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Optical Properties of CdS/CuInGaSe$_2$ hetero-structures irradiated by MeV electrons

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The stability of solar cells with CuInSe$_2$(CIS) -based absorber layers under high-energy electron- and proton-radiation combined with the radiation hardness of bare CIS and CuInGaSe$_2$ (CIGS) make these materials very attractive for use in spacecraft power generators. To retain and enhance these advantageous properties as CIS-based technology is developed requires an understanding of the origin of these phenomena. CIS-based technology has taken a lead in terms of performance amongst thin-film technologies for mass production of solar cells, with a conversion efficiency close to 20% achieved [1]. A number of studies of the physical properties of ZnO/CdS/CIGS hetero-structures suggest that the main obstacle to further progress towards the theoretical maximum of 30% is unwanted defects generated during the growth process of the CIGS absorber layer due to deviations from the ideal stoichiometry. The high performance and stability of CIGS-based solar cells make them likely candidates not only for terrestrial applications but also for outer space, on near-earth orbits [3]. Such an application requires studies of their radiation hardness and in particular of effects of irradiation by high-energy electrons [4, 5]. This issue is closely linked to improving the general understanding of defect physics in CIS and CIGS. In addition establishing the nature of radiation defects can facilitate understanding of the nature of the growth defects.

CIGS thin films were deposited on Mo coated soda-lime glass substrates by the co-evaporation technique and then coated with 50 nm of CdS using a standard chemical bath deposition process. The studied hetero-structures consist of ~50nm CdS buffer-layer, ~ 1.5 μm CIGS absorber grown upon a 0.8 μm thick molybdenum back contact deposited on a 2 mm soda-lime glass substrate. Chemical composition and the depth profile were determined by energy dispersive X-Ray analysis (EDX) and Auger electron spectroscopy (AES). CIGS films with the same chemical composition were also deposited on soda-lime glass substrates as reference samples for comparison. The crystalline structure and the phases in the films were investigated by X-Ray diffraction (XRD) with CuK_α (λ = 1.5414 Å) radiation. The surface morphology of the films was analyzed by scanning electron microscopy (SEM).

The CIGS films were irradiated with 5 MeV electrons (doses from 10^{16} to $5\cdot10^{17}$ cm^{-2}) at a rate of 10^{12} cm^{-2}s^{-1} and at a temperature below 50 °C. The transmittance (T) and reflectance (R) of the reference CIGS films on glass substrates were measured at 300 and 4.2 K over the spectral range 200 – 3000 nm using a Cary 500 UV-Vis-NIR spectrophotometer. Photoluminescence (PL) measurements were carried out at 4.2 K using a 200 mW Ar ion laser ($\lambda_{exc.}$ ~ 488 nm) as the excitation source. The PL was detected by an InGaAs p-i-n detector (Hamamatsu, Japan) in conjunction with a 0.6 m single-grating monochromator with a 600 grooves/mm grating. The photoluminescence excitation (PLE) spectra were measured using a 400 W halogen tungsten lamp combined with a grating monochromator (600 grooves/mm, focal length of 0.3 m) as an excitation source. The samples were immersed into liquid helium during the optical measurements.

Table 1 contains the average concentrations of Cu, In, Ga and Se measured by EDX and AES methods in the CIGS

Table 1. Elemental composition of CIGS thin films deposited upon Mo/glass and glass substrates.

Sample notation	Method of analysis	Substrate type	Cu at, %	In at, %	Ga at, %	Se at, %	Ga/Ga+In at, %
4	AES	Mo/glass	25.1	18.6	6.8	49.5	0.268
4	EDX	Mo/glass	24.1	18.8	7.2	49.9	0.277
2	AES	glass	23.0	19.9	7.1	50.0	0.263
2	EDX	glass	23.0	19.6	7.4	50.0	0.274

films deposited on Mo coated glass (Mo/glass substrates) (sample 4) or CIGS layers deposited on bare glass substrate (sample 2). Each elemental composition measured by EDX is an average of the concentrations measured at five different points of each film. For AES the averaging uses the atomic concentrations measured after different ion-beam sputtering times. The results of these measurements as well as relative percentages of Ga are shown in Table 1.

Fig.1 shows an example of the depth profiles of the elemental compositions of Cu, In, Ga and Se through the CIGS layer for sample 4 measured by AES. It can be seen that Se and Cu are uniformly distributed with depth down to the Mo layer.

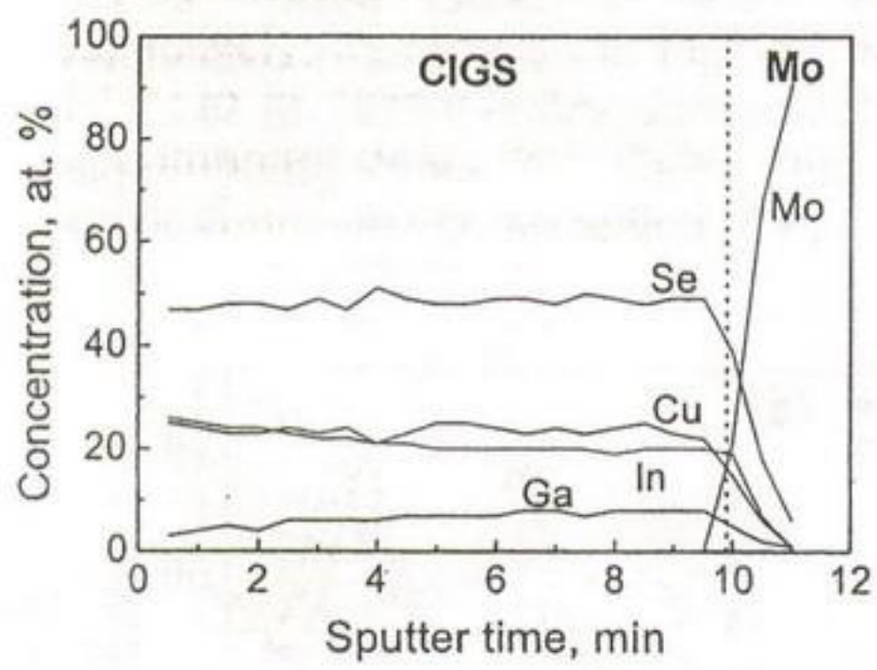

Fig.1. AES depth profiles of Cu, In, Ga and Se in CIGS film.

The concentrations of In and Ga are less uniform. The content of Ga is gradually increasing towards the Mo layer, whereas the In concentration is decreasing. Very similar trends have been found in the Cu, In, Ga and Se depth profiles in the CIGS film of sample 2 deposited upon bare glass substrate.

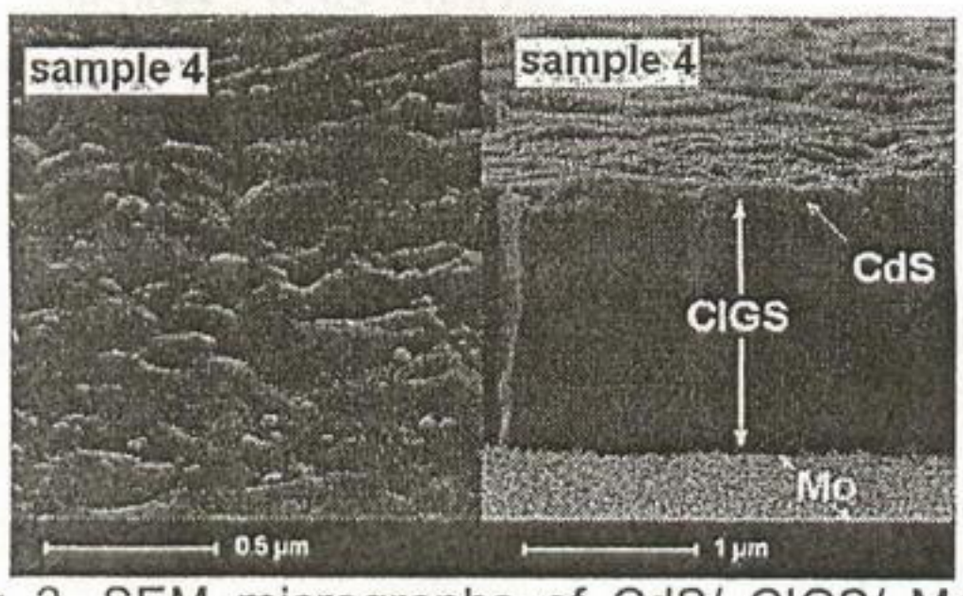

Fig. 2. SEM micrographs of CdS/ CIGS/ Mo/ glass hetero-structure.

Fig.2 shows SEM images of the surface morphology and a cross-section of the CdS/CIGS layer of sample 4. The crystalline grain sizes are seen to reach 0.3 – 1.2 µm, which is comparable with the thickness of the CIGS layer whereas the CdS layer is thin and dense. The images demonstrate large, well-faceted grains of CIGS with small porosity at the grain boundaries. Comparative analysis of the morphology of the CdS/CIGS/Mo/glass (sample 4) and CIGS/Glass (sample 2) interface layers demonstrates a good uniformity of the structure as well as good adhesion of the layers for both samples.

The crystalline structure of the samples has been studied by XRD. The results of these measurements manifest that the CIGS layers formed on both Mo/glass and bare glass substrates have a good single-phase chalcopyrite structure. As an example, Fig. 3 shows a XRD pattern of a CdS/CIGS hetero-structure fabricated upon Mo coated glass substrate (sample 4). The major diffraction reflections – (112), (204)/(220) and (116)/(312) are associated with the chalcopyrite CIS phase. The degree of preferred orientation for sample 4 estimated from the intensity ratio $I_{112}/I_{204,220}$ is about 3.1 suggesting that a significant degree of the (112) preferential orientation has been achieved for sample 4.

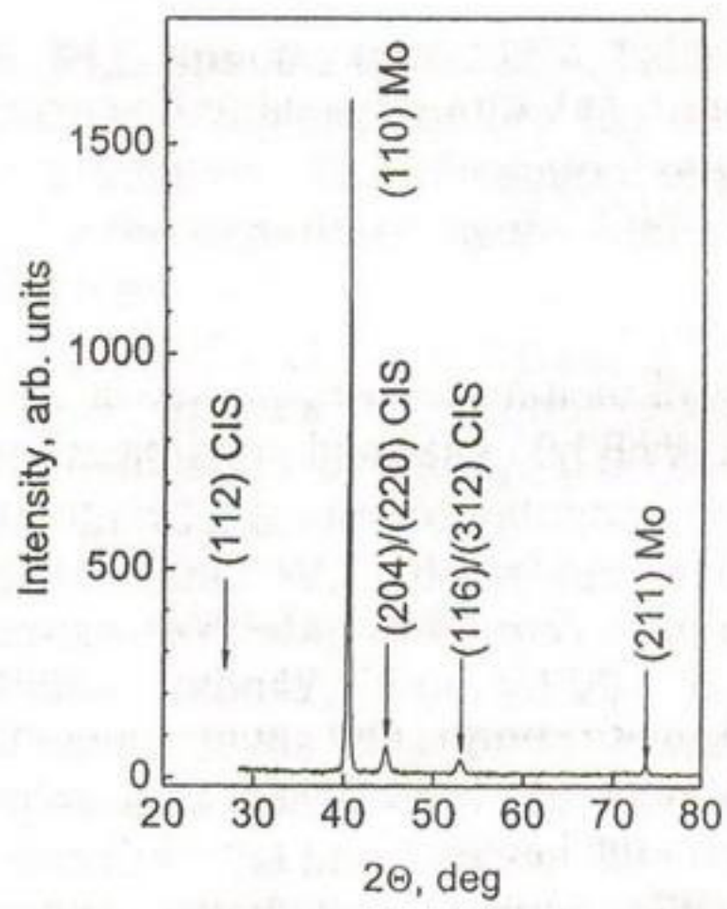

Fig. 3: XRD diffraction pattern of CdS/ CIGS/ Mo/ glass hetero-structure.

The optical characteristics of sample 2 on glass substrate have been determined from transmission (*T*) and reflection (*R*) spectra at 4.2 K and 300 K. The transmission spectra are shown in Fig. 4(a). It can be seen that sample 2 has a high transparency reaching ~ 70% in the near-infrared region, with intensive interference fringes. A relatively sharp edge of the intrinsic absorption can be seen in Fig. 4(b). These experimental data confirm a high quality of CIGS films on glass substrate. Reflectance was measured in the photon energy region 0.8 – 1.3 eV and was about 0.18 for sample 2. The absorption

coefficient of the films has been calculated using the following equation [6]:

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

where α is the absorption coefficient, *d* is the thickness of the film. For the allowed direct transitions the spectral dependence of the absorption coefficient can be calculated as follows [7]:

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2}, \qquad (2)$$

where *A* is a constant and E_g is the optical band gap. Thus the optical band gap E_g of CIGS films, is determined by extrapolating the linear part of the spectrum $\alpha^2 \sim f(h\nu)$ to the phonon energy axis. E_g = 1.28 eV and E_g = 1.21 eV were found for 4.2 K and 300 K, respectively, as shown in Fig. 4. These values of E_g are in satisfactory agreement with other experimental data for CIGS thin films with similar chemical composition [8,9].

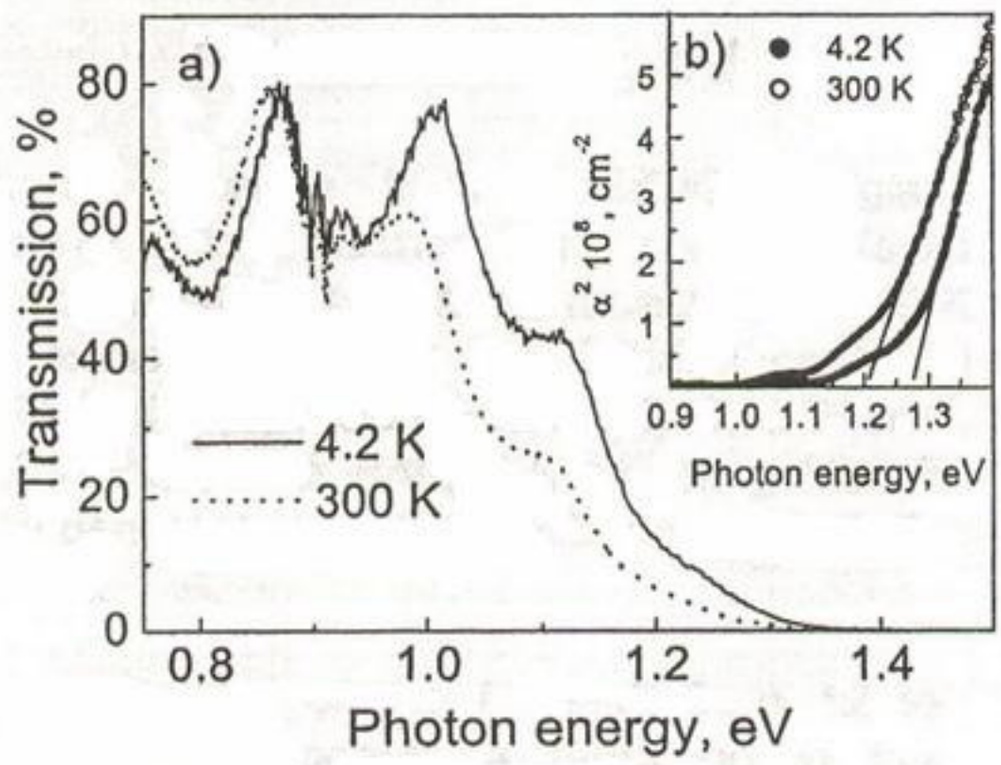

Fig.4. Transmission (a) and absorption (b) spectra taken at 4.2 and 300 K measured in sample 2 (CIGS/glass).

The CIGS layer in sample 4 has been deposited upon Mo/glass substrate. The non-transparent Mo makes it impossible to measure the band gap in this layer using transmission. Thus, the E_g in this sample was measured using PLE. The PL and PLE spectra, measured at 4.2 K in CdS/CIGS/Mo/glass hetero-structures (sample 4) before and after irradiation by electrons with a dose of 5×10^{17}cm^{-2} are shown in Fig.5. Similar spectra were also taken at 4.2 K for CIGS/glass (sample 2). The spectral position of the maximum in the PLE spectra is 1.26 – 1.29 eV which is close to the band gap measured in sample 2 by the transmission method at 4.2 K. For the irradiated structures PLE measurements were carried out at three detection energies E_{det}, at the energies of maxima of the main bands of luminescence P1 and P2, associated with radiation defects, as well as at the maximum of the donor-acceptor pair band (DAP) shown in Fig.5.

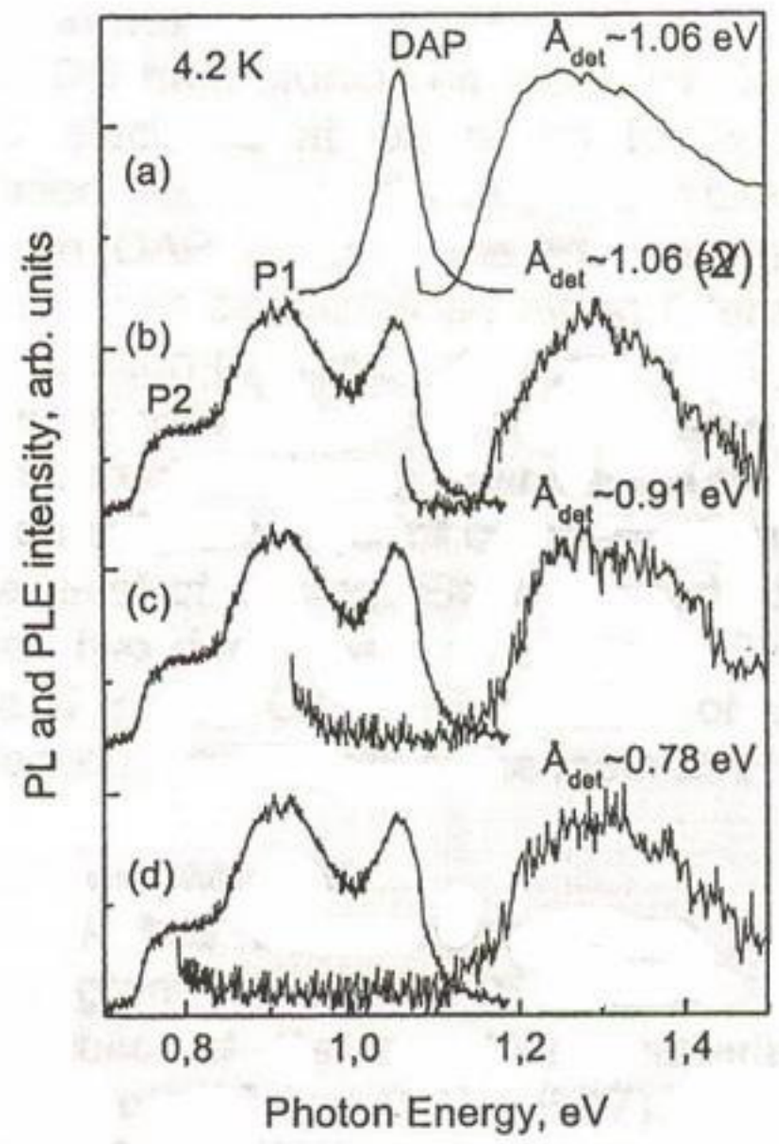

Fig.5. PLE spectra taken at 4.2 K in sample 4 (CdS/CIGS/Mo/glass) before (a) and after (b, c, d) irradiation. The detection energies E_{det} used for the experiment were 1.06 eV, 0.91 eV and 0.78 eV.

The PL spectra, taken prior to irradiation at 4.2 K (excitation intensity 0.08 W·cm^{-2}) and shown in Fig. 6, are dominated by a broad band at 1.052 eV, with a full width at half maximum (FWHM) of 55 meV. Increasing the excitation intensity from 0.006 to 2 W/cm^2 significantly shifts this band towards higher energies at a rate (*j* -shift) of 12 meV/decade. The shape of the band shows little change with increasing excitation power. The spectral positions of the PL band, ~ 0.2 eV below the band gap E_g, and the value of the blue shift suggest that this band is associated with deep donor-acceptor pair (DAP) recombination influenced by strong spatially fluctuating potentials (SFP). Statistically distributed lateral potential fluctuations due to inhomogeneity of the elemental composition on a micro-scale generate high concentrations of charged defects. These SFP cause fluctuations of the band gap, widen the impurities levels and generate band tails. The observed DAP band can be tentatively associated with copper vacancies (V_{Cu}) as the acceptor and selenium vacancies (V_{Se}) as the deep donor. Irradiation by electrons decreases the rate of the blue shift with increasing excitation (down to

8 meV/decade at $5x10^{17}$ cm^{-2} as shown in Fig. 6)

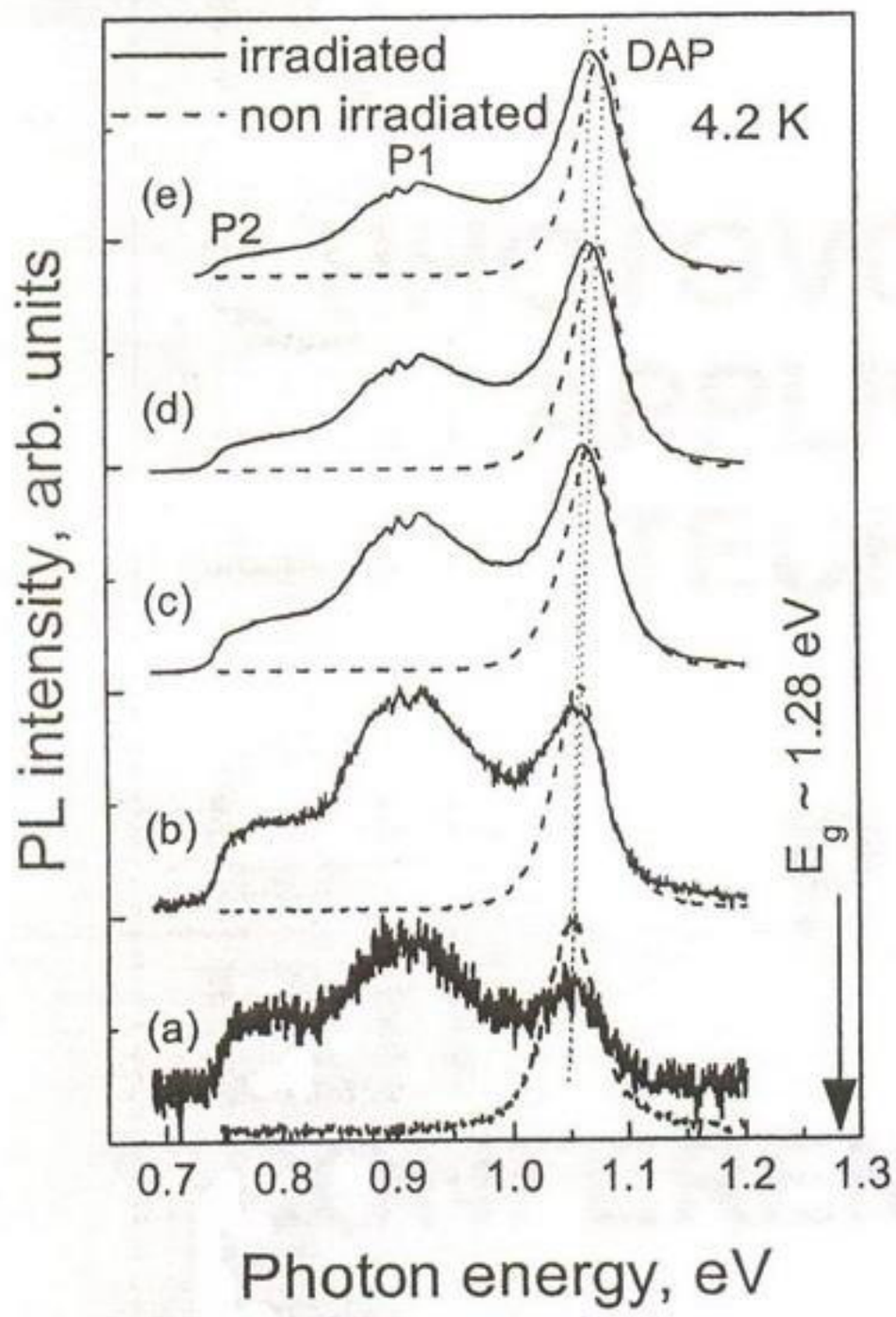

Fig.6. PL spectra from CdS/CIGS/Mo/glass (sample 4) before (dashed lines) and after (solid lines) irradiation with electrons measured at 4.2 K and excitation powers (a) 0.006 $W \cdot cm^{-2}$, (b) 0.028 $W \cdot cm^{-2}$, (c) 0.26 $W \cdot cm^{-2}$, (d) 0.78 $W \cdot cm^{-2}$, (e) 2.0 $W \cdot cm^{-2}$. The straight lines are guides for the eye demonstrating the *j*-shifts before and after irradiation.

The reduction of the *j* - shift from 12 to 8 meV/decade suggests a reduction in the mean value of the potential fluctuation. This reduction can be explained by an interaction of the radiation-induced defects with growth defects. Such an interaction results in annihilation of some of the growth defects reducing their concentration and consequently the level of compensation as well as the level of doping. Improvements in the performance of CIGS-based solar cells after irradiation with doses of about $10^{16}cm^{-2}$ of 1 MeV electron has been reported earlier [10] confirming that at low doses electron irradiation can be beneficial for the performance of solar cells.

The electron irradiation also generates two additional deeper bands P1, at 0.91 eV, and P2, at 0.77 eV, in the PL spectra as shown in Fig. 6. At high doses irradiation reduces the intensity of the main DAP band and increases the intensity of the P1 and P2 bands. These bands do not shift with variations of the excitation intensity and correspond to defects with levels at about 0.37 eV and 0.51 eV in the band gap of CIGS. The deep levels are tentatively associated with copper at indium site Cu_{In} and indium vacancies V_{In} (or indium at copper site In_{Cu}), respectively, induced by the radiation defects.

Conclusions

CdS/CIGS heterojunctions were irradiated with 5 MeV electrons at doses up to $5x10^{17}$ cm^{-2}. Irradiation decreased the rate of the blue shift of the main DAP band in the PL spectra. This reduction can be explained by an interaction of the radiation-induced defects with growth defects resulting in annihilation of some of the growth defects reducing their concentration and consequently the level of compensation as well as the level of doping. Electron irradiation also induced two deep levels at 0.37 and 0.51 eV in the band gap of CIGS. High doses of electrons also reduce the intensity of the main DAP band.

Acknowledgements

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