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INFLUENCE OF γ–IRRADIATION ON OPTICAL AND ELECTRICAL PROPERTIES OF AMORPHOUS CuInSeTe, CuInSTe AND CuInSeS THIN FILMS

LAILA I. SOLIMAN

Solid State Physics Laboratory, National Research Centre, Cairo, Egypt

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Thin films of quaternary CuInSeTe, CuInSTe and CuInSeS, of thickness 180 nm, were deposited on glass or quartz substrates at 300 K by thermal evaporation under vacuum of 0.13 MPa (10^{-6} Torr) with a deposition rate of about 6 nm/s. The bulk and thin films of the samples were tested by X-ray diffraction, which revealed that the bulk samples have a polycrystalline structure whereas the thin films are amorphous. The X-ray fluorescence analysis as well as the chemical analysis indicates very slight variations of the film constituents after γ-irradiation. The dependence of the absorption coefficient on photon energy showed the existence of an indirect energy gap in all quaternary films. Moreover, these optical band gaps decreased after increasing the γ-ray doses at room temperature. The validity of the Urbach rule was investigated and the respective parameters were estimated. Resistivity and Hall effect measurements showed that the CuInSeTe, CuInTeS and CuInSeS thin films are p-type semiconductors. The resistivity decreased after increasing the γ-ray doses. The decrease of the values of energy gaps and the resistivity at room temperature of the films with increased γ-ray doses are interpreted in terms of the variation of the density of states model of Mott and Davis, and explained as due to the unsaturation of bonds in amorphous solid.

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Keywords: thin films of CuInSeTe, CuInSTe and CuInSeS, amorphous, γ-irradiation, optical band gaps, resistivity, Hall effect, unsaturation of bonds

1. *Introduction*

Among the quaternary compounds, the pseudo-binary alloys (CuIn)(SeTe) and (CuIn)(SeS) are of potential interest as promissing materials for photovoltaic solar energy conversion devices since the band gaps of these compounds are well adapted to the solar spectrum [1,2]. It is possible to obtain p-type semiconductors [3] which in combination with CdS allow one to obtain hetero-junctions with a low defect content and low recombination of carriers at the interface. In spite of the importance of these quaternary compounds (CuInSeTe, CuInSeS and CuInTeS), little is known about their bulk properties [4–6]. On the other hand, few data are available about the properties of thin films of these compounds [2,7–9], which may be due to the amorphous nature as well as the dependence of their properties on the ambient conditions. Soliman et al. have studied the electrical [10] and optical [11] properties of CuInTeSe, CuInTeS and CuInSeS thin films.

This work is devoted to the study the effect of γ-radiation on the optical and electrical properties of CuInTeSe, CuInTeS and CuInSeS thin films after irradiation with 0.85, 1.2, 0.2 and 2.8 Mrad.

2. *Experimental*

Spectroscopically pure Cu, Te, Se, S and In (99.999% Mathey Chemical Ltd.) were used, in proper ratios, for preparing solid solutions of the quaternary systems CuInTeSe, CuInTeS and CuInSSe by the fusion method [10]. Thin films of these systems were deposited by thermal evaporation of bulk materials onto ultasonically-cleaned glass substrates under vacuum of 0.13 mPa (10^{-6} Torr). The rate of deposition was 6 – 8 nm/s, monitored by a quartz-crystal thickness monitor. The film thickness was re-determined using the multiple beam interference method. The thickness of the films was 180 nm.

The structure of the films was studied by X-ray diffraction (XRD) analysis using a Philips diffractometer. Atomic absorption GBC 980 and Perkin-Elmer Model 1100 have been used to determine the compositions of the as-deposited thin films.

A Gamma Chamber 4000 A was used to expose the specimens of CuInSeTe, CuInTeS and CuInSeS films to γ-ray doses of 0.85, 1.2, 2 and 2.8 Mrad.

The optical transmittance (T) and reflectance (R) of the films were measured in the wavelength range 300–2500 nm using the UV.VIS.NIR spectrophotometer Schimadzu Type–3100.

The electrical conductivity ot the thin films was measured by the conventional four-probe method using direct current. The Hall-effect measurements were carried out by the traditional DC method. An electromagnet with truncated pole faces of 5 cm diameter was used to provide a uniform magnetic field up to 0.85 T (tesla) for an air gap of 3 cm between the poles faces. The Hall constant was calculated using the relation

$$R_H = \frac{V_H t}{IB} \,,$$

where V_H is the Hall voltage, I is the current, t is the thickness of the film and B is the magnetic field strength. The experimental error was estimated at less than 2%.

3. Result and Discussion

3.1. Structure

X-ray studies demonstrate the amorphous nature of the investigated thin films of the three prepared quaternary systems (see Fig. 1a). The X-ray fluorescence quantitative spectra of the bulk compounds and of the amorphous films are shown in Fig. 1b. From these patterns, it is clear that all thin films and the corresponding bulk samples have nearly the same intensity within a 3% error.

The chemical analysis of both the bulk compounds and of the thin films was carried out to detect any minute changes of the constituents which could not be detected by the other methods owing to their limited sensitivity. The results are illustrated in Table 1. From these results, it is clear that the differences in the composition between the bulk and thin film materials are very small.

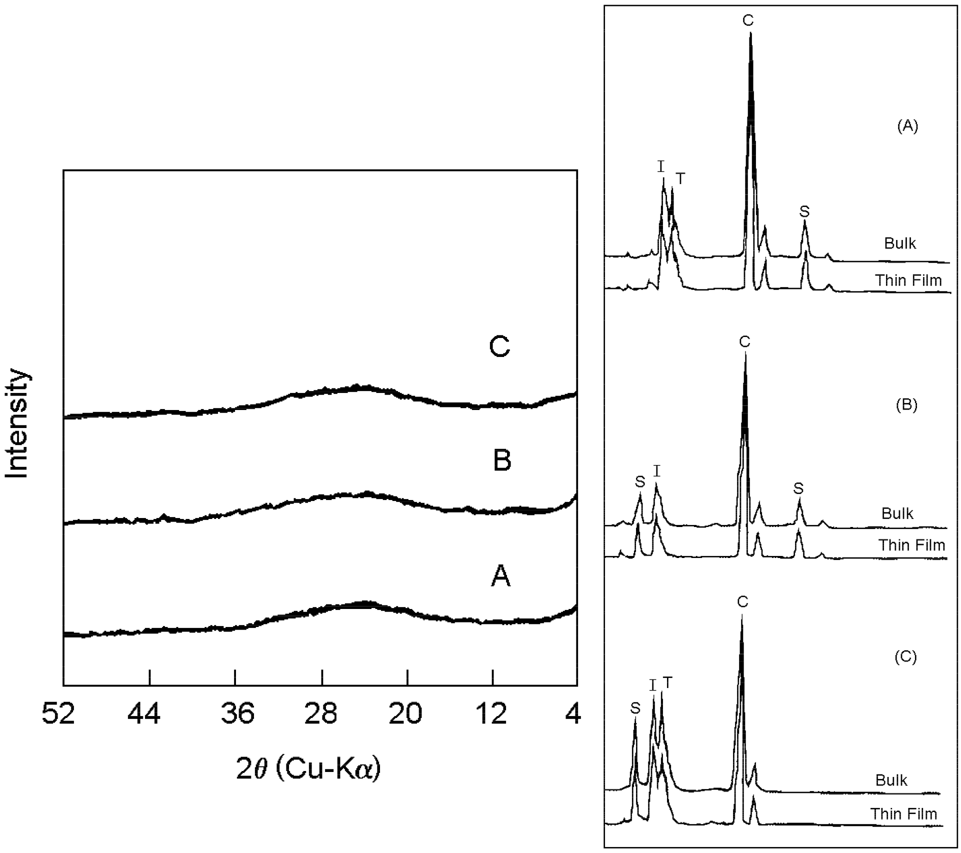


Fig. 1. (left) X-ray diffraction patterns of CuInTeSe, CuInTeS *and* CuInSeS *thin films, (right) X-ray fluorescence analysis of* CuInTeSe, CuInTeS *and* CuInSeS *bulk compounds and thin films.*

TABLE 1. Chemical analysis of powder and of thin films of CuInTeSe, CuInTeS *and* CuInSeS.

Element	Powder	Thin film γ-irradiated	Bulk compound
1. CuInSeTe			
Cu	16.463	17.102	16.509
In	29.790	29.788	29.663
Se	20.661	20.124	20.513
Te	33.086	32.988	33.149
2. CuInSeS			
Cu	22.028	22.031	21.958
In	39.620	39.460	39.677
Se	27.306	27.849	27.258
S	11.0444	10.65	11.080
3. CuInSTe			
Cu	19.187	19.23	18.799
In	34.018	33.84	33.968
S	9.051	8.95	9.485
Te	37.757	37.91	37.748

3.2. Optical band gap and Urbach tail

Study of the optical absorption spectra has been one of the most productive methods in developing and understanding the structure and energy gap of amorphous non-metallic materials.

In the high-absorption region (where absorption is associated with interband transitions), the form of the absorption coefficient $\alpha(\omega)$ was given in quadratic form by Tauc et al. [12] and discussed in more general terms by Davis and Mott [13], who use the equation of the form

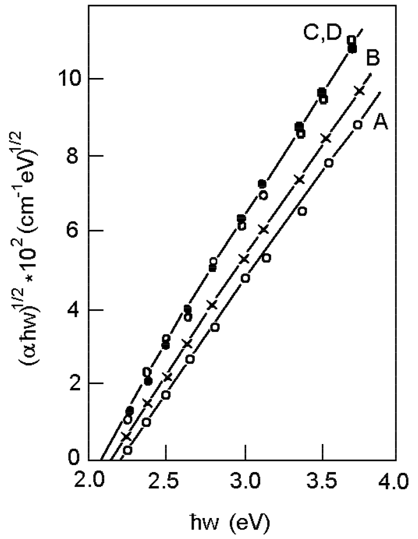
$$\alpha(\omega) = \frac{B_\alpha(\hbar\omega - E_g)^r}{\hbar\omega}\,, \qquad (1)$$

where B_α is a constant, E_g is the optical band gap, $\alpha(\omega)$ is the absorption coefficient at an angular frequency of $\omega = 2\pi\nu$, $\hbar$ is the Planck constant divided by 2π and r is an index which can assume values of 0.5, 1.5, 2 and 3, depending on the nature of the electronic transitions responsible for the absorption. r is equal to 0.5 for allowed direct transitions, 1.5 for direct forbidden transitions, 2 for allowed indirect transitions and 3 for forbidden indirect transitions.

Fundamental absorption edge in most amorphous semiconductors follows an exponential law [14]. Above the exponential tail, the absorption coefficient of any amorphous semiconductor has been observed to obey an equation similar to Eq. (1). The range of validity of this equation is very small and, hence, it is very difficult to determine the exact value of the exponent r [15].

The authors of Refs. [16–21] have suggested different values of r for different glasses. Theoretically, an equation similar to Eq. (1) has been derived for amorphous materials for which k-conservation no longer holds. Davis and Mott [13] obtained $r = 2$ which is experimentally valid for most amorphous semiconductors. However, for more complicated materials, Fagen and Fritzsche [22] obtained $r = 3$.

The value of E_g in any amorphous material is obtained by plotting $(\alpha\hbar\omega)^{1/r}$ versus $\hbar\omega$ (where r has the values 2 or 3) in the high-absorption range and extrapolating the linear region of the plots of $(\alpha\hbar\omega)^{1/r}$ to zero. This extrapolated value is used to define the so-called optical gap in amorphous materials.



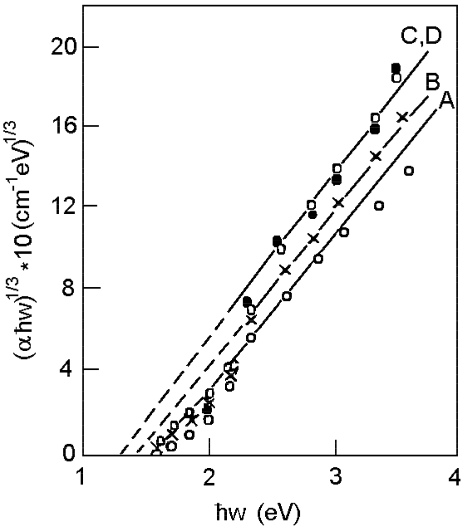


Fig. 2. $(\alpha\hbar\omega)^{1/2}$ *versus* $\hbar\omega$ *of* CuInSeS *thin films for* γ*-doses 0.85 (A), 1.2 (B) , 2.0 (C) and 2.8 (D)* Mrad.

Fig. 3 (right). $(\alpha\hbar\omega)^{1/3}$ *versus* $\hbar\omega$ *of* CuInSeS *thin films for* γ*-doses 0.85 (A), 1.2 (B), 2.0 (C) and 2.8 (D)* Mrad.

Figures 2 and 3 show plots of $(\alpha\hbar\omega)^{1/2}$ and $(\alpha\hbar\omega)^{1/3}$ versus $\hbar\omega$ for $r = 2$ and $r = 3$ of CuInSeS irradiated with γ–ray doses of 0.85, 1.2, 2 and 2.8 Mrad as a representative example of the three quaternary films (CuInTeSe, CuInTeS and CuInSeS). By comparing the fits for both these different values of r (2 and 3) of CuInSeS as shown in Figs. 2 and 3, one can conclude that $r = 2$ gives a slightly better fit than $r = 3$ for these film.

From Figs. 2 and 3, it was found that the width of the optical gaps of CuInSeS decreased when γ–irradiation doses were increased from 0.85 to 1.2, 2, and 2.8 Mrad, as shown in Table 2. That was also found for CuInTeSe and CuInTeS thin films, i.e., the optical energy gaps decreased when increasing the γ-ray doses. The results are summarized in Table 2. This decrease of energy gaps with γ-ray doses can be explained to as due the variation of disorder and defects present in amorphous materials [23].

It is known that unsaturated bonds are produced as a result of an insufficient number of atoms deposited in the amorphous films [24]. The unsaturated bonds are responsible for the formation of some defects in the films. Such defects produce localized states in the amorphous solids. The presence of high concentration of localized states in the band structure is responsible for low values of optical energy gap E_g in the case of as-deposited amorphous films [25]. In the process of γ-irradiation, the unsaturated defects produce a large number of unsaturated bonds. The increase in the number of unsaturated defects increases the density of localized states in the band structure and consequently decreases the optical energy gap E_g.

Figure 4 shows the plot of $\ln\alpha$ versus $\hbar\omega$ for different γ-ray doses in CuInSeS thin films as a representative example of the quaternary films. The straight line in the figure confirms the exponential dependence of the absorption coefficient ($\alpha(\hbar\omega)$) on photon energy $\hbar\omega$, in accordance with the Urbach rule [14]

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/E_e)\,, \tag{2}$$

where α_0 is a constant, ω the angular frequency of the incident photon and E_e is calculated from the slopes of the straight lines. E_e is interpreted as the width of the tails due to localized states in the forbidden gap, associated with the amorphous state. However, an Urbach tail has been also observed in crystalline materials. Therefore, nothing can be said with certainly about the origin of this exponential dependence.

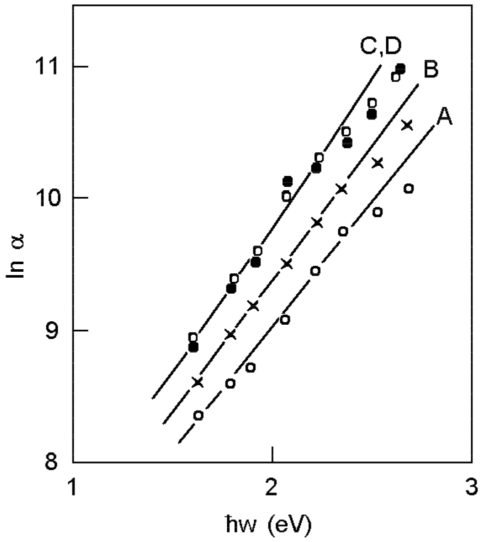


Fig. 4. $\ln\alpha$ *versus* $\hbar\omega$ *for* CuInSeS *thin films for* γ*-ray doses 0.85 (A), 1.2 (B), 2.0 (C) and 2.8 (D)* Mrad.

The values of E_e obtained in our samples of CuInSeS, CuInTeSe and CuInTeS thin films are given in Table 2. From these results, it is clear that the optical energy gap (E_g) in CuInSeTe decreases from 1.82 eV to 1.57 eV, in CuInTeS from 1.63 eV to 1.42 eV while in CuInSeS from 2.2 eV to 2.05 eV as γ-ray doses increase from 0.85 to 2.8 Mrad. This decrease of energy gaps with increasing γ-ray doses can be explained by the disorder and defects present in amorphous materials [23].

The valence-band density of states g_i may be estimated, as given by Biswas et al. [26], from the following relation

$$g_i(E_i - \hbar\omega) = const. \frac{nc}{k_s \hbar^2 \omega^2} \left\{ 2\omega[\hbar\omega\alpha(\omega)] + \omega\hbar\omega \frac{\mathrm{d}(\hbar\omega\alpha)}{\mathrm{d}(\hbar\omega)} \right\}, \tag{3}$$

Representing ($\alpha\hbar\omega$) as a function $g_i(\hbar\omega)$, the valence band density of states was estimated for different photon energies for CuInTeS, CuInTeS and CuInSeS thin films, exposed to different γ-ray doses.

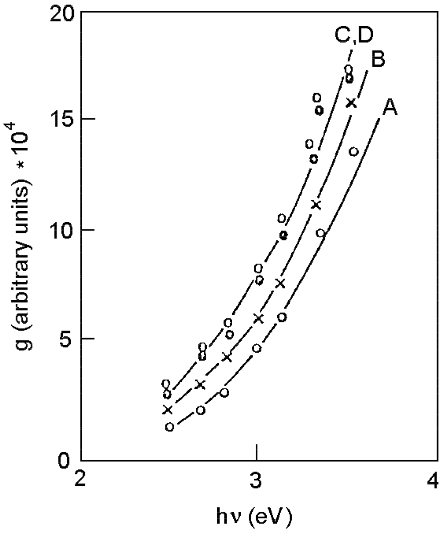


Fig. 5. Valence band density of state g_i versus $h\nu$ for CuInSeS *thin film at γ-ray doses 0.85 (A), 1.2 (B), 2.0 (C) and 2.8 (D)* Mrad.

Figure 5 presents this relation for CuInSeS as an example of the three quaternary thin films, irradiated with different γ-ray doses. Figure 5 also shows an increase of the density of localized states when increasing the γ-ray doses. The increase of the number of the density of localized state, due to the increased γ-ray doses, may be due to the increase of unsaturated defects, leading to a decrease in the optical energy gap [24].

3.3. Electrical conductivity and Hall effect

The room temperature resistivities of the three quaternary thin films CuInSeTe, CuInTeS and CuInSeS were calculated using the equation

$$\sigma = \sigma_0 \exp(-E_a/kT), \tag{4}$$

where σ is the electrical conductivity, σ_0 is the pre-exponential factor and E_a is the activation energy.

Figure 6 shows the dependence of the resistivity on γ-ray doses at room temperature for the three quaternary films. It is clear from this figure that the resistivity decreases when increasing the γ-ray doses. The decrease of the resistivity, ρ, with increasing γ-ray doses can be explained through the presence of a great number of

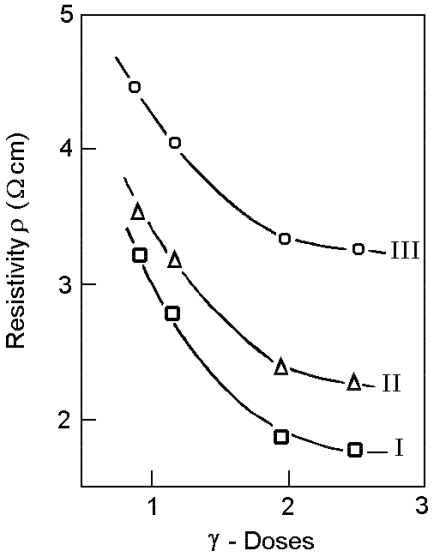


Fig. 6. Resistivity (r) for different γ-ray doses for CuInTeS *(I),* CuInTeSe *(II) and* CuInSeS *(III) thin films.*

TABLE 2. The values of the energy gap, E_g, activation energy, E_a and the width of the tail E_e for CuInSeS, CuInTeS *and* CuInTeSe *thin films for different γ-ray doses.*

Sample	γ–dose [Mrad]	E_g [eV]	E_e [eV]	E_a [eV]
CuInSeS	0.85	2.2	1.6	0.583
	1.2	2.12	1.4	0.563
	2.0	2.05	1.2	0.515
	2.8	2.05	1.2	0.515
CuInTeS	0.85	1.63	1.43	0.495
	1.2	1.54	1.22	0.453
	2.0	1.42	1.115	0.432
	2.8	1.42	1.15	0.432
CuInTeSe	0.85	1.82	1.42	0.406
	1.2	1.76	1.25	0.383
	2.0	1.57	1.13	0.333
	2.8	1.57	1.13	0.333

defects and disorder in amorphous films [27]. It was also found that the values of the activation energy, E_a, in CuInTeS, CuInSeS and CuInTeSe thin films decrease when increasing γ-ray doses, as illustrated in Table 2.

Hall effect measurements indicated that CuInTeSe, CuInTeS and CuInSeS films have p-type conductivity. The calculated dependence of the carrier concentration and the mobility on γ-ray doses from the measurement of the Hall effect is illustrated in Figs. 7 and 8, respectively.

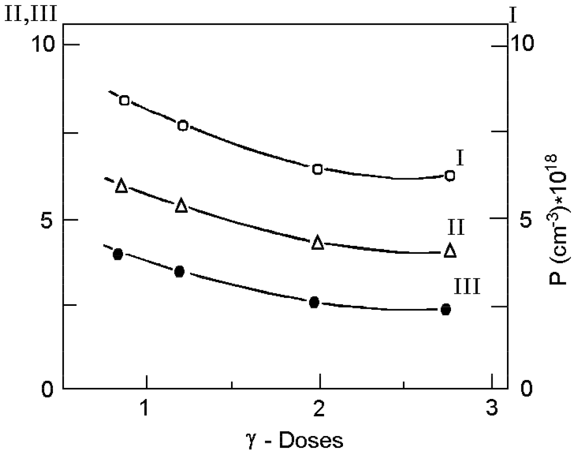


Fig. 7. Carrier concentration P for different γ-ray doses for CuInTeS *(I),* CuInTeSe *(II) and* CuInSeS *(III) thin films.*

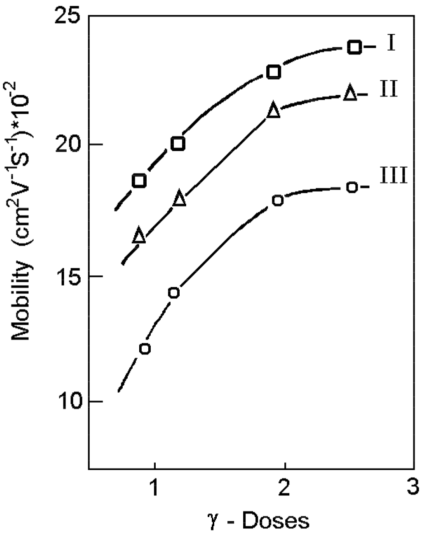


Fig. 8. Mobility m for different γ–doses for CuInTeS *(I),* CuInTeSe *(II) and* CuInSeS *(III) thin films.*

From Fig. 7, it is clear that the carrier concentration decreases when increasing the γ-ray doses, while the mobility increases, as shown in Fig. 8. So, we may say that the main factor affecting the conductivity in these quaternary films is the mobility of the charge carriers. However, this decrease in the number of free carriers may be attributed to a slight increase of the metal content (as indicated by the chemical analysis) which may cause an increase of the number of free electrons. This increase of the number of free electrons increases the number of compensated part, which leads to a decrease in the number of free carriers when increasing γ-ray doses.

4. Conclusions

Thin films of the three quaternary compounds, CuInTeSe, CuInSeS and CuInTeS, are p-type amorphous semiconductors. These films posses an indirect energy gap and this energy gap decreases when increasing γ-ray doses. The decrease of the energy gaps when increasing γ-ray doses may be attributed to an increase of unsaturated defects and disorder as well as the increase of the density of localized states.

The resistivity decreases as the γ-ray doses increase. The variation in the resistivity is mainly limited by the variation of the mobility. Such a variation of the transport properties is mainly due to the variation of defects and a very slight variations of the film constituents, which lead to minute changes in its microstructure.

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UTJECAJ γ-ZRAČENJA NA NEKA FIZIČKA SVOJSTVA AMORFNIH TANKIH SLOJEVA CuInSeTe, CuInSTe I CuInSeS

Naparavali smo četvero-komponentne tanke slojeve CuInSeTe, CuInSTe i CuInSeS, debljine 180 nm, na podloge od stakla i kremena na 300 K, pri tlaku 10^{-6} Torr, brzinom od oko 60 nm/s. Ispitivali smo masivne uzorke i tanke slojeve difrakcijom rendgenskog zračenja, koja je pokazala polikristaliničnu strukturu masivnih uzoraka, dok su tanki slojevi amorfni. Analize rendgenskom fluoroscencijom i kemijske analize pokazale su vrlo male promjene sastavnih elemenata nakon γ-ozračivanja. Ovisnost apsorpcijskog koeficijenta o energiji fotona ukazuje na postojanje posrednog energijskog procjepa u svim uzorcima tankih slojeva. Ti se energijski procjepi smanjuju s povećanjem doza γ-zračenja na sobnoj temperaturi. Provjeravali smo Urbachovo pravilo i odredili odnosne parametre. Mjerenja otpornosti i Hallovog efekta pokazala su da su tanki slojevi CuInSeTe, CuInTeS i CuInSeS poluvodiči p-tipa. Njihova se otpornost smanjila s povećavanjem doza γ-zračenja. Smanjenje energijskih procjepa i otpornosti na sobnoj temperaturi s povećavanjem doza γ-zračenja tumači se promjenama gustoće stanja prema modelu Motta i Davisa, i objašnjava nezasićenim vezanjima u amorfnom sloju.