely studied to create active optical interference filers [19,20] or to write Bragg grating in planar waveguides [21–24].

In this work we have investigated the deposition of $Ge_{33}As_{12}Se_{55}$ thin films. This glass has been selected due to its commercial availability and known photosensitivity. Some previous works have already shown that it can be deposited into thin films using by pulsed laser deposition [25–27] or thermal evaporation [28–30] or electron beam deposition (EBD) [31], because it allows producing homogeneous thick and large aperture films that will be compatible with the production of multilayer optical interference filters. Using reverse engineering coupled with a Tauc Lorentz model, the optical properties of single layers were determined and a precise study of the photosensitive effects is presented. Finally a systematic study of the stability of the fabricated films is performed, showing that these layers are compatible with the production of complex optical elements.

2. Experiments

Chalcogenide glasses with composition $Ge_{33}As_{12}Se_{55}$ and commonly known as AMTIR-1 were used in this study. These glasses were produced by the Amorphous Material Company. Cylindrical samples with 25 mm diameter and thickness of about 12 mm were placed on a Mo liner inside a BALZERS BAK600 system with residual pressure within the chamber of ~10^{-6} mBar. Thin single-layers were fabricated by EBD on fused silica substrates which were cleaned in an ultrasonic bath. Various films with thicknesses ranging between 300 and 700 nm were fabricated. AMTIR-1 having a low glass transition and melting temperatures (e.g. T_g = 362 °C), very low and stable deposition rate could not be achieved. The deposition rate was thus set to 10 A/s and was controlled by an Inficon quartz crystal monitor XTC/2. This speed allowed securing stable deposition speed with fluctuations not exceeding ± 20% after optimizing the PID parameters.

Transmission and reflection spectra of each single-layer were measured with a Perkin Elmer Lambda 1050 spectrophotometer in the spectral range from 600 to 1800 nm at an angle of incidence of 8°. A special module from OMT solutions was used to perform this measurement. This module allows accurate and absolute measurement of both transmission and reflection spectra of a sample, without moving or replacing

http://dx.doi.org/10.1016/j.jnoncrysol.2016.03.018
0022-3093/

the sample and without reflection etalons as transmission baseline is used to both calibrate the transmission and reflection spectra. Such a system is crucial for obtaining high accuracy measurements and determinations of the optical properties of the layers. Typical precision of the measured transmission and reflection intensity is no larger than 0.1%. Composition of the thin films compare to the bulk material was also studied using Energy-dispersive X-ray spectroscopy (EDS).

AMTIR-1 being a photosensitive material, kinetics of refractive index change on dosage of actinic radiation were studied. Radiation from a 200 μm-fiber-coupled laser diode centered at 808 nm, with a spectral bandwidth of 2 nm and a beam diameter of 10 mm was used to perform exposure. Power density in place of the sample was 15 W/cm^2. Samples were exposed with dosages up to 1.1×10^2 kJ/cm^2. Between exposures, samples were kept into dark boxes in order to secure that no parasitic exposure from external source would modify the layers properties. After each exposure, reflection and transmission spectra were measured using the procedure that was described above. Customs algorithms were finally developed in order to extract the optical parameters of the single layers: the refractive index dispersion $n(\lambda)$, the extinction coefficient dispersion $k(\lambda)$, the thickness t, and the bandgap E_0.

3. Determination of AMTIR-1 single layer optical constants

3.1. Tauc-Lorenz model

We used reflection and transmission spectra measured on AMTIR-1 single layers to determine their optical constants. Typical spectra measured on a 500 μm thick layer is presented in Fig. 1. One can see two distinct regions, one above 700 nm that presents oscillations of the signal, typical of the interferences occurring within the layer, and a second region below 700 nm, where the layer presents high absorption. Optical constants of thin film materials, are generally determined using the Swanepoel method [32]. This method involves determining the envelopes T_M and T_m describing respectively the spectral dependence of the amplitude of the maxima and the minima of the measured interference pattern. This method provides with a simple method for evaluating the constants of single layers in low absorbing regions i.e. where $k << 0.01$. However, as illustrated on Fig. 1, AMTIR-1 thin films have large absorption in the spectral regions below 900 nm due to intrinsic absorption of the glass matrix. In addition, this study is intended to provide an accurate determination of the optical properties of these layers that will be further used for the design of complex multilayer filters. To achieve, the Tauc-Lorentz (TL) [33–36] method was implemented for modeling the dispersion of optical constants. It is important to stress that this method was shown to be an accurate method for modeling interband absorption [37] and high absorbing optical coating materials [38], e.g. silicon (Si) [39,40], hydrogenate silicon (a-Si:H) [41].

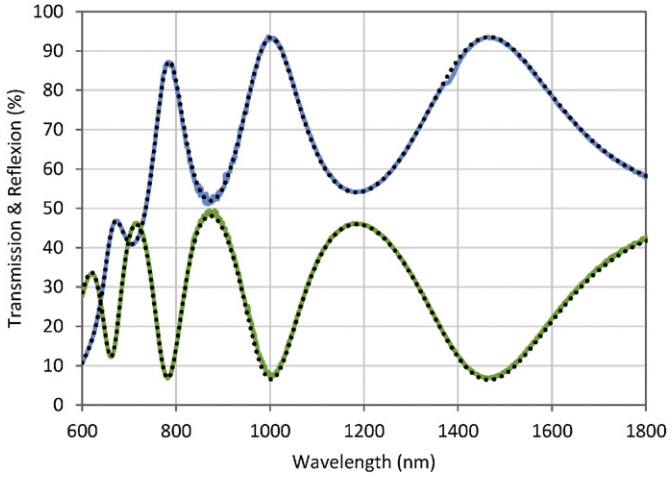

Fig. 1. Measured and theoretical (resulting from TL fitting) spectral dependences of the transmission and reflection of an AMTIR-1 single layer.

TL optical model is derived from Kramers-Kronig [42] expression where electric permittivity can be express as:

$$\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$$

and N the complex refractive index is linked with electric permittivity by the following formula:

$$\varepsilon(E) = N(E)^2 = (n(E) + ik(E))^2.$$

Real and imaginary part of electric permittivity $\varepsilon_1(E)$ and $\varepsilon_2(E)$ are given by:

$$\varepsilon_2(E) = \begin{cases} \sum_{i=1}^{q} \frac{A_i E_{0i} C_i (E-E_{TL})^2}{\left(E^2-E_{0i}^2\right)^2 + C_i^2 E^2} \frac{1}{E}, & E > E_{TL} \\ 0, & E \le E_{TL} \end{cases}$$

$$\begin{aligned} \varepsilon_1(E) = \varepsilon_\infty + \sum_{t=1}^{q} & -A_i E_{0i} C_i \frac{E^2+E_{TL}^2}{\pi \varsigma_{4i} E} \ln\left(\frac{|E_{TL}-E|}{E_{TL}+E}\right) \\ & + \frac{2A_i E_{0i} C_i E_{TL}}{\pi \varsigma_{4i}} \ln\left(\frac{|E_{TL}-E|(E_{TL}+E)}{\sqrt{\left(E_{0i}^2-E_{TL}^2\right)^2 + C_i^2 E_{TL}^2}}\right) \\ & + \frac{A_i C_i a_{Li}}{2\pi \varsigma_{4i} \alpha_i E_{0i}} \ln\left(\frac{E_{0i}^2+E_{TL}^2+\alpha_i E_{TL}}{E_{0i}^2+E_{TL}^2-\alpha_i E_{TL}}\right) \\ & - \frac{A_i \alpha_{Ai}}{\pi \varsigma_4 E_0}\left[\pi - \arctan\frac{2E_{TL}+\alpha_i}{C_i} - \arctan\frac{2E_{TL}-\alpha_i}{C_i}\right] \\ & + 4A_i E_{0i} E_{TL} \frac{E^2-\gamma_i^2}{\pi \varsigma_{4i} \alpha_i}\left[\frac{\pi}{2} - \arctan\frac{2\left(E_{TL}^2-\gamma_i^2\right)}{\alpha_i C_i}\right] \end{aligned}$$

where:

$$a_{Li} = \left(E_{TL}^2 - E_{0i}^2\right)E^2 + E_{TL}^2 C_i^2 - E_{0i}^2\left(E_{0i}^2 + 3E_{TL}^2\right)$$

$$\alpha_{Ai} = E^2 - E_{0i}^2\left(E_{0i}^2 + E_{TL}^2\right) + E_{TL}^2 C_i^2$$

$$\gamma_i = \left(E_{0i}^2 - \frac{C_i^2}{2}\right)^{1/2}$$

$$\alpha_i = \left(4E_{0i}^2 - C_i^2\right)^{1/2}$$

$$\varsigma_{4i} = \left(E^2 - E_{0i}^2\right)^2 + C_i^2 E^2.$$

In case of AMTIR-1 single layers, the parameters of interest are: E_{TL}, the bandgap energy of the materials, E_0, the central peak of energy, C the broadening parameter, A the amplitude, ε_∞ the high frequency dielectric constant and t the thickness. The total number of parameters to determine is equal to $p = 3$ (E_{TL}, ε_∞, t) + 3q (A_i, C_i, E_{0i}) where q is the number of oscillators used in Tauc-Lorentz formalism. Generally, the q parameter is equal to one, e.g. for Ta_2O_5 [39], HfO_2 [43], but sometimes, increasing the number of oscillators is required in order to get an optimal estimation of optical functions, e.g. Ag_2O [44]. However, one must keep in mind that like in any other mathematical decomposition of a physical curve, the number of free parameters must be kept to minimum in order to provide an error function between model and experimental curve equal to the measurement precision.

Optimization of the model was performed using Matlab and more precisely the programmed "fmincon" function. This algorithm allows for searching the minimum of constrained functions. As it's an optimization program, a converging error function (EF) needs to be defined. A