Microwave Irradiation Effects on Structural and Optical Investigations of Nanostructured Ge$_{25}$Se$_{75}$ Glassy Films

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Received: 31.01.2020 & Accepted: 22.04.2020
Doi: 10.12693/APhysPolA.138.434
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Ge$_{25}$Se$_{75}$ binary glass is prepared using melt-quenching technique. Thin films of 250 nm Ge$_{25}$Se$_{75}$ are thus evaporated using thermal evaporation method on a cleaned glass substrate. Energy dispersive X-ray analysis confirmed the starting percentage of the element. The effect of microwave irradiation on Ge$_{25}$Se$_{75}$ thin film with different illumination times (0–90 min) is studied. As confirmed by X-ray diffraction and scanning electron microscopy measurements, the nature of the as-prepared Ge$_{25}$Se$_{75}$ thin films appears to be amorphous. The type of optical transition has been demonstrated to be allowed indirect transitions. Moreover, the rest of the optical parameters have changed as a result of the microwave irradiation. It can be observed that, for Ge$_{25}$Se$_{75}$ thin films, the optical band gap increases as the illumination time increases. In terms of bond adjustments and changes in these films’ microstructure, this post-light increment in the band gap was decoded. Furthermore, while increasing the illumination time of microwave irradiation, the dispersion parameters of Ge$_{25}$Se$_{75}$ films were diminished.

1. Introduction

Chalcogenide glasses consist of group VI components (S, Se, and Te) in the periodic table. These glasses can be regarded to be semiconductor materials [1]. Recently, these glasses are gaining an increasing interest owing to their potential applications in solid-state electronic and optical devices, such as phase-change optical recording, optical imaging, memory exchanging, nondirect optics, and photolithography [2]. Ge–Se is a common chalcogenide semiconductor, which can be effectively arranged either in glass or in crystalline structure. Recently, numerous researches on Ge–Se glass have been conducted to examine rigidity percolation and short and transitional range order of the structure [3–5]. The microwave energy has become an intriguing branch for studying [6–8]. The developing interest during the past decade is basically due to the plausibility of assembly, cost reduction through energy reserve, shorter preparation times, and improved product consistency and yields. For the most part, microwave processing differs in that the heat is created within the material rather than in an external heating source, a reality that is responsible for the one of a kind microstructure and consistency. Microwave processing has been employed in annealing ferroelectric films [9]. Microwave irradiation has shown rapid development in its application in material science owing to its unique response impacts, for example, quick volumetric heating and the ensuing sensational increment in response rates. This paper presents the effect of microwave irradiation on the Ge$_{25}$Se$_{75}$ thin films with different illumination times (0–90 min). X-ray diffraction (XRD) has been utilized to study the structural nature. Optical reflection and transmission spectra of Ge$_{25}$Se$_{75}$ chalcogenide thin films have been obtained in the range 200–2500 nm at room temperature. The optical parameters have changed with the microwave irradiation.

2. Experimental techniques

Ge$_{25}$Se$_{75}$ bulk chalcogenide glasses were set up by the melt-quenching system. Materials (99.999% pure) were weighted by their atomic rates and were fixed in an evacuated silica tube, which was heated...
at 1100°C for 15 h. The tube was shocked at
temperature in order to make the solu-
tion homogeneous; this took place in ice water.
Films were prepared using thermal evaporation at
vacuum in 10⁻⁵ Torr by an Edwards E-306 coating
unit. The evaporation rates and film thick-
ness were restricted using a quartz screen, Ed-
wards model FTMS. The chemical composition of
the samples was determined using the standard en-
dergy dispersive X-ray (EDX) analysis technique,
JEOL JSM-T200 type, Japan.

X-ray examination of the as-prepared films was
carried out using Philips Diffractometer 1710 with
Ni with CuKα source (λ = 0.154 nm). A microwave
with 650 W power (Sanle General Electric Corp.
Nanjing, China) was utilized for different illumina-
tion times (0–90 min).

The scanning electron microscopy (SEM) images
were recorded on a JEOL JEM200CX scanning elec-
tron instrument.

Transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were
recorded at room temperature using a double beam
spectrophotometer (Shimadzu UV-2101).

3. Results and discussions

3.1. Structural properties

EDX spectra of Ge$_{25}$Se$_{75}$ films show the ele-
ment percentage in Fig. 1. The percentage of
these elements nearly agrees with the starting bulk
material. Figure 2 shows the XRD patterns for
the as-prepared Ge$_{25}$Se$_{75}$ thin films at different mi-
crowave illumination times (0–90 min). In Fig. 2a
the amorphous nature of the as-prepared Ge$_{25}$Se$_{75}$
thin film is illustrated. Figure 2b and 2c reveals that
the amorphous nature still exists in time, but there
were some peaks after the 45 min illumination time.
Additionally, some peaks appeared after the 90 min
illumination time. These peaks suggested that there
are certain bonds appearing, being Ge–Se bonds, in-
dicating that the microwave illumination time had
an impact on the structural figure of these films.

The surface morphology of the studied films
was analyzed before and after illumination time
of 90 min. Figure 3 displays the SEM images for

4. Optical investigations

4.1. Absorption coefficient

At different induced microwave irradiation times
(0–90 min), the transmittance $T$ and reflectance $R$
were captured for 250 nm Ge$_{25}$Se$_{75}$ films and shown
in Fig. 4. It is found that $T$ increases with $R$ de-
creasing as time increases. In addition, the trans-
mittance edge is shifted towards a lower wave-
length indicated that the energy gap will increase
as the time increases.

Therefore, the absorption coefficient ($\alpha$) should
be calculated using both values of $T$ and $R$ accord-
ing to the following equation [10]:

$$\alpha = \frac{1}{d} \ln \left( \frac{(1 - R)^2}{2T} + \sqrt{R^2 + \frac{(1 - R)^4}{4T^2}} \right),$$

where $d$ [cm] is the film thickness.
Fig. 4. Transmittance $T$ and reflectance $R$ for Ge$_{25}$Se$_{75}$ film with different illumination time (0–90 min).

Fig. 5. The absorption coefficient vs. photon energy of Ge$_{25}$Se$_{75}$ film with different illumination time.

Figure 5 shows the dependence of $\alpha$ on the incident photon energy $h\nu$ for the as-prepared Ge$_{25}$Se$_{75}$ thin films illuminated at different times. A decreasing behavior of $\alpha$ with induced time is observed. To understand these behaviors in more detail, the $\alpha$ values less than $10^4$ cm$^{-1}$ are called the Urbach tail. In this range, $\alpha$ is depending exponentially on $h\nu$ which is captured with the formula [11]:

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_e),$$

(2)

where $\nu$ is radiation frequency, $E_e$ is a localized states tails’ width.

Figure 6 shows the dependence of $\ln(\alpha)$ on the incident photon energy $h\nu$ for the as-deposited glass Ge$_{25}$Se$_{75}$ illuminated at different times. Using a linear regression the straight line is drawn to better estimates behaviour of the plotted points. Thus, the values of $m$ are $2 \pm 0.05$. When the value of $m$ is closed to 2, this indicates that the electronic transition responsible for the photon absorption is a nondirect process. Figure 6 illustrates linear plot of $\sqrt{\alpha h\nu}$ versus photon energy $h\nu$ of the two films with different film thickness. The intercept of the straight line with the photon energy axis at $\sqrt{\alpha h\nu} = 0$ gives the optical band gap $E_g$. The results collected for Ge$_{25}$Se$_{75}$ in Table I indicate that $E_g$ values increase for increasing values of illumination time.

In case of the optical band gap, it was shifted slightly from 2 eV to 2.13 eV due to irradiation. Microwave irradiation leads to the breaking of bonds and formation of new ones, in turn resulting in the decrease of dangling bonds and defects and trapping generated carriers. This triggers the decrease

$$\alpha(h\nu) = A(h\nu - E_g)^m,$$

(3)

where $E_g$ is an optical band gap, and $m$ is a power indicated in the transition process. If $m = 2$, one has an indirect allowed transition. Otherwise, if $m = 1/2$, a direct allowed transition occurs. Figure 7 explains the dependence of $\sqrt{\alpha h\nu}$ on the incident photon energy $h\nu$ for the as-deposited Ge$_{25}$Se$_{75}$ illuminated at different times. Using a linear regression the straight line is drawn to better estimates behaviour of the plotted points. Thus, the values of $m$ are $2 \pm 0.05$. When the value of $m$ is closed to 2, this indicates that the electronic transition responsible for the photon absorption is a nondirect process. Figure 6 illustrates linear plot of $\sqrt{\alpha h\nu}$ versus photon energy $h\nu$ of the two films with different film thickness. The intercept of the straight line with the photon energy axis at $\sqrt{\alpha h\nu} = 0$ gives the optical band gap $E_g$. The results collected for Ge$_{25}$Se$_{75}$ in Table I indicate that $E_g$ values increase for increasing values of illumination time.

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### Table I

| Illumination time [min] | $E_g$ [eV] | $E_e$ [meV] | $\epsilon_L$ [$10^{56}$ kg$^{-1}$ m$^{-3}$] |
|-------------------------|-----------|------------|-------------------------------------------|
| 0                       | 2         | 16         | 23                                        |
| 15                      | 2.05      | 15         | 22                                        |
| 45                      | 2.07      | 14         | 20                                        |
| 60                      | 2.1       | 12         | 21                                        |
| 75                      | 2.11      | 11         | 16                                        |
| 85                      | 2.12      | 10.3       | 15                                        |
| 90                      | 2.13      | 10.2       | 15                                        |

$E_g$ is an optical band gap, and $m$ is a power indicated in the transition process.
in band tail width, then the energy gap expands as the homopolar bond decreases [14]. These homopolar bonds, such as Se–Se bonds defects, are related to localized states on the band structure. Due to annealing, these unsaturated defects are gradually annealed out, and thus the optical band gap increases. Moreover, the annealing sources, such as thermal, light, or microwave annealing, cause a decrease in homopolar bonds, indicating the increase of the optical band gap [15].

The extinction coefficient $k$ could be represented in the form [16, 17]:

$$a = \frac{4\pi k}{\lambda}. \quad (4)$$

The dependence of $k$ on $\lambda$ is observed in Fig. 7. It is observed that $k$ values for the as-deposited Ge$_{25}$Se$_{75}$ films are less (or decreased) than the irradiated Ge$_{25}$Se$_{75}$ films. This can be attributed to the reason mentioned previously — to the absorption coefficient that has the same behavior.

3.2.2. Dispersion analysis

Refractive index is considered to be one of the key properties of an optical material, since it is closely associated with the electronic polarizability of ions and the local field inside materials. In some applications, especially in optical devices, the assessment of the refractive file of optical material is important.

The refractive index $n$ can be calculated using [18, 19]:

$$n = \left(1 + \frac{R}{1 - R}\right) + \frac{4 R}{(1 - R)^2} k^2. \quad (5)$$

Figure 8 displays the refractive index $n$ as a function of wavelength for Ge$_{25}$Se$_{75}$ films with different illumination times. It is clear from Fig. 9 that there are two regions of refractive index $n$ spectrum for the irradiated film. The first region occurs at $\lambda = 1000$–1700 nm, and the second region starts where $\lambda$ exceeds 1700 nm. The refractive index $n$ increases in the first region, resulting from the electronic transitions of the valence band and the impurities (or an increase of the compactness of the films) and the transitions of energy bands. These values are reduced with increase in wavelengths. In the second region of the spectrum, the variation of refractive index $n$ with wavelengths becomes slightly decreased and its values are very close at cut-off wavelength. On the other hand, a deviation from the linear behavior is seen at a longer wavelength, which is attributable to the negative contribution of the lattice vibration [20]. Real and imaginary dielectric constants for Ge$_{25}$Se$_{75}$ at different illumination times can be calculated using the following equations [21, 22]:

$$\epsilon_r = n^2 - k^2, \quad (6)$$

$$\epsilon_i = 2nk. \quad (7)$$

Figures 10 and 11 show the variation of real and imaginary dielectric constants for Ge$_{25}$Se$_{75}$ films at different illumination times. The variation of $\epsilon_i$ and nearly ignoring $n$ are because of the ignored values of $k^2$ compared to $n^2$. On the other hand,
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Fig. 10. Real part of dielectric constant $\varepsilon_r$ vs. wavelength $\lambda$ of Ge$_{25}$Se$_{75}$ film with different illumination time.

Fig. 11. As in Fig. 10, but for imaginary part.

$\varepsilon_r$ mainly depends on the value of $k$, illustrating the radiation absorption by free carriers [24]. It is observed that $\varepsilon_r$ increases and decreases with irradiation, and this is attributed to the same reason mentioned previously for the refractive index, while $\varepsilon_r$ increases with increase in the irradiation, and this is due to the similar interpretation discussed previously for the extinction coefficient. Single oscillator model [17, 18] is used for analyzing the data of refractive index in the normal dispersion area, describing the dielectric response for the transition below the band gap.

High-frequency dielectric constant is very important because of its contribution of free carriers and dispersion lattice vibration modes. Therefore, it could be determined by analyzing the data of refractive index. The dependence of the real dielectric constant ($\varepsilon_r = n^2$) on $\lambda$ in the normal dispersion area could be given by the following [18, 23]:

$$\varepsilon_r = \varepsilon_L - \frac{e^2}{4\pi^2 c^2 \varepsilon_0 m^*} \frac{N}{\lambda^2}$$

(8)

where $\varepsilon_L$ is the lattice dielectric constant, $e$ is electronic charge, $\varepsilon_0$ is permittivity of free space, $N/m^*$ is the ratio of carrier concentration to the effective mass.

The dependence of $n^2$ on $\lambda^2$ appears in Fig. 12 and it is seen that the reliance of $n^2$ on $\lambda^2$ is linear at longer wavelengths. Extrapolating the direct parts of this reliance to zero wavelengths gives the estimations of $\varepsilon_L$. From the slope of the linear parts, one could obtained the values of $N/m^*$ which were listed in Table I. The values of $N/m^*$ (related to the internal microstructure) diminish with expanding microwave-induced time. Such behavior is interpreted as the creation of additional trapping carriers, uniting with the original carriers in the films.

4. Conclusion

Nanostructured Ge$_{25}$Se$_{75}$ films were set up by thermal evaporation procedure. XRD studies show that, upon microwave-induced time, an adjustment in the microstructure of the films happens due to their adaptable structure. The absorption coefficients of these films, upon illumination, are of the order for $10^5$ cm$^{-1}$. As a consequence, such materials may have an industrial application as optical recording media. The Ge$_{25}$Se$_{75}$ band gap has an allowed indirect transition of increments of 2–2.13 as the microwave-induced increments 0–90 min. The impact of microwave induction should be associated with bond adjustments and changes in the microstructure of these films. The refractive index diminishes with the expansion of the microwave-induced time. Investigation of the experimental results highlights that the dispersion parameters of Ge$_{25}$Se$_{75}$ at various induced times diminished with increments in those times.

Acknowledgments

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through research groups program under grant no. R.G.P. 2/33/40.
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