ISSN 1330–0008
CODEN FIZAE4

JUNCTION FORMATION AND CHARACTERISTICS OF n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ POLYCRYSTALLINE THIN FILMS

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Received 23 January 2003; revised manuscript received 17 September
Accepted 29 September 2003   Online 19 April 2004

$CuGa_{0.3}In_{0.7}Se_2$ polycrystalline thin films were prepared by thermal evaporation under vacuum of about 10^{-4} Pa, with a deposition rate of about 200 nm/min. The selenization of these films at 723 K improves their properties. The activation energy as well as the optical energy gap of the investigated samples decreased with annealing and selenization. Polycrystalline thin film n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ heterojunctions were fabricated and the current density-voltage and capacitance-voltage characteristics of the junction were studied. The heterojunctions were exposed to light, and under illumination of 1000 $mWcm^{-2}$, the open circuit voltage was 580 mV, the short circuit current density 4.8 $mAcm^{-2}$, the fill factor 0.682 and the electrical conversion efficiency was 1.898% for cells of active area of 1 cm^2.

PACS numbers: 42.79.Ek, 73.40.Kp, 84.60.Jt   UDC 53.082.52
Keywords: $CuGa_{0.3}In_{0.7}Se_2$, polycrystalline thin film, n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$, heterojunction, solar cell, conversion efficiency

1. Introduction

Chalcopyrites are well suited as absorber materials for the preparation of highly-efficient thin-film solar cells [1,2]. $CuGa_xIn_{1-x}Se_2$ solid solutions have received considerable interest for photovoltaic applications, because their band gap can be adjusted to obtain an optimum match with the solar spectrum [3]. By increasing the value of x from 0.25 to 0.3, the optical band gap can be changed from 1.15 to 1.2 eV [4,5]. A higher Ga content ($x > 0.3$) yields a higher open-circuit voltage V_{oc}, but the efficiency of the solar cells is reduced [6]. $CuGa_xIn_{1-x}Se_2$ has a poor lattice match with CdS, but it can be almost matched if $Cd_{0.9}Zn_{0.1}S$ is used instead of CdS [7]. Hence, in the present investigation, the n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ thin-film polycrystalline heterojunctions were used as solar cells. Several processing techniques for the preparation of $CuGa_xIn_{1-x}Se_2$ thin films have been investigated, including co-evaporation, three-stage process, spray technique and selenization [8–13]. The film characteristics depend on the methods and the growth conditions. The aim of our work is to obtain good quality polycrystalline films of $CuGa_{0.3}In_{0.7}Se_2$ and study their physical properties. This paper presents and discusses also the results of X-ray diffraction (XRD), composition analysis (EDX) and of electrical and optical properties of these films. Also, the deposition techniques of n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ thin film heterojunctions and their characteristics were studied.

2. *Experimental*

2.1. *Preparation of* $Cd_{0.9}Zn_{0.1}S$ and $CuGa_{0.3}In_{0.7}Se_2$

$CuGa_{0.3}In_{0.7}Se_2$ polycrystalline compounds were synthesized by fusing high-purity elements (Cu, In, Ga and Se) in stoichiometric ratio in quartz ampoule under a pressure of about 10^{-4} Pa ($\sim 10^{-6}$ Torr, 1 Torr = 133 Pa). Polycrystalline $Cd_{0.9}Zn_{0.1}S$ were prepared using the method described elsewhere [14]. Thin films of $Cd_{0.9}Zn_{0.1}S$ and $CuGa_{0.3}In_{0.7}Se_2$ were prepared by the conventional thermal evaporation technique using a Leybold-Heraeus high-vacuum coating unit of type Univex-300 provided with INFICON XTC thin-film thickness and rate controller. Thin films of $Cd_{0.9}Zn_{0.1}S$ and $CuGa_{0.3}In_{0.7}Se_2$ were deposited at substrate temperature of 450 K under vacuum of about $\sim 10^{-4}$ Pa, and a rate of deposition between about 60 and 200 nm/min, respectively. The thickness of the films was measured by a quartz thickness monitor and confirmed by multiple-beam interferometry. The selenization of $CuGa_{0.3}In_{0.7}Se_2$ was carried out by setting the compound in a vacuum-sealed quartz ampoule with Se shot and crystallized by annealing for one hour in a Se atmosphere in the temperature range from 573 to 773 K [15].

2.2. *Preparation of heterojunctions*

The n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ cells were prepared in a superstrate configuration so that light enters the cell through a gold grid over the glass substrate. The Cd and Zn proportions are chosen so that the $\sqrt{2}a$ lattice parameter of $Cd_{0.9}Zn_{0.1}S$ matches the lattice parameter a of $CuGa_{0.3}In_{0.7}Se_2$. The x value of $CuGa_xIn_{1-x}Se_2$ was chosen 0.3 so that the energy gap is equal to 1.28 eV [16]. First, about 200 nm of $Cd_{0.9}Zn_{0.1}S$ was deposited at substrate temperature 423 K onto a gold-grid coated glass. Prior to $CuGa_{0.3}In_{0.7}Se_2$ deposition, the prepared $Zn_{0.1}Cd_{0.1}S$ films were heat treated with $CdCl_2$ vapour to reduce optical absorption [14]. $CuGa_{0.3}In_{0.7}Se_2$ of thickness 850 nm were then evaporated on top of the $Cd_{0.9}Zn_{0.1}S$ layer at a growth rate of about 6200 nm/min and a substrate temperature of 473 K. These deposition conditions as well as selenization processes yielded uniform single-phase $CuGa_{0.3}In_{0.7}Se_2$ thin films. Silver paint contacts on $CuGa_{0.3}In_{0.7}Se_2$ were used.

2.3. Structural characteristics

The X-ray diffraction (XRD) patterns of $CuGa_{0.3}In_{0.7}Se_2$ samples in both powder form and thin films, deposited on glass substrates, were recorded by Philips PW 1373 X-ray diffractometer. The composition of the powder and thin films of these compounds analysed by the energy dispersive X-ray analysis (EDX).

2.4. Optical measurements

The transmittance $T(\lambda)$ and reflectance $R(\lambda)$ of the as-deposited and of treated films were measured at normal incidence in the spectral range of 300 to 2500 nm, using the JASCO model V-570 UV-VIS NIR double-beam spectrophotometer.

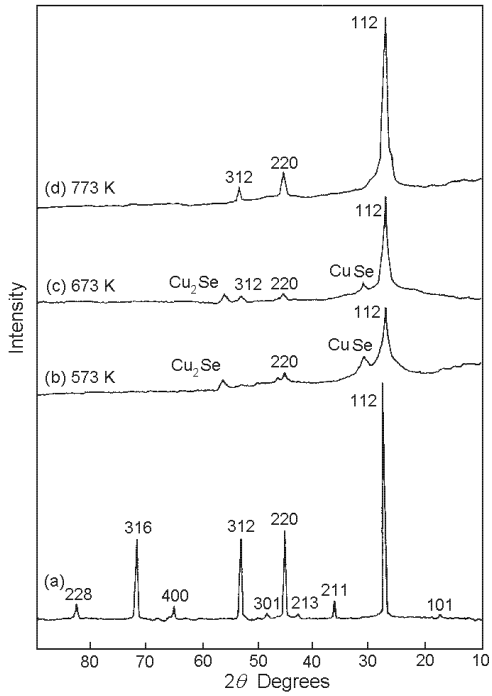
2.5. Electrical measurements

Electrical resistivity measurements of the prepared thin films were performed by coplanar four-probe technique in the temperature range from 300 to 500 K using Keithley 616 digital electrometer. From Hall effect measurements with $CuGa_{0.3}In_{0.7}Se_2$ and $Cd_{0.9}Zn_{0.1}S$, it was found that the values of the donnor (N_D) and acceptor (N_A) densities are 4.2×10^{17} cm^{-3} and 8.15×10^{15} cm^{-3}, respectively. The dark current-voltage (I–V) characteristics of the heterojunctions n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ were carried out at room temperature, while the illuminated I–V characteristics were performed at room temperature under 1000 mWcm^{-2} incident light power. The dark capacitance-voltage characteristics of the n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ heterojunctions were measured at room temperature using a FLUKE programmable automatic RCL meter model PM 6306. Measurements were performed at different frequencies with the reverse DC bias voltage scanned from 0 to 2 V ib steps of 200 mV.

3. Results and discussion

3.1. X-ray analysis (XRD)

From the compositional analysis of both bulk and thin films of $CuGa_{0.3}In_{0.7}Se_2$, as-deposited and annealed at 773 K as well as the films annealing in a Se atmosphere at 773 K, it was found that the compositions of the samples in both bulk and thin films were very close. On the other hand, the compositions of these thin films (Cu, In + Ga, Se) contents are closely equal to 25 %, 25 % and 50 %, respectively, which is the stoichiometric composition in $CuGa_{0.3}In_{0.7}Se_2$. Typical X-ray diffraction patterns of bulk and thin films of thickness 850 nm, as-deposited and crystallized either in nitrogen or selenium atmosphere under vacuum of about 0.1 Pa for one hour at different annealing temperatures (573 – 773 K), are shown in Figs. 1a – d and Figs. 2a – d. The calculated interplaner spacing (d_{hkl}) and relative intensities of the bulk sample are compared with the standard values recorded in the JCPDS cards, which confirm the chalcopyrite structure. The lattice parameters



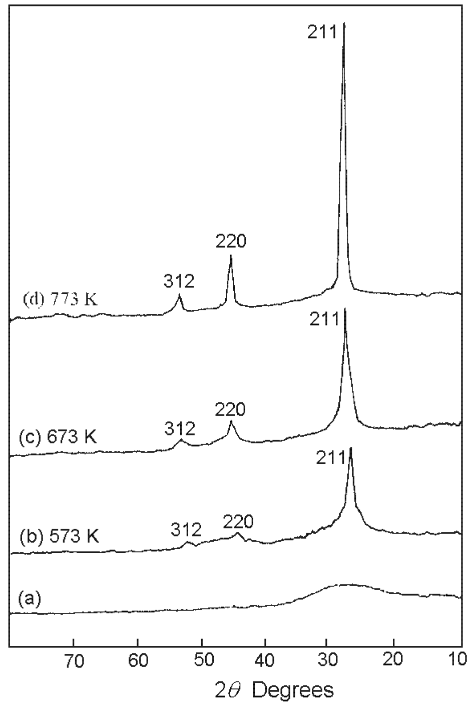


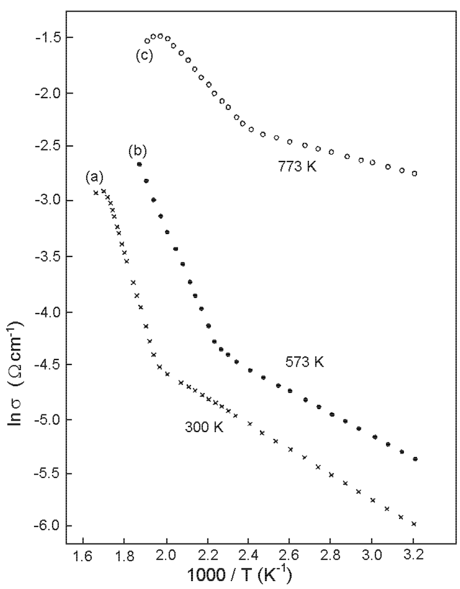
Fig. 1 (left). XRD patterns of $CuGa_{0.3}In_{0.7}Se_2$ *(a) of bulk, and of thin films annealed in* N_2 *atmosphere at (b) 573, (c) 673 and (d) 773* K.

Fig. 2. XRD patterns of $CuGa_{0.3}In_{0.7}Se_2$ *thin films (a) as-deposited, and annealed in* Se *atmosphere at (b) 573, (c) 673 and (d) 773* K.

calculated from the XRD data are in good agreement with the given values in the standard cards. From Fig. 2a, it is clear that the as-deposited $CuGa_{0.3}In_{0.7}Se_2$ thin films are poorly crystalline as seen by the absence of any sharp peak, i.e., the peak intensity is below the detectable limits. However, the degree of crystallinity increases as the annealing temperature increases, as indicated by the increase of the peak intensities. From Figs. 1b and c, it is clear that the $CuGa_{0.3}In_{0.7}Se_2$ thin films, crystallized at 573 K and 673 K, show diffraction peaks which correspond to (112), (220) and (312) faces, and in addition to two foreign peaks are seen which correspond to CuSe and Cu_2Se. On the other hand, the spectrum of the films crystallized at 773 K (Fig. 1d) exhibit many peaks ((112), (220) and (312)), corresponding to diffraction lines of the chalcopyrite phase in $CuGa_{0.3}In_{0.7}Se_2$, and no foreign peaks are observed. Also, the thin films crystallized in Se atmosphere at different temperatures (573 – 773 K) indicate the preferred orientation along the (112) direction and low intensity (220) and (312) peaks, as shown in Figs. 2b – d. Moreover, the full-width at half-maximum of the (112) diffraction peak decreases with increasing annealing temperature in Se atmosphere, an indication of grain growth in $CuGa_{0.3}In_{0.7}Se_2$ thin films. Hence, thin films crystallized at annealing temperature 773 K and selenization temperature in the range 573 – 773 K, are required in order to obtain single-phase $CuGa_{0.3}In_{0.7}Se_2$ with chalcopyrite structure.

3.2. Electrical properties

The electrical dark conductivity σ was measured as a function of temperature in the temperature range 300 – 550 K, of $CuGa_{0.3}In_{0.7}Se_2$ thin films of thickness 850 nm, as-deposited and annealed in nitrogen as well as Se atmosphere, under vacuum of about 0.1 Pa for one hour, at different annealing temperatures (573 – 773 K). Figs. 3a – c and 4 present the temperature dependence of σ of the as-deposited $CuGa_{0.3}In_{0.7}Se_2$ films and of those annealed in nitrogen and Se atmosphere at 573 K and 773 K for one hour under vacuum (about 0.1 Pa), respectively. From Figs. 3 and 4, it is found that σ increases with increasing temperature of annealing and



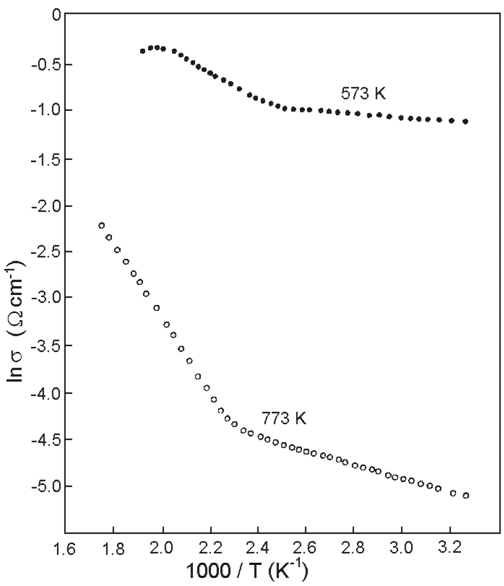


Fig. 3 (left). Temperature dependence of DC conductivity σ of $CuGa_{0.3}In_{0.7}Se_2$ *thin films, (a) as-deposited and annealed in* N_2 *atmosphere at (b) 300, (c) 573 and (d) 773* K.

Fig. 4. Temperature dependence of the DC conductivity σ of $CuGa_{0.3}In_{0.7}Se_2$ *thin films selenized at (b) 573 and (c) 773* K.

selenization. The activation energy ΔE can be calculated from the relation between $\ln \sigma$ and $1/T$ from the equation

$$\sigma = \sigma_0 \exp(-\Delta E/k_B T), \tag{1}$$

where σ_0 is the pre-exponential factor and k_B is the Boltzman constant. The increase of the conductivity σ may be attributed to the transformation of the films from the amorphous state to crystalline state and to the decrease of the number of defects by annealing. The results agree well with structural investigations by X-rays, which indicate the increase of crystallinity. As seen in Figs. 3a – c and 4, the plot of $\ln \sigma$ versus $1000/T$ shows two linear regions, both obeying Eq. (1). The rate of the increase in conductivity in the high-temperature region (350 – 550 K) is greater than that in the low temperature region (300 – 350 K). The electrical conductivity activation energies at high temperature, ΔE_1, and at low temperature, ΔE_2, are determined from the corresponding slopes in the $\ln \sigma$ versus $1000/T$ plots. Their values are listed in Table 1. From this table, it is clear that the high activation energy ΔE_1 values of the as-deposited films are almost half the optical energy gap, indicating that the conduction at this range of temperature is intrinsic, while in the temperature range 300 – 350 K, the low activation energy ΔE_2 is attributed to the shallow acceptor levels of copper vacancies [17–20]. The activation energies ΔE_1 and ΔE_2 decrease when increasing the annealing temperature. From Figs. 3 and 4, it is also clear that the selenized $CuGa_{0.3}In_{0.7}Se_2$ thin films, annealed at 573 K and 773 K, have higher conductivity than those annealed in nitrogen atmosphere. The high value of conductivity of the selenized samples may be attributed to the increase of crystallinity and improvement of the grain growth of these samples.

TABLE 1. The electrical conductivity activation energies at high temperature, ΔE_1, and at low temperature, ΔE_2, determined from the slopes in the $\ln \sigma$ versus $1000/T$ plots of electrical dark conductivity of $CuGa_{0.3}In_{0.7}Se_2$ thin films of thickness 850 nm annealed in nitrogen and Se atmosphere at 573 K and 773 K.

Samples	ΔE_1 (eV)	ΔE_2 (eV)
As-deposited	0.565	0.108
Annealed at 573 K	0.369	0.0869
Annealed at 773 K	0.165	0.0464
Selenized at 573 K	0.273	0.072
Selenized at 773 K	0.13	0.032

3.3. Optical properties

To study the optical properties of $CuGa_{0.3}In_{0.7}Se_2$ thin films, the dependence of both transmission T and reflection R at normal incidence at wavelengths in the spectral range from 500 to 2500 nm were recorded of the as-deposited $CuGa_{0.3}In_{0.7}Se_2$ thin films of the same thickness 850 nm and annealed either in N_2 or Se atmosphere at different temperatures (573 K and 773 K). The absorption coefficient α could be calculated using the measured values of R and T from the following relation [21]

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

where d is the film thickness. The absorption coefficient α is related to the energy gap E_g according to the equation

$$\alpha h\nu = A\sqrt{h\nu - E_g}\,, \tag{3}$$

where A is a constant and h is the Planck constant. Figs. 5 and 6 show the variation of $(\alpha h\nu)^2$ with the photon energy $h\nu$ of the as-deposited and of the annealed films in N_2 and Se atmosphere at annealing temperatures 573 K and 773 K. The intercepts of the extrapolation to zero absorption with the photon energy axis are taken as the values of the direct energy gap E_g. It is found that the direct energy gaps of both films annealed in N_2 and in Se decrease with increasing annealing temperature. This may be due to the increase of crystallinity as indicated by the X-ray studies. Moreover, the decrease of the direct energy gap in the case of selenization is lesser

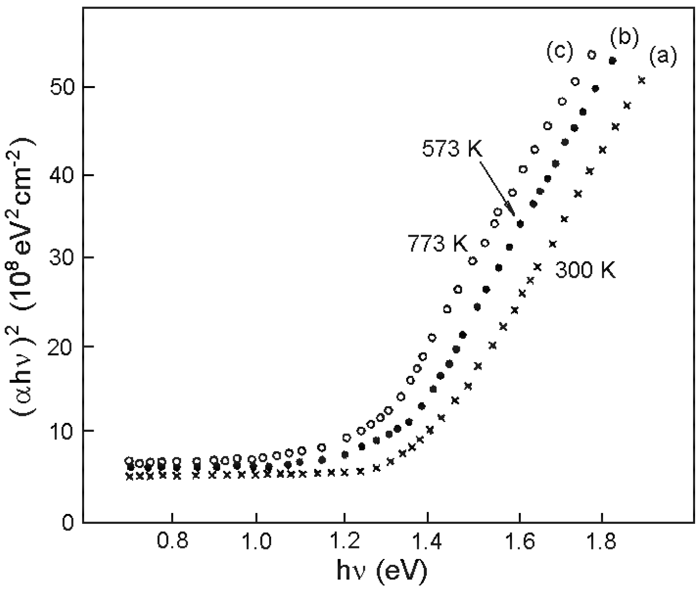


Fig. 5. $(\alpha h\nu)^2$ *vs.* $h\nu$ *of* $CuGa_{0.3}In_{0.7}Se_2$ *films, (a) as-deposited (300* K*) and annealed in* N_2 *atmosphere at 573 and 773* K.

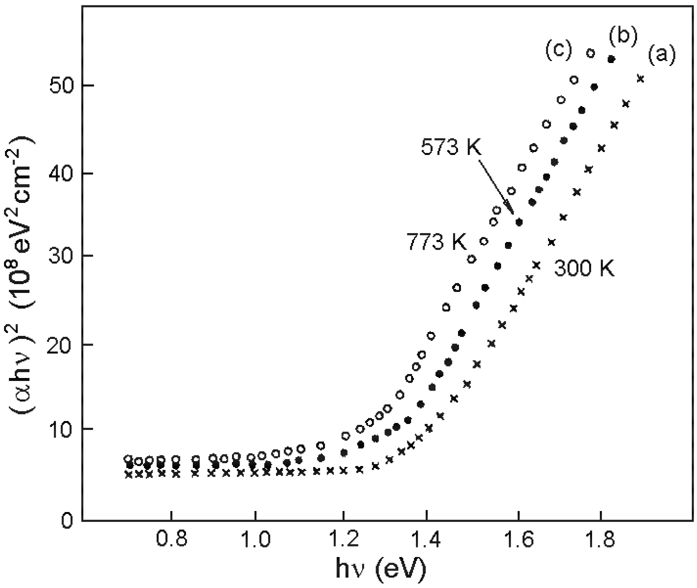


Fig. 6. $(\alpha h\nu)^2$ *vs.* $h\nu$ *of* $CuGa_{0.3}In_{0.7}Se_2$ *films selenized at 573 and 773* K.

than that of the annealing, which indicates that the selenization improves optical properties of $CuGa_{0.3}In_{0.7}Se_2$ thin films more than the annealing in nitrogen atmosphere.

3.4. Characterization of n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ *heterojunctions*

From the studies of the optical and electrical properties of $CuGa_{0.3}In_{0.7}Se_2$ thin films, it is found that the selenization of these films at 773 K under vacuum of about 0.1 Pa for one hour, is much more effective in improving the film properties than annealing at the same temperature in nitrogen atmosphere. Also, the $Cd_{0.9}Zn_{0.1}S$ thin films heat treated with $CdCl_2$ vapour are used as a window layer instead of CdS. Therefore, the p-$CuGa_{0.3}In_{0.7}Se_2$ films selenized at 773 K and the n-$Cd_{0.9}Zn_{0.1}S$ thin films heat-treated with $CdCl_2$ vapour were chosen for fabrication of heterojunction solar cells.

3.5. Current-voltage characteristics

To determine the junction parameters of the cells, their characteristics were studied while shielded from light and while exposed to light, as shown in Fig. 7. The forward dark current shows exponential increase with the applied voltage. However, at high forward bias ($V > 0.5$ V) the I–V characteristics show a linear behaviour. The rectification ratio (RR) of a cell can be calculated from the ratio

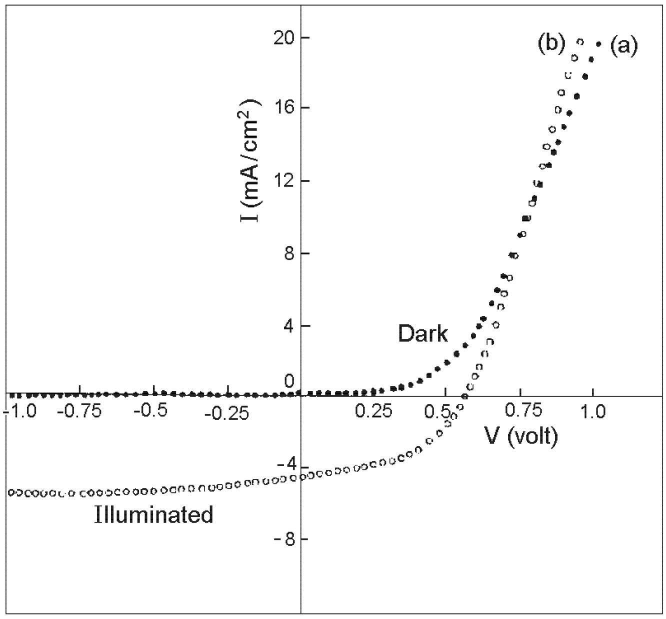


Fig. 7. Current-voltage characteristics of n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ *thin films heterojunction, (a) dark and (b) illuminated.*

of the forward current to the reverse current at a certain value of the applied voltage and the value $RR = 300$ was obtained. The value of the series resistance R_S of the cell can be determined from the slope of the linear part of the forward I–V characteristics at high bias and the value $R_S = 30.4\ \Omega$ was obtained. Similarly, the shunt resistance R_p can found from the reverse I–V characteristics, and the result is $R_p = 10.8\ M\Omega$. The I–V characteristics of the n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ heterojunctions under illumination with sun light were also studied. These I–V characteristics of the cell, with a cell total area of 1 cm^2 are shown in Fig. 7. The observed open-circuit voltage (V_{oc}) value, determined from the intercept of the curve with the voltage axis ($I = 0$), is equal to 580 mV, and the short circuit current (I_{sc}) value, calculated from the intercept with the current axis ($V = 0$), is equal to 4.8 mA. The poor collection efficiency (1.898 %) is probably due to the recombination losses in the bulk and in the interface region as well as to the lattice thermal and electron affinity mismatch between $Cd_{0.9}Zn_{0.1}S$ and $CuGa_{0.3}In_{0.7}Se_2$ layer [23,24].

3.6. Capacitance-voltage characteristics

The capacitance-voltage characteristics of n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ heterojunctions were measured at 100 kHz in dark and at room temperature. Fig. 8 shows the C^{-2} versus the applied bias V plot for the heterojunctions. At a reverse

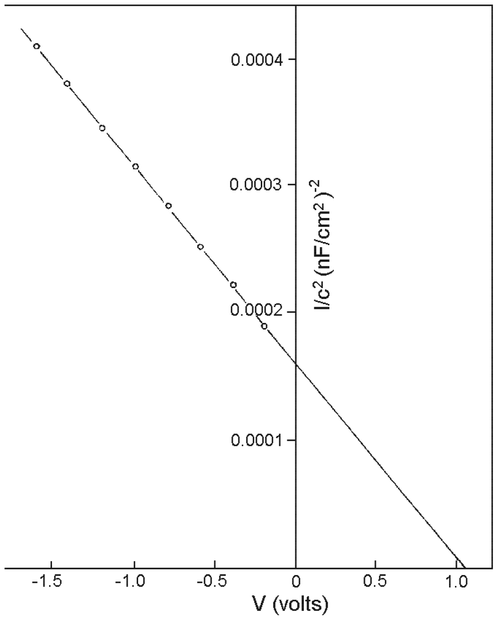


Fig. 8. Capacitance-voltage characteristic of n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ *thin films heterojunction at 100* kHz.

bias (V) the capacitance of the heterojunctions is primarily determined by the capacitance of the depletion region. The capacitance per unit area is given by [25]

$$C = \sqrt{\frac{e\varepsilon_n N_D \varepsilon_p N_A}{2(V_D - V)(\varepsilon_n N_D + \varepsilon_p N_A)}}\,, \tag{4}$$

where ε_n and ε_p are the permitivities, and N_D, N_A are the ionized impurity densities in the n-type and p-type materials, respectively. The value of N_A was determined from the slope of the C^{-2} versus V curve, and this value is in agreement with the value determined from the Hall effect measurements. The voltage intercept in the C^{-2} versus V plot gives the built-in voltage $V_D = 1.05$ V.

4. Conclusion

$CuGa_{0.3}In_{0.7}Se_2$ polycrystalline thin films were grown by thermal evaporation at substrate temperature of 450 K under vacuum of about 10^{-4} Pa and the rate of deposition of about 200 nm/min. The selenization temperature was between 573 and 773 K. The X-ray diffraction studies confirm the chalcopyrite structure of $CuGa_{0.3}In_{0.7}Se_2$ annealed at 773 K in N_2 atmosphere and when selenized at different temperatures with single phase. It was found that the activation energy decreases upon selenization or annealing in N_2 atmosphere of the $CuGa_{0.3}In_{0.7}Se_2$

thin films. The optical absorption spectra of the investigated films reveal the existence of a direct energy gap. It was found that the optical energy gap decreases with increasing temperature of both annealing and selenization. From the dark *I–V* characteristics of n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ heterojunctions at room temperature, the diode quality factor, the rectification ratio, the series resistance and the shunt resistance were found to be 2.1, 300, 30.4 Ω and 10.8 MΩ, respectively. The as-deposited n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ heterojunction cells exhibited an electrical conversion efficiency of 1.898 %. From the *C–V* measurements at room temperature, it was found that the built-in voltage and the acceptor state density are 1.05 V and 8.15×10^{15} cm^{-3}, respectively.

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IZRADA I ZNAČAJKE TANKIH POLIKRISTALINIČNIH HETERO-SPOJEVA n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$

Tanke polikristalinične slojeve $CuGa_{0.3}In_{0.7}Se_2$ pripremali smo naparavanjem u vakuumu oko 10^{-4} Pa, brzinom polaganja oko 200 nm/min. Seleniranje tih slojeva na 723 K poboljšava im svojstva. Aktivacijska energija i optički energijski procijep smanjuju se opuštanjem i seleniranjem. Pripremali smo i polikristalinične tankoslojne hetero-spojeve n-$Cd_{0.9}Zn_{0.1}S$/p-$CuGa_{0.3}In_{0.7}Se_2$ i proučavali njihova značajke: gustoća struje – napon i kapacitet – napon. Ćelije ploštine 1 cm^2 hetero-spojeva osvijetlili smo svjetlošću jakosti 1000 mW/cm^2 i izmjerili napon otvorenog kruga od 580 mV, gustoću struje kratkog spoja 4.8 $mAcm^{-2}$, faktor punjenja 0.682 i učinkovitost pretvorbe 1.898%.