Influence of hydrogen incorporation on the optical properties and crystallization of GeTe₂ thin films

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Thin films of GeTe₂ were deposited on glass substrates using radio-frequency magnetron sputtering with various hydrogen flow rates in the growth chamber. Transmission data of deposited films were taken and used to determine optical constants [refractive index (n), extinction coefficient (k), and absorption coefficient (α)] and the energies corresponding to absorption coefficients of 10⁴ and 10⁴ cm⁻¹ (E₀₁, E₀₃), Tauc band gap Eₜauc, and Urbach energy Eₚ. An increase in these energies was observed as a function of the hydrogen flow rate. An increase in the disorder in the hydrogenated GeTe₂ thin films was determined from Tauc’s slope B¹/² parameter, Urbach energy, and full width at half maximum of Raman vibrational modes. Crystallization of GeTe₂ occurs via a phase separation into Te and GeTe crystalline phases. The crystallization temperature increases with the addition of hydrogen. A large change (~60% decrease) in the optical transmission occurs after the phase change from amorphous to crystalline. © 2008 American Institute of Physics.

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I. INTRODUCTION

Chalcogenide glasses are an important class of amorphous semiconductors. They are recognized as promising materials for infrared optical elements, infrared optical fibers, xerography, switching and memory devices, photolithography and in the fabrication of inexpensive solar cells, and more recently for reversible phase-change optical recording. Ge₂Sb₂Te₅ has attracted interest in recent years because it has applications in phase-change memories and optical disks. In the phase diagram of GeSbTe alloys, there are two pseudobinary tie lines passing through Ge₂Sb₂Te₅:GeTe₂−Sb₂Te and GeTe₂−Sb₂Te₅. Therefore, the studies of the properties of these pseudobinary compounds help us to understand the properties of Ge–Sb–Te compounds, particularly Ge₂Sb₂Te₅. In this work, we present a study of the optical properties of GeTe₂ as well as the influence of hydrogen on these properties. To the best of our knowledge, there is only one early report about the properties of GeTe₂ thin films and none on the influence of hydrogen on the optical properties of GeTe₂ thin films, which is presented and discussed in this work. The properties studied in this work are the Tauc band gap, refractive index, and extinction and absorption coefficients. The other aim of the present work is to investigate the crystallization under thermal annealing of amorphous GeTe₂ thin films and to study how the addition of hydrogen modifies the crystallization process. The change in optical properties of GeTe₂ thin films after amorphous-crystalline transformation is also studied.

II. EXPERIMENTAL DETAILS

Amorphous films of GeTe₂ were deposited on borosilicate glass substrates at room temperature by radio-frequency (rf) magnetron sputtering at 13.56 MHz using an AJA ORION system in a sputter-up configuration. Each substrate was hand washed with acetone and methanol and blow dried with high purity nitrogen gas. The GeTe₂ target was supplied by AJA International with a purity of 99.99%. The base pressure of the sputtering system was (2–3) × 10⁻⁶ Torr and the pressure in the chamber during the deposition was 3 mTorr with a sputtering power of 75 W. The growth rate under these conditions was 2–3 Å/min as recorded by the single crystal thickness monitor Maxtek TM-350. The resulting films had thicknesses of 1–3 μm. Ar and hydrogen gas flows were controlled using mass flow controllers. The argon flow was kept at 13 SCCM (SCCM denoted cubic centimeter per minute at STP) while the addition of hydrogen injected into the chamber was varied between 0.5 and 2.0 SCCM.

X-ray diffraction (XRD) results were obtained using Bruker AXS D8 Focus x-ray diffractometer system with scanning speed of 1°/min. The as-grown sample films were characterized by XRD measurements and found to be amorphous in nature as no prominent peak was observed in the spectra. Energy-dispersive spectroscopy measurements, performed in an Oxford INCA X-sight spectrometer, verified that the composition of deposited films was GeTe₂. The normal incidence transmission measurements were performed at room temperature (300 K) in the photon energy range 0.75–1.25 eV. Room temperature Raman spectroscopy measurements were taken with a micro-Raman system, LabRAM HR from JY-Horiba, using a spot size of 2 × 2 μm² and a 632.81 nm HeNe laser.

To investigate the crystallization temperature of GeTe₂ thin films, the samples prepared with various hydrogen flow rates were annealed for 30 min. at several temperatures, either up to 500 °C or until XRD patterns indicated complete crystallization. The heat treatment process was carried out under a vacuum of 10⁻⁶ Torr in order to minimize oxidation of the investigated thin films.

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III. RESULTS AND DISCUSSION

A. Optical band gap

Figure 1 shows the optical transmission spectra of non-hydrogenated and hydrogenated GeTe$_2$ thin films. The interference fringes in the plot proved the film thickness uniformity. The transmission spectrum shifts to a higher photon energy region with increasing hydrogen flow rate into the vacuum chamber during deposition. The transmission data were used to determine the optical constants [refractive index ($n$) and extinction coefficient ($\kappa$)] using the method suggested by Swanepoel.\textsuperscript{12-14} This data analysis was done using a computer program based on unconstrained optimization.\textsuperscript{15} The obtained refractive index and extinction coefficient, as a function of the hydrogen flux in the growth chamber are presented in Figs. 2(a) and 2(b), respectively. The absorption coefficients were obtained from extinction coefficients according to the equation $\alpha = 4\pi \kappa / \lambda$, where $\alpha$ is the absorption coefficient, and $\lambda$ is the wavelength. Figure 3 shows a plot of the absorption coefficient versus incident photon energy, from which we determined the values for $E_{04}$ and $E_{03}$ in order to examine the effect of hydrogen incorporation. $E_{04}$ and $E_{03}$ are defined as the energy corresponding to absorption coefficients of $10^4$ and $10^5$ cm$^{-1}$, respectively. Figure 4(a) shows the values corresponding to $E_{04}$ and $E_{03}$ in hollow triangles and squares, respectively. Although $E_{04}$ and $E_{03}$ are commonly used, they do not provide further information about the structural properties of the material. For this reason, it is more favorable to use Tauc’s optical band gap as given by\textsuperscript{16}

$$(\alpha \hbar \omega)^{1/2} = B^{1/2}(\hbar \omega - E_{\text{Tauc}}),$$

where $B^{1/2}$ is the Tauc parameter, $E_{\text{Tauc}}$ is the Tauc band gap, and $\hbar \omega$ is the incident photon energy. The Tauc parameter $B^{1/2}$ is a measure of the steepness of density of states (DOS) band tail. High values of $B^{1/2}$ are due to less structural disorder.\textsuperscript{17,18} Figure 4(b) shows a plot of $(\alpha \hbar \omega)^{1/2}$ versus photon energy $\hbar \omega$. The Tauc band gap, $E_{\text{Tauc}}$, can be obtained by extrapolating the linear portion of this curve to the $x$-axis (Tauc extrapolation).\textsuperscript{19} The results are shown in Fig. 4(a) in solid dots.

Tauc’s plot is based on the assumption that transition matrix element, $p_{ex}$, is independent of the energy and that the DOS in the conduction and valence bands have a three-dimensional (3D) character (parabolic dependence on the energy).\textsuperscript{20} Some authors\textsuperscript{21} argued that $p_{ex}$ is energy independent, however others pointed out that the matrix element has energy dependence.\textsuperscript{22} In the last case and assuming that the DOS in the conduction and valence bands are 3D, $(\alpha / \hbar \omega)^{1/2}$ and not $(\alpha \hbar \omega)^{1/2}$, will have a linear dependence on the photon energy.\textsuperscript{20} We investigated the dependence of $(\alpha / \hbar \omega)^{1/2}$ on the photon energy and found that the dependence is not
linear. It is therefore concluded that the matrix element of GeTe₂, \( p_{cv} \), does not depend on the energy and Tauc’s plot is appropriate for this material.

The values of \( E_{04} \), \( E_{03} \), and \( E_{\text{Tauc}} \), summarized in Fig. 4(a), show the increase in the optical band gap with increasing hydrogen incorporation. This behavior is explained on the basis of the DOS model.²¹ According to this model, chalcogenide thin films always contain a high concentration of unsaturated bonds or defects, which are responsible for the presence of localized states in the amorphous band gap. The incorporation of hydrogen produces a large number of saturated bonds and reduces the number of unsaturated bonds, which decrease the density of localized states in the band structure and consequently increase the optical band gap.

B. Network disorder: Urbach energy, \( B^{1/2} \), and Raman full width at half maximum

In the low absorption region (\( \alpha < 10^4 \text{ cm}^{-1} \)), known as the Urbach edge region, the absorption coefficient increases exponentially with energy and it is described by \( \alpha \propto \exp(h\omega/E_U) \), where \( E_U \) is the Urbach edge energy. This energy is related to the width of the localized tail states and it is considered a measure of the total disorder in the amorphous material.²² The top part of Fig. 5 shows a plot of the Urbach edge energy versus the Tauc slope \( B^{1/2} \) parameter. In order to correlate these two parameters, \( B^{1/2} \) and \( E_U \), with the network disorder, we have studied their relationship with the full width at half maximum (FWHM) of Raman modes. The

Raman spectra of the GeTe₂ samples presented two vibrational modes at 117 and 138 cm⁻¹. The data presented in the middle and in the bottom part of the Fig. 3 correspond to the FWHM of the peaks at 117 and 138 cm⁻¹, respectively, as a function of the \( B^{1/2} \) parameter. According to Fig. 5, the introduction of hydrogen (flow rate < 2.0 SCCM) into the amorphous GeTe₂ increases the network disorder, the Urbach edge energy \( E_U \) and the FWHM of Raman modes, while it decreases \( B^{1/2} \). Also, the straight lines shown in this figure indicate a linear relationship between \( E_U \), \( B^{1/2} \), and the FWHM of Raman modes.

C. Annealing effects on optical transmission and crystallization process

The crystallization process and its effects on the optical and electrical properties of chalcogenide materials are important in applications such as information storage by either optical or electrical means. We have studied the crystallization process of the GeTe₂ films as a function of the annealing temperature and flux of hydrogen in the chamber during the deposition process. Figure 6 shows the transmission spectra of a 1 \( \mu \text{m} \) thick GeTe₂ film, grown under a 1 SCCM flux of hydrogen, before annealing and after complete crystallization. These data show that GeTe₂ films have extremely low transmission in the spectral region 0.75–1.25 eV after

![FIG. 4. (a) Band gaps as a function of hydrogen flow rate. (b) Plot of \((\alpha h\omega)^{1/2}\) as a function of photon energy.](image)

![FIG. 5. Plot of Urbach edge energy (square), FWHM of Raman mode at 117 cm⁻¹ (circle), and 138 cm⁻¹ (triangle) vs Tauc slope parameter \( B^{1/2} \).](image)

![FIG. 6. Transmission spectra for a 1 \( \mu \text{m} \) thick GeTe₂ film grown with 1 SCCM hydrogen flow rate before and after annealing.](image)
amorphous-crystalline transformation. This great transmission contrast in the spectral region 0.75–1.25 eV after phase change was also observed for other hydrogenated and nonhydrogenated GeTe$_2$ samples (not shown here). For the GeTe$_2$ film grown with the highest hydrogen flow rate, 2 SCCM, the transmission spectrum remained the same as the one before annealing because the substrate softening temperature did not allow us to attain the crystallization temperature in this case. This agrees with the XRD results which showed that the film did not crystallize at temperatures lower than 500 °C.

In order to investigate the details of the crystalline phase producing the large transmission contrast, XRD studies and computer simulations of the transmission, reflectivity, and absorption were performed. Figure 7 shows the XRD spectra corresponding to a GeTe$_2$ film with 1 SCCM hydrogen flow rate. Similar spectra were observed for other samples. This graph indicates that the sample remains amorphous up to 300 °C and partially crystallizes with increasing annealing temperature from 350 to 400 °C, as indicated by the intensity increase of the peaks between 23° and 30°. The complete crystallization was monitored by tracking whether or not significant changes in the peaks intensity were occurring and therefore was determined to have occurred at annealing temperatures between 450 and 480 °C. The analysis of the XRD data in Fig. 7 reveals a phase separation during the crystallization process. The identified crystalline phases are the following: (i) Te phase with hexagonal structure of unit cell constants $a=4.445$ Å and $c=5.910$ Å and (ii) GeTe rhombohedral structure of lattice constants $a=8.427$ Å and $c=10.710$ Å. These unit cell constants are in agreement with previous reports. The phase separation in GeTe$_2$ system occurs because only one Te atom is required for GeTe phase and the other Te atom is left to form an elemental phase. The phase separation was also observed in nonhydrogenated GeTe$_2$ films which are not shown here.

Crystalline GeTe and Te have optical gaps of 0.2 and 0.335 eV, respectively, and hence a large absorption in the spectral range 0.75–1.25 eV is expected. Figure 8 shows the experimental transmission, and calculated reflectivity and absorption for the sample without hydrogen incorporation before the phase separation. The reflectivity and absorption coefficients presented in Fig. 2. After the phase separation, the transmission, reflectivity, and absorption have to be calculated using the effective medium approximation. However, the optical constants $(n, k)$ for crystalline GeTe are only available for wavelengths shorter than 0.83 μm, therefore in our calculations (Fig. 9) we used only the optical constants of tellurium to approximate the constants of the crystallized film. A comparison of the transmission presented in Figs. 6 and 9 shows that the use of the optical constants of tellurium is reasonable and allows us to conclude that an increase in both the reflectivity (∼10%) and the absorption (∼20%) occur due to the phase change. Due to this reason, a large transmission decrease was observed after the amorphous-crystalline transformation, as shown in Fig. 4.

XRD results for nonhydrogenated GeTe$_2$ films showed a crystallization temperature of 350 °C, while hydrogenated GeTe$_2$ films grown with 2 SCCM hydrogen flow rate did not crystallized up to temperatures as high as 500 °C. No higher temperatures were investigated due to the limitations imposed by the substrate softening temperature (550 °C). From the XRD experiments, we observed that the crystallization temperature of GeTe$_2$ films increases monotonically with the hydrogen flow rate used in the film growth. This increase in crystallization temperature can be interpreted in terms of...
dangling bonds. The incorporated hydrogen atoms in the films reduce the density of dangling bonds available for re-engagement during the crystallization and consequently increase the crystallization temperature. Therefore, as hydrogen concentration increases, crystallization temperature shifts to a higher temperature.

IV. CONCLUSION

This work presented the effect of hydrogen incorporation on the optical properties and crystallization temperature of sputtered GeTe$_2$ films. The optical gaps ($E_{04}, E_{03}$, and $E_{\text{Tauc}}$), Urbach energy $E_U$, and FWHM of Raman modes increase while the Tauc parameter $B^{1/2}$ decreases with increasing hydrogen flow rate from 0.5 to 2 SCCM. According to the FWHM of Raman modes, the inclusion of hydrogen atoms into the amorphous GeTe$_2$ network produces more disorder. There have been observed linear relationships between the Raman FWHM, $B^{1/2}$ and $E_U$. Our investigated nonhydrogenated GeTe$_2$ films have a crystallization temperature of 350 °C. The crystallization temperature shifts to a higher temperature with increasing hydrogen flow rate in the growth chamber because the incorporated hydrogen atoms reduce the density of dangling bonds available for the network re-arrangement. Phase separation has been observed in both nonhydrogenated and hydrogenated GeTe$_2$ films. The identified crystalline phases are hexagonal structure Te phase and rhombohedral structure GeTe phase. After amorphous-crystalline transformation, both nonhydrogenated and hydrogenated GeTe$_2$ films experienced large transmission decrease (~60%) in the spectral region 0.75–1.25 eV due to the narrow band gaps of the constitutive crystalline phases and the associated increases in reflectivity and absorption.

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