Optical properties of chalcogenide Ge-Te-In thin films

A Zaidan1,2,3, V Ivanova1 and P Petkov1

1 Thin Film Technology Laboratory, Department of Physics, University of Chemical Technology and Metallurgy, 8, Kl. Ohridski Blvd., 1756 Sofia, Bulgaria
2 Department of Physics, Faculty of Science and Technology, Airlangga University, 60115 Surabaya, Indonesia
E-mail: zaidan@unair.ac.id

Abstract. Thin films of the chalcogenide (GeTe)1-xInx with various compositions (x = 0, 5, 10, 15, 20 at %) were deposited under vacuum on glass substrates by thermal evaporation. The optical transmission and reflection spectra of the films at normal incidence were investigated in the spectral range from 800 to 2600 nm. Using the transmission spectra, the optical constants (refractive index (n) and extinction coefficient (κ)) were calculated based on Swanepoel’s method. The optical band gap (Eg_opt) was also estimated using Tauc’s extrapolation procedure.

1. Introduction
Chalcogenide glasses have received much consideration because of their interesting applications in optics, optoelectronics and electronics due to their unique properties (optical transparency in the infrared region, high refraction index, low phonon energies). Chalcogenide glasses applications include phase-change materials [1, 2, 3, 4], sensors [5, 6], optical circuits, gratings, waveguides [7, 8, 9], and many others.

Chalcogenides based on Ge-Te have been extensively studied by many authors because of their potential for use as phase-change materials for optical recording. The Ge-Te system has the ability to form glasses at timescales and temperatures that are appropriate for certain data-transfer rates and laser powers available [10].

In the present study, thin films of the system (GeTe4)1-xInx with x = 0, 5, 10, 15, and 20 at % were deposited by thermal evaporation onto floatglass substrates. The transmission and reflection spectra of the thin films were measured. Using the transmission spectra, the optical constants and film thickness were determined using Swanepoel’s method. The absorption coefficient and the optical band gap were also estimated and discussed.

2. Experimental details

2.1. Sample preparation and characterization
Various compositions of bulk samples of the system (GeTe4)1-xInx with x = 0, 5, 10, 15, and 20 at % were prepared by melt quenching using 5N purity elements of Ge, Te and 4N purity of In. All

3 To whom any correspondence should be addressed.
elements were heated in evacuated ampoules at a constant heating ratio of 3 K/min up to 1200 K. Finally, the ampoules were quenched into ice-cooled water to avoid crystallization.

All thin films in this study were deposited by conventional thermal evaporation at a residual gas pressure of $1.33 \times 10^{-4}$ Pa and temperature 800-900 K onto floatglass substrates using the respective bulk composition as a source material. The thickness of the films obtained was about 400-600 nm. The transmission and reflection spectra of the thin films were measured using a Jasco UV-VIS-NIR spectrophotometer (Model V-670) at room temperature in the wavelength range from 800 nm to 2600 nm.

2.2. Calculation of the thickness, optical constants, absorption, and optical band gap

The optical constants (refractive index, $n$, and extinction coefficient, $\kappa$) of the thin films were determined based on a method proposed by Swanepoel [11], which use the interference fringes from the optical transmission data. In this method, the thin film considered is a homogeneous and uniform film with thickness $d$, refractive index $n$ and absorption $\alpha$ deposited on a thick transparent substrate. The transparent substrate has thickness several orders of magnitude larger than $d$, refraction index $n_s$ and absorption coefficient $\alpha_s = 0$.

Swanepoel [11] has shown that the transmittance $T$ of a uniform thin film of thickness $d$, refractive index $n$, and absorption coefficient $\alpha$, deposited on a substrate with a refractive index $n_s$, is given by:

$$T = \frac{Ax}{B + Cx \cos \phi + Dx^2},$$

where $A = 16n^2n_s$, $B = (n + 1)^3$, $C = 2(n^2 - 1)(n^2 - n_s^2)$, $D = (n^2 - 1)^3(n - n_s^2)$, $\phi = 4\pi nd/\lambda$ and $x = \exp(-\alpha d)$. From equation (1), the transmission values at maxima and minima of the interference fringes can be obtained by setting the interference condition $\cos \phi = 1$ for maxima ($T_M$) and $\cos \phi = -1$ for minima ($T_m$). Using $T_M$ and $T_m$, approximate value of the optical constants, film thickness and absorption coefficient can be obtained [11].

3. Results and discussion

3.1. Transmission spectra and refractive index of the thin films

Transmission spectra of the system $(\text{GeTe}_4)_{1-x}\text{In}_x$, with $x = 0, 5, 10, 15$, and 20 at % in the wavelength range from 800 nm to 2600 nm are shown in figure 1. It is obvious that the system is transparent in the near infrared and infrared ranges and has transmission spectra edge from 900 nm to 1200 nm. This infrared transmittance behavior can be explained by the high percentage of tellurium in the system. It is known that most glasses containing tellurium are opaque in the visible region and have a wide transparency range in the infrared region [12]. The wide infrared region is the reason why the transmission of the system $(\text{GeTe}_4)_{1-x}\text{In}_x$ in the wavelength range from 800 nm to 2600 nm is only up to 85 %.

Using the transmission spectra, the optical constants and the thickness of the films were calculated numerically using the PUMA (Pointwise Unconstrained Minimization Approach) code [13]. The
numerical calculation of the refractive index shows that for the chalcogenide system (GeTe4)\(_x\)In\(_x\) with \(x = 0, 5, 10, 15, \) and 20 at \%, the refractive index in the wavelength range from 1000 nm to 2600 nm is following an exponential relation. At 2600 nm, our thin films have high refractive index (2.41 < \(n\) < 3.36). This makes Ge-Te-In films suitable for infrared optics applications, such as waveguides in the infrared region. The thin Ge-Te-In film has a high refractive index because it contains germanium which has a very high refractive index in the infrared region and is one of the most common infrared materials.

3.2. Absorption coefficient and optical band gap

The absorption coefficient of thin films can be obtained using the extinction coefficient, \(k\), and the expression \(\alpha = 4\lambda k / \lambda\).

The absorption spectra in figure 2 show that absorption is lower at higher wavelengths and almost zero in the infrared region. This perfectly makes sense due to the film transparency in the infrared region. Using the absorption coefficient obtained, the optical band gap can be calculated by means of Tauc’s equation [14]:

\[
\alpha h\nu = B (h\nu - E_{opt}^{\text{gap}})^n,
\]

where \(B\) is a parameter that depends on the transition probability, \(E_{opt}^{\text{gap}}\) is the optical band gap energy and \(n\) is equal to 1/2 for allowed direct optical transitions and 2, for indirect transitions. The results of the optical band gap calculation are summarized in table 1.

Generally, for the system (GeTe4)\(_x\)In\(_x\), the optical band gap value decreases upon adding indium from 0% to 20%. This decrease suggests a structural change in the films. Another reason for the decrease may be the generation of an impurity band because of indium doping in the band tails region. The impurity band merges with the conduction or valence band and causes the formation of a new band tail. This new formation of a band tail narrows down the band gap.

Conclusions

The study of the optical properties of chalcogenide systems (GeTe4)\(_x\)In\(_x\) with \(x = 0, 5, 10, 15, \) and 20 at \% shows that the thin films are opaque in the visible region and highly transparent in the near infrared and infrared region. The refractive index of the films is high (2.41 < \(n\) < 3.36) and follows an exponential relation in the wavelength range from 1000 nm to 2600 nm. The films’ optical band gap depends on the composition; its value decreases from 0.84 eV to 0.41 eV upon the addition of indium from 0% to 20%.

References

[1] Boniardi M et all 2011 Solid-State Electr. 58 11-6
[2] Sousa V 2011 Solid-State Electr. 88 807-13
[3] Kozyukhin S A, Popov A I and Voronkov E N 2010 *Thin Solid Films* **518** 5656-8
[4] Abrutis A, Plausinaitiene V, Skapas M, Wiemer C, Salicio O, Longo M, Pirovano A, Siegel J, Gawelda W, Rushworth S and Giesen C 2008 *Microelectron. Eng.* **85** 2338-41
[5] Kolev K, Popov C, Petkova T, Petkov P, Mihailescu I N and Reithmaier J P 2009 *Sensors and Actuators B: Chemical* **143** 395-9
[6] Vassilev V S and Boycheva S V 2005 *Talanta* **67** 20-7
[7] Rode A V, Zakery A, Samoc M, Charters R B, Gamaly E G and Luther-Davies B 2002 *Appl. Surf. Sci.* **197/8** 481-5
[8] Hu J, Tarasov V, Carlie N, Petit L, Agarwal A, Richardson K and Kimerling L 2008 *Optical Mater.* **30** 1560-6
[9] Florea C, Sanghera J S and Aggarwal I D 2008 *Optical Mater.* **30** 1603-6
[10] Meinders E R, Mijiritskii A V, van Pieter son L and Wuttig M 2006 *Optical Data Storage Phase-Change Media and Recording* (Dordrecht Springer)
[11] Swanepoel R 1983 *J. Phys. E: Sci. Instrum.* **16** 1214
[12] Ray Hilton A 2010 *Chalcogenide Glasses for Infrared Optics* (New York The McGraw-Hill)
[13] Birgin E G, Chambouleyron I and Martnez J M 1999 *J. Computational Phys.* **151** 862
[14] Morigaki K 2010 *Physics of Amorphous Semiconductors* (London Imperial College Press)