LASER INDUCED CHANGES ON BAND GAP AND OPTOELECTRONIC PROPERTIES OF CHALCOGENIDE GLASSY $Cu_{0.11}Cd_{0.40}S_{0.49}$ THIN FILMS

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Thin amorphous chalcogenide films of $Cu_{0.11}Cd_{0.40}S_{0.49}$ glasses were prepared by chemical bath deposition technique. Some samples were irradiated with continuous wave He-Ne 632.8 nm laser beam for 20 minutes and characterized. Results showed that the energy band gap decreased by 0.18 eV after irradiation. The dissipation factor, extinction coefficient, high frequency dielectric constant and the ratio of carrier concentration to effective interaction mass also varied after irradiation. These changes have been identified to be as a result of structural defects introduced on Cu-Cd-S chalcogenide systems, induced by intense laser irradiation.

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Keywords: Cu-Cd-S system, He-Ne laser, Optoelectronic properties, Energy band gap

1. Introduction

Chalcogenide glasses are among the most widely known families of amorphous materials and have been studied extensively over the past few decades because of their interesting fundamental properties and wide commercial applications [1- 3]. They behave as semiconductors and exhibit amorphous semiconductor behavior with band gap energy ranging from 1 to 3 eV [2]. Thin film chalcogenide glasses are also known to be sensitive to the absorption of electromagnetic radiation and show a variety of photon- induced effects as a result of illumination [3]. On exposure to light or other radiations capable of exciting electron-hole pairs, chalcogenide glassy materials can exhibit structural changes. These structural changes are predominantly due to modifications in the atomic configuration, which consequently affect their physico-chemical properties [4, 5] such as the morphology, optical constants, energy bands and electronic transport phenomena of the semiconductor materials. Another important laser interaction effects on semiconductors is that it can induce drift of electrons, which can in turn change the refractivity of the materials. This can trigger changes in surface output of the semiconducting crystals [6].

In the present paper, we investigated the interaction of laser radiation with ternary amorphous chalcogenide Cu-Cd-S system and its effects on the energy band gap and some optoelectronic constants.

2. Experimental

The deposition of Cu-Cd-S ternary thin film took place at room temperature. The bath contained [1 M $CdCl_2$.21/2+0.08 M $CuSO_4$], 0.01 M EDTA, 25% NH_3 1 M SC $(NH_2)_2$ and deionized water was added to make it up to 50 ml. A pre- cleaned glass slide was immersed into the bath and was allowed to stand for 24 hrs. The films were removed from the solution, washed with deionized water and dried. Some of the films were irradiated for 20 minutes with He-Ne laser operating at wavelength 632.8 nm placed 1m from the film.

The optical transmissions of the films were performed with a Jenway 6405 UV-VIS spectrophotometer. Thin film compositions and were determined with a 2.2 MeV $^4He^+$ ion beam tandem accelerator with Rutherford backscattering (RBS) cross-section detector.

3. Results and discussions

The thin film reflection spectra (R) (fig. 2), were calculated directly from using the well known equation [8];

$$R = \frac{[(n-1)^2 + (K)^2]}{[(n+1)^2 + (K)^2]} \tag{1}$$

The extinction coefficient (K) was calculated from the absorption data curves using the relation [7], and the plot of extinction coefficient versus photon energy is displayed in fig. 1.

$$k = (\alpha\ \lambda)/\ (4\pi) \tag{2}$$

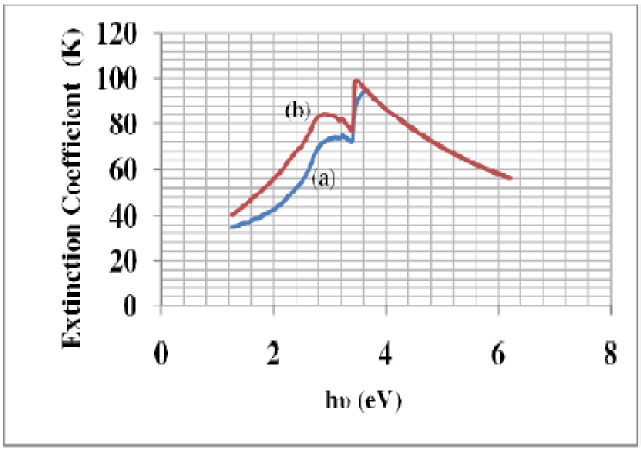
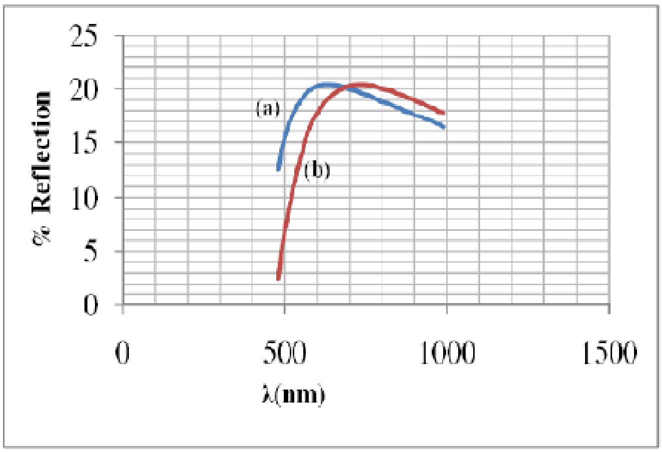


Fig. 1 Plot of extinction coefficient versus energy (a) unirradiated, (b) irradiated



u *Unirradiated (b) irradiated $Cu_{0.11}Cd_{0.40}S_{0.49}$ films.*

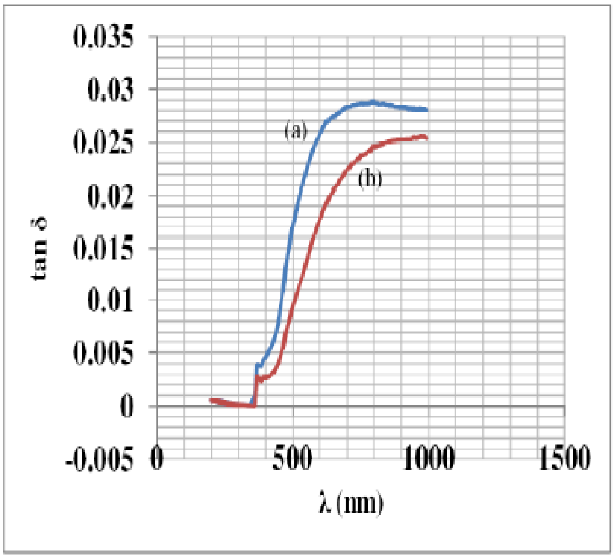


Fig. 3. Plot of $\tan\delta$ *versus* λ *(a) unirradiated, (b) irradiated*

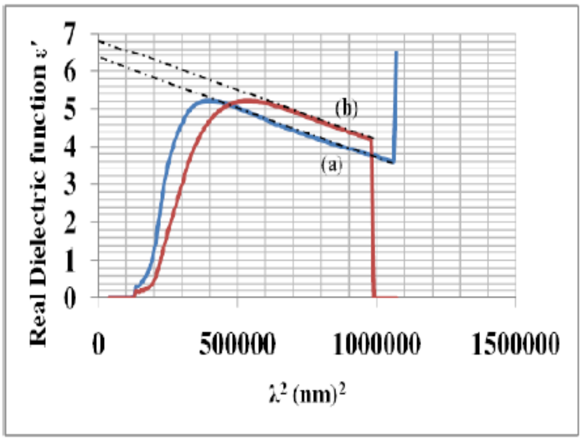


Fig. 4. Plot of ε' *versus* λ^2 *(a) unirradiated, (b) irradiated*

The values of the extinction coefficient were observed to increase after laser irradiation. Similar trend was also observed for the thin films of amorphous Se_{96}-xTe4Gax semiconductors [4].

The dissipation factor of the thin films semiconductor is defined as [8];

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{3}$$

Where ε' *and* ε'' are the real dielectric constant and imaginary dielectric constant. The plot of $\tan\delta$ against photon wavelength is shown in figure 3. It is clearly observed that the dissipation factor, tan δ, of both He-Ne laser irradiated and unirradiated thin films increased in the visible spectrum and was steady at high values ~0.028 for unirradiated sample and ~0.024 for the irradiated sample.

The dependence of ε' on λ^2 can be examined using the relation [8]

$$\varepsilon' = \varepsilon'_\infty + \left(\frac{e^2}{\pi c^2}\right)\cdot\left(\frac{N_c}{m^*}\right)\lambda^2 \tag{4}$$

Where, ε'_∞, is the high frequency dielectric, e is the electronic charge, c is the speed of light in vacuum, N_c is carrier concentration, and m^*, is the effective mass of the carrier. The plot of ε', against λ^2 (fig. 4), allows the determination of ε'_∞, as the intercept and $\left(\frac{N_c}{m^*}\right)$, can be evaluated from the gradient of the plot. The values of ε'_∞ and the ratio of the carrier concentration to the effective mass, $\left(\frac{N_c}{m^*}\right)$ is shown in table 1. Observation shows that the ratio of the carrier concentration to effective interaction mass of the sample increased on laser irradiation.

Also the relation between absorption coefficient (α) and the incident photon energy (hν) can be written as [7], ie, Tauc relation;

$$\alpha = A\,(h\upsilon - E_g)^m / h\upsilon \quad (5)$$

Where A is a constant and E_g is the energy band gap of the semiconductor material. The values of m depends upon the type of the transition; which may have values 1/2, 2, and 3/2 corresponding to the allowed direct, allowed indirect, and forbidden direct transitions respectively [12]. From the above equation, it is clear that the plot of $(\alpha h\upsilon)^2$ versus hυ (fig. 5), will indicate a divergence of an energy values, E_g where the transition takes place. The values of optical band gap energies E_g were obtained by extrapolating the straight portion to the hυ axis at (αhυ) = 0. From table 1, it is clear that the band gap of the un- irradiated sample is wider than the laser irradiated sample. Similar band gap red shift has been observed for other chalcogenide glasses. This can be attributed to the high-energy ions, which were sufficient to cause electron excitations from the lone pair and bonding states to higher energy states [4]. It is expected that the vacancies created in these transition energy states can be immediately reoccupied by the outer electrons by the process of Auger recombination. This can lead, off course to production of more holes and subsequently electron vacancy cascades. This effect always brings about ionizations of atoms due to structural defects, hence reduction of energy band gap of the semiconductor irradiated with laser. This has equally been observed to be responsible for the changes in the magneto- optical properties in some multilayer heterostructures [9].

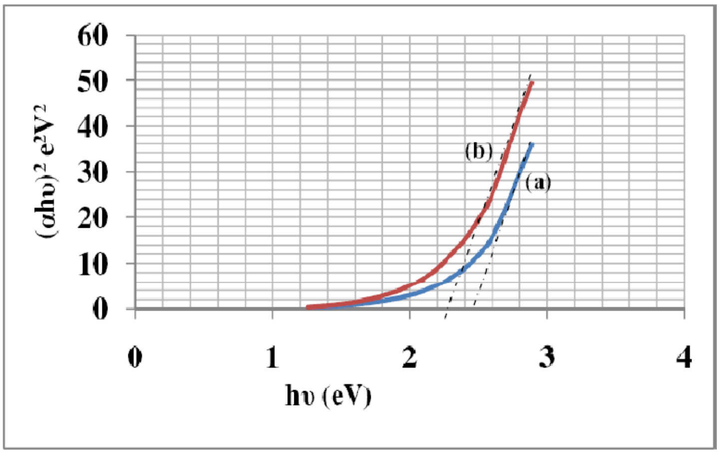


Fig. 5. Plot of $(\alpha h\upsilon)^2 e^2V^2$ versus hυ (a) unirradiated, (b) irradiated

Table 1. Values of optoelectronic and energy band gaps of un-irradiated and laser irradiated

$Cu_{0.11}Cd_{0.40}S_{0.49}$	$\langle \tan\delta \rangle$	$\langle K \rangle$	E_g(eV)	ε'_{∞}	$\frac{N_c}{m^*}$ (10^{47}) $(kg^{-1}m^{-3})$
Not-irradiated	0.018	52.82	2.48	6.4	5.51
Irradiated	0.014	61.33	2.30	6.8	7.71

The elemental compositions determined by RBS spectrometry [fig. 6] revealed that the thin films on glass matrix were stoichiometric with the formation of ternary system of the type $Cu_{0.11}Cd_{0.40}S_{0.49}$. The continuous line is the simulated one while dotted line represents the RBS spectrum of $Cu_{0.11}Cd_{0.40}S_{0.49}$ thin films on soda lime glass.

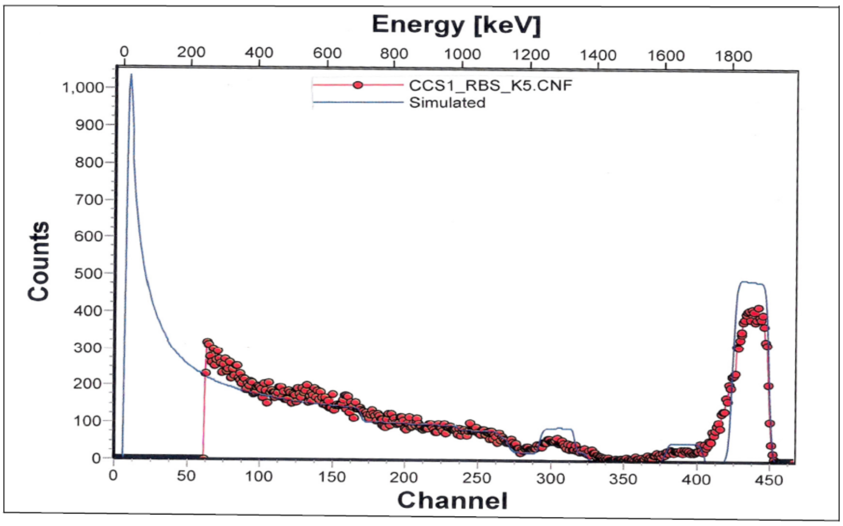


Fig. 6. Rutherford backscatterimg spectrometry of $Cu_{0.11}Cd_{0.40}S_{0.49}$ chalcogenide glass. Un-irradiated

4. Conclusion

In this work, we examined the effects of He-Ne continuous wave laser-irradiation on the band gap and optoelectronic properties of glassy chalcogenide thin films of $Cu_{0.11}Cd_{0.40}S_{0.49}$. Post irradiation effects were observed in the variations of band gap and some optoelectronic properties of amorphous $Cu_{0.11}Cd_{0.40}S_{0.49}$ thin films.

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