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Dedicated to Professor Ioan-Iovitz Popescu's 80th Anniversary

EFFECT OF PROTONS IRRADIATION ON THE PERFORMANCES OF CdS/CdTe PHOTOVOLTAIC CELLS FOR SPACE APPLICATIONS

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Abstract. Photovoltaic cells based on cadmium sulphide and cadmium telluride thin films were prepared by thermal vacuum evaporation in superstrate configuration. Thin films of indium tin oxide or indium zinc oxide deposited on optical glass substrates were used as transparent and conductive electrodes. The structures were irradiated with protons (3 MeV, 10^{14} protons/cm^2 fluency), electrical characterizations being performed both before and after irradiation. The photovoltaic parameters were extracted and the effect of irradiation is discussed. The structures using indium zinc oxide are more stable against protons irradiation than those based on indium thin oxide as transparent and conductive electrode.

Key words: cadmium sulphide, cadmium telluride, photovoltaic cells, protons irradiation.

1. INTRODUCTION

$A^{II}B^{VI}$ semiconductors were widely investigated, as potential candidates for optoelectronic applications [1], particularly for photovoltaic cells [2]. The materials in this class, especially cadmium chalcogenides, have physical properties well suited for such type of applications: direct bandgaps [3], with values suited for both window layers – as in the case of cadmium sulfide (CdS) – or absorber layers due to high absorption coefficients – as in the case of cadmium telluride (CdTe) or cadmium selenide [4, 5], good mechanical and chemical stability [6]. Moreover, CdS, CdSe and CdTe can be cast into thin films by several techniques: electrodeposition [7, 8], sputtering [9], screen printing [10], spray pyrolysis [11] or thermal vacuum evaporation [12–18]. CdS/CdTe thin film based photovoltaic cells are well suited both for terrestrial and space applications, too, due to their reduced weight and good physical and chemical stability. The power conversion efficiency of such type of cells has increased significantly in last years from 8.8% [19] to 16.7% in AM 1.5 conditions [20, 21].

The physical and chemical properties of component layers of CdS/CdTe photovoltaic cells can be improved by chemical treatments with cadmium chloride ($CdCl_2$) [4], either by using a "dry" method or a chemical "wet" one, with samples immersed in a properly chosen solution. The main consequences of cadmium chloride treatment are the increase of CdTe crystallite grains and decrease of defect states at the interface CdS/CdTe, then improving the performances of the photovoltaic cells generally, and in the case of those used in space applications, their stability against the ionizing radiations, respectively [22–25].

In this paper we report on the influence of irradiation with energetic protons on photovoltaic cells based on CdS/CdTe heterojunction, in superstrate structure using indium tin oxide (ITO) or indium zinc oxide (IZO) as transparent and conductive oxide (TCO), deposited on optical glass substrates. Protons represent 87% of cosmic rays, so such studies are of great interest for using such structures in space applications. The samples were characterized before and after protons irradiation and the cells parameters were compared.

2. EXPERIMENTAL PROCEDURES

Photovoltaic cells based on CdS/CdTe heterojunction were prepared by thermal vacuum evaporation technique (TVE), in superstrate configuration. A CdS "window" layer, 250 – 800 nm thick, was deposited onto optical glass substrates covered with indium zinc oxide (75 nm thick) and indium tin oxide (50 nm thick), respectively. CdS powder (Aldrich, 99.99%) was sublimated at 740°C form a single source; the residual pressure in the deposition chamber was 1.4×10^{-5} Torr and the substrate temperature was maintained at 250°C during film deposition. A thermal treatment was performed immediately after deposition for 15 minutes at 300°C. CdTe thin films were also deposited by TVE, at 600°C. The CdTe powder (Aldrich 99.99%) was used without further purification. The substrate temperature was maintained at 250°C, during the deposition. Both IZO/CdS/CdTe and ITO/CdS/CdTe prepared structures were thermally treated for 25 minutes at 300°C, to improve the crystalline structure of the as prepared thin films.

Chemical treatments with $CdCl_2$ were then performed for both ITO/CdS/CdTe and IZO/CdS/CdTe structures, by their immersion in a $CdCl_2/CH_3OH$ solution for 5 seconds and then were thermally treated at 200°C, in an evacuated chamber (~10^{-4} mbar).

To complete the photovoltaic structure, back electrodes were deposited onto CdTe absorber layer, consisting of a thin layer of copper, (50 nanometers thickness), followed by another thin film of gold (100 nanometers thickness), both deposited by TVE. The whole structures were thermally treated again for 30 minutes at 150°C.

The samples were subjected to protons irradiation using a Van der Graaf accelerator, the radiation beam being directed along the normal to the sample's surface. Irradiation was performed in an evacuated chamber, at room temperature; the energy of the incident particles was 3 MeV and the fluency was 8×10^{14} protons/cm^2.

The morphology for the CdS/CdTe interfaces were analyzed by Cross Section Scanning Electron Microscopy (Cross-Section SEM), using a Tescan Vega XMU-II microscope with secondary electrons as signal (the acceleration voltage was between 200 V up to 30 kV, the resulting magnification being from 3 × up to 500.000 ×). The SEM had also an adjustable scanning speed between 160 ns / pixel to 10 ms / pixel.

Electrical measurements were performed before and after protons irradiation. Dark I-V measurements were done covering the devices with a black paper. Photoelectrical characterization was performed using a Newport-Oriel 150 solar simulator, in AM 1.5 conditions. The current was measured using a 2400 Keithley Source Metter. The range of the sweeping voltage across the devices is set using a labview program which is connected with the source meter. The samples' active area was 0.6 cm^2.

For action spectra and external quantum efficiency (EQE) measurements, an experimental setup containing a Newport Oriel monochromator, controlled by a computer, was used. Optical properties of the CdS and CdTe films were characterized by performing transmittance and absorption measurements. The data were recorded at room temperature, with a Perkin-Elmer Lambda 35 spectrometer.

Short-circuit current, open-circuit voltage, fill factor and maximum power were determined from I-V characteristics in forth quadrant, at illumination in AM 1.5 conditions, and compared for irradiated and as grown samples.

3. RESULTS AND DISCUSSIONS

For the surface morphology investigations we have used the Cross-Section SEM technique, using a Tescan Vega XMU-II SEM microscope.

Figures 1 and 2 show SEM micrographs recorded for a Au:Cu/$CdCl_2$/CdTe/ CdS/IZO and Au:Cu/$CdCl_2$/CdTe/CdS/ITO structure, respectively.

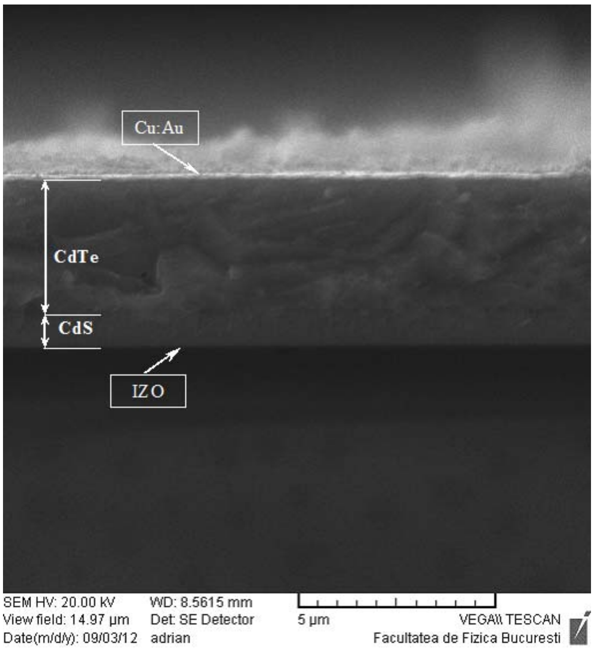


Fig. 1 – SEM micrograph of a Au:Cu/$CdCl_2$/CdTe/CdS/IZO structure (cross section).

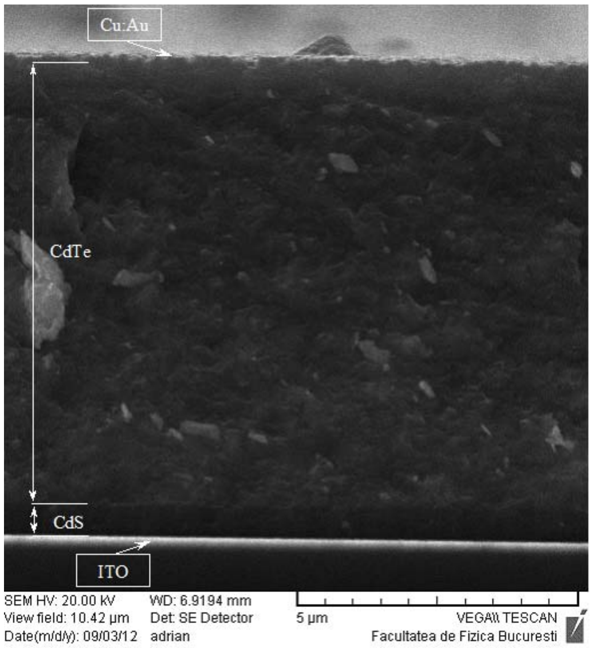
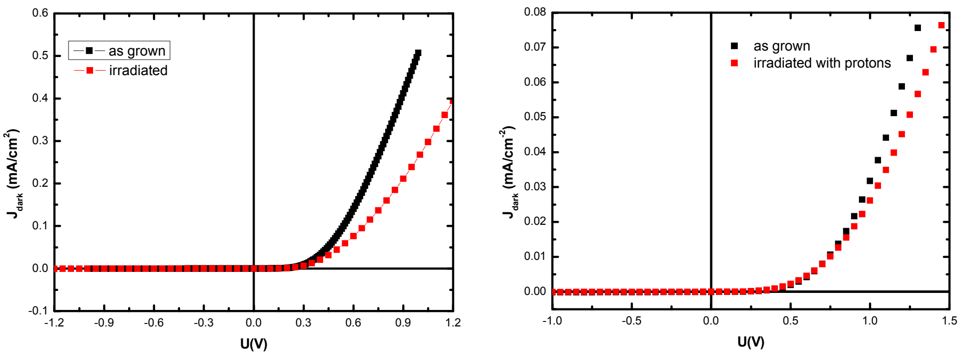


Fig. 2 – SEM micrograph of a Au:Cu/$CdCl_2$/CdTe/CdS/ITO structure (cross section).

As one can observe easily from these figures, all the layers of the structures are present in the structures, they are compact and larger grains can be observed in CdTe layers.

The current-voltage (*I-V*) characteristics of the prepared solar cells have been measured in dark, at room temperature, in both forward and reverse bias conditions, before and after protons irradiation as they are shown in Fig. 3. One can notice that the *I-V* characteristics are highly asymmetric and nonlinear. As expected, the forward bias conditions lead to an increase of the current density with the positive voltage between the gold electrodes with respect to the ITO or IZO front contact electrode. Their asymmetry is due to the presence of a barrier at the interface CdS/CdTe.



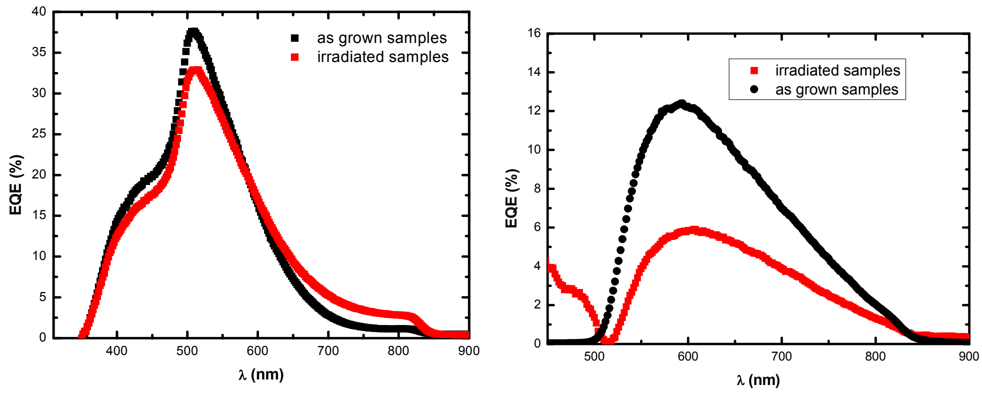
(a) (b)

Fig. 3 – *I-V* characteristics in dark of: a) IZO/CdS/CdTe/Cu/Au; b) ITO/CdS/CdTe/Cu/Au.

Using the modified Shockley equation [23–25], the series and shunt resistances and the quality factor of the junction, *n,* were determined, before and after protons irradiation. The calculated values for series and shunt resistances for ITO/CdS/CdTe/Cu/Au as grown samples were 1.8 kΩ and 0.11 MΩ. After irradiations, the series resistance increased by a order of magnitude, to 10 KΩ, while the shunt resistance increase slightly to 0.17 MΩ. Series and shunt resistances of IZO/CdS/CdTe/Cu/Au, were 4.9 kΩ (as grown), and 10 kΩ (after proton irradiation), and 0.17 MΩ (as grown) and 1.27 MΩ (after proton irradiation), respectively.

Figure 4 shows the action spectra of the prepared samples, before and after accelerated protons irradiation.

The external quantum efficiency (EQE) was measured at room temperature for all samples. Notice that proton irradiation results in decreased values of EQE. In the case of IZO/CdS/CdTe/Cu/Au the difference between EQE values, for as grown and irradiated samples, is not significant, from 37% to 32%, but for the sample ITO/CdS/CdTe/Cu/Au the decrease is sharp (EQE values after irradiation are almost half of those obtained for as grown structures). This behavior suggests that the stability against the protons irradiation of the IZO/CdS/CdTe/Cu/Au structures was significantly improved with respect of ITO/CdS/CdTe/Cu/Au cells.



(a) (b)

Fig. 4 – Action spectra of: a) IZO/CdS/CdTe/Cu/Au; b) ITO/CdS/CdTe/Cu/Au structures.

In Fig. 5 the *I*-*V* characteristics of ITO/CdS/CdTe/Cu/Au samples, in fourth quadrant, before and after irradiation are presented.

The main parameters of the cells (short-circuit current, open circuit voltage, fill factor and maximum power) were determined; the corresponding values were summarized in Table 1.

The same measurements were performed for IZO/CdS/CdTe/Cu/Au and the obtained results are presented in Fig. 6.

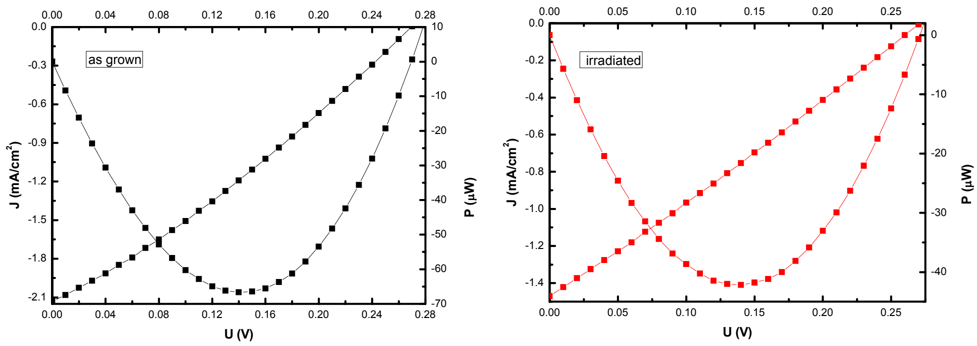


Fig. 5 – *I*-*V* characteristics in fourth quadrant before (black lines) and after irradiation (red lines) for ITO/CdS/CdTe/Cu/Au structures.

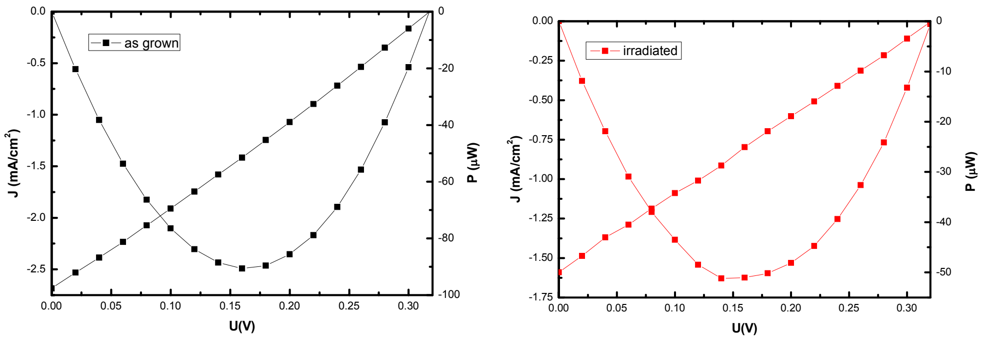


Fig. 6 – *I-V* characteristics in fourth quadrant before (black lines) and after irradiation (red lines) for IZO/CdS/CdTe/Cu/Au.

Table 1

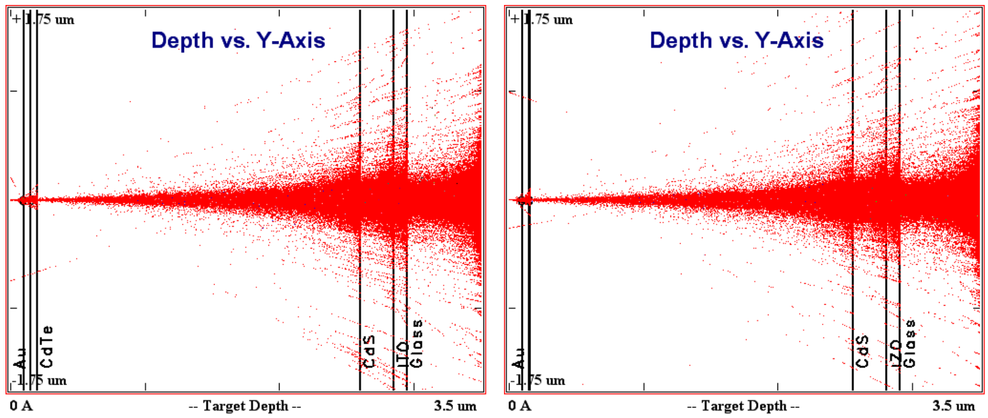
Parameters describing the photovoltaic response, before and after irradiation

Structure	I_{sc} (mA)	V_{oc} (mV)	P_{max} (µW)	FF (%)
Glass/ITO/CdS/CdTe/Cu/Au (as grown)	0.8	270	66	28
Glass/ITO/CdS/CdTe/Cu/Au (protons irradiation)	0.5	270	42	26
Glass/IZO/CdS/CdTe/Cu/Au (as grown)	1	320	90	28
Glass/IZO/CdS/CdTe/Cu/Au (protons irradiation)	0.6	310	51	25

For all samples the maximum output power decreased after protons irradiation, but not significantly. Also, the fill factor was not much affected by irradiation with protons.

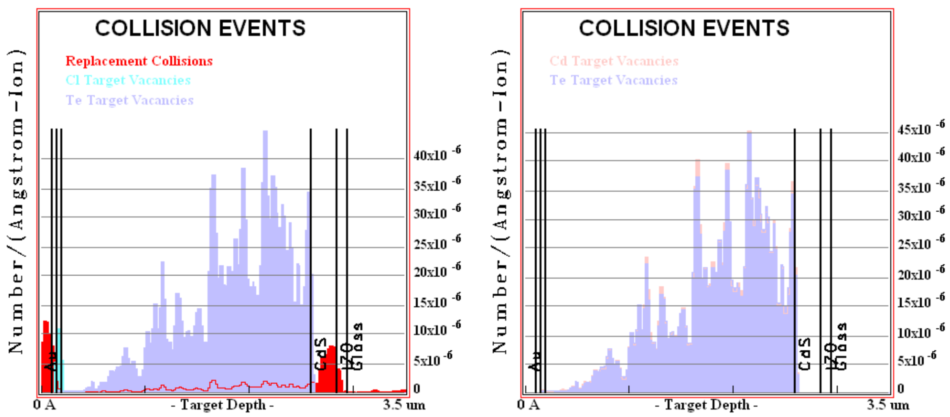
Figures 7 and 8 show ion distributions with recoils as determined with SRIM 2008 [26] package in full cascade mode. Most of defects are introduced near interfaces; inter-diffusion occurs, affecting the quality of CdTe/CdS hetero-junction (see also Fig. 8). The distribution of selected point defects, *e.g.*, Te and Cd vacancies (V_{Te} and V_{Cd}, respectively) introduced by irradiation is shown in Fig. 8.

As the irradiation was performed at ambient temperature, it is expected that some of the Frenkel pairs created by irradiation will disappear. Those created near interfaces have better chances to survive, due to the above-mentioned inter-diffusion. V_{Te} is a negative-U deep donor in CdTe, while V_{Cd} (with a distribution similar to V_{Te} , see Fig. 8b) is the most important shallow acceptor (indicated as responsible for setting the intrinsic limit for *n*-type doping in CdTe [27]). Such type of defects may alter the distribution of the electrostatic potential in the space charge region.



(a) (b)

Fig.7 – Monte Carlo simulations of the effect of proton irradiation (3 MeV) on Au: a) Cu/CdTe/CdS/ITO; b) Au:Cu/CdTe/CdS/IZO structures.



(a) (b)

Fig. 8 – a) Defect introduction rates for V_{Te}, V_{Cl} . Replacement collisions are also plotted, as a reference; b) defect introduction rates for V_{Te} and V_{Cd}.

4. CONCLUSIONS

Photovoltaic cells based on CdS/CdTe heterojunction were prepared by thermal vacuum evaporation, in superstrate configuration using two kind of the transparent and conductive oxides (IZO and ITO) deposited on the optical glass substrates.

To improve the physical and chemical properties of the component layers was made a wet chemical treatment with cadmium chloride.

Electrical and photoelectrical measurements were performed for "as grown" and after protons irradiation with energy of 3 MeV and 10^{14} protons/cm^2 fluency, respectively.

Irradiation with protons resulted in a decrease of the external quantum efficiency, due to electrically active defects introduced at CdS/CdTe interface. The same behavior was observed for short-circuit current, and except for structures having indium tin oxide as anode, for open-circuit voltage. Maximum output power and the fill factor decreased only slightly after irradiation.

The conventional ITO used as TCO for the solar cells based on CdS/CdTe heterojunction, for space applications, could be replaced with IZO, which is cheaper and a nontoxic material. In addition, IZO/CdS interface seems to be more stable against the effect of energetic protons irradiation.

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