

# EFFECTS OF D<sup>+</sup> IMPLANTATION ON THE PROPERTIES OF CdS/CIGS AND ZnO/CdS/CIGS HETEROSTRUCTURES

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## Abstract

Cu(InGa)Se<sub>2</sub> thin films with a Mo back contact and coated with a 30nm of CdS layer, were implanted with doses from 10<sup>14</sup> to 10<sup>18</sup> cm<sup>-2</sup> of 2.5keV D<sup>+</sup> at room temperature. Implanted and non-implanted area were characterised using low temperature photoluminescence (PL). ZnO dot-contacts were then deposited by r.f. sputtering to produce ZnO/CdS/CIGS/Mo photovoltaic devices and the spectral photo-response measured. A broad band (A) at 1.07eV dominated the PL spectra from the non-implanted material. Implantation of D<sup>+</sup> generated four new transitions in the PL spectra: three low energy peaks and a new peak at 1.1eV. A considerable reduction in the blue shift (*j*-shift) of the main band with increasing excitation power followed implantation and was attributed to passivation effects of D<sup>+</sup>. Annealing at 100°C for 30 min increased both the PL intensity and *j*-shift although the effect of passivation by D<sup>+</sup> on the *j*-shift was only observed for the highest implanted dose following anneal.

## Introduction

Cu(InGa)Se<sub>2</sub> (CIGS) based photo-voltaic (PV) devices hold the world record efficiency for solar energy conversion (18.8%) for thin film solar cells [1]. One of the ways to improve the characteristics of semiconductor materials is to passivate electrically active defects using hydrogen. Hydrogen can be delivered through a CdS window layer directly into the interface region. Excess energy is absorbed by the polycrystalline CdS and the implantation of hydrogen can be then done using a conventional ion implanter. A CIGS layer coated with CdS will also be protected against any possible detrimental effects of exposure to atmosphere. A study of the effects of energetic ions in CdS/CIGS heterostructures will help to understand the physics of radiation damage in CIGS and illuminate the origins of the remarkable high radiation hardness exhibited by CIGS-based photo voltaic (PV) devices. In

this work D ions were used for modelling H behaviour because depth profiling of deuterium can be done with much higher accuracy.

## Experiment

CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> thin films (with *x*≈0.7 and a deficiency of copper, the standard elemental composition for high efficient CIGS solar cells) were deposited on Mo coated soda-lime glass substrates by the co-evaporation technique and coated with 30nm of CdS using a standard chemical-bath deposition process at Stuttgart. The films were implanted with doses 10<sup>14</sup>, 10<sup>15</sup> and 10<sup>18</sup> cm<sup>-2</sup> of 2.5keV D<sup>+</sup> (ion current 1.5μA/cm<sup>2</sup>) at room temperature using an ion implanter with magnetic separation. ZnO dot-contacts were deposited by r.f. sputtering to produce photovoltaic devices. The open-circuit photovoltaic response spectra of these devices were measured at room temperature using a 100W quartz halogen light source and lock-in amplifier. The illuminated area on the sample surface was focused to about 2mm diameter. Subsequently the samples were annealed for 30 min at 100°C in air. CdS deposited using the chemical-bath process forms a continuous layer [2], which protects the CIGS from oxygen in air and from the loss of selenium. Photoluminescence and photo-response measurements were repeated following the annealing. Implanted and non-implanted areas of the films were also characterised using low temperature photoluminescence (PL) excited by the 488nm line from an Ar ion laser. The PL emission was detected using a liquid nitrogen cooled Ge detector. The samples were mounted on a 10K to 300K cold finger supported on a stage allowing two-dimensional translations of the sample without re-optimisation of the light collection optics. This enables comparative measurements of the emission intensity from different areas of the same sample. The laser excitation power for the intensity dependencies was varied from 2 to 50mW.

## Results

PL spectra taken at 10K are shown in Fig.1. A single broad band (A) at 1.07eV dominates the spectrum from non-implanted area. The PL intensity from the sample before annealing was found to be quite low at temperatures above 30K. This limited the use of the temperature dependence of the PL measured from non-annealed material for identification of the origin of the observed recombination. However, information was gained by monitoring changes in the PL spectra taken at different laser excitation intensities. Increase in the excitation intensity generated a significant blue shift ( $j$ -shift) of the A-band, shown in Table 1. Room temperature implantation of  $D^+$  with a dose  $10^{14} \text{ cm}^{-2}$  was seen to increase the width of the dominant band and shift its centre towards higher energies. After higher  $D^+$  doses the width of this band narrows again and is seen to be slightly narrower than in the non-implanted PL. The dominant band is now centred at 1.10 eV and we interpret the changes in shape following implantation in terms of the appearance of a new higher energy peak which replaces the 1.07 eV peak. The broad peak in the  $10^{14} \text{ cm}^{-2}$  sample results from the merging of the two co-existing peaks.

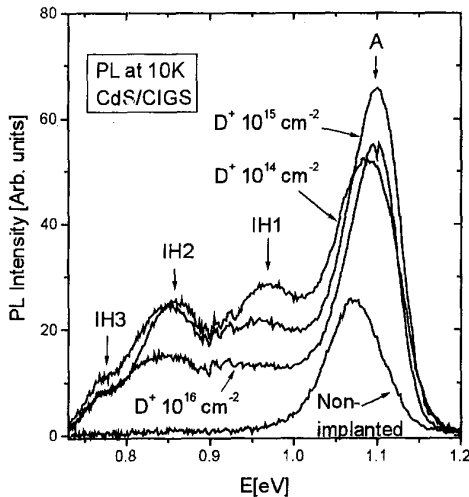


Fig.1. PL spectra from CdS/CIGS thin films implanted with different doses of 2.5keV  $D^+$ . PL was measured at 10K and excitation laser intensity 14mW.

Implantation of deuterium with doses up to  $10^{15} \text{ cm}^{-2}$  also led to a considerable increase in the intensity of the dominant band. The  $j$ -shift of the dominant band after implantation is significantly smaller than that before implantation, as shown in Table 1. In addition to the changes in the dominant PL band the  $D^+$  implantation induced three broad, low energy peaks IH1, IH2 and IH3, which achieve their maximum intensity after a dose of  $10^{15} \text{ cm}^{-2}$ . These low energy bands did not show any shift with excitation power change.

The spectral open circuit photo-voltage responses, measured for each dose, are shown in Fig.2. The implantation is seen to result in improved photo-

response. Initially the response increases with the dose, with a maximum for  $10^{14} \text{ cm}^{-2}$ . For higher doses the photo-response saturates and then decreases.

Table 1. The blue  $j$ -shift of the A band with excitation intensity for non-implanted and  $D^+$  implanted CdS/CIGS before and after 100°C ½ hr annealing.

Dose [ $\text{cm}^{-2}$ ]	non-impl.	$10^{14}$	$10^{15}$	$10^{16}$
$j$ -shift before annealing [meV/decade]	23	11	12	10
$j$ -shift after ½ hr 100°C anneal [meV/decade]	31	31	26	18

Annealing at 100°C for half an hour in air significantly changed the PL spectra. The intensity of the dominant band increased by about one order of magnitude in the PL spectra from both non-implanted and deuterium implanted areas. The intensity of the three deep bands

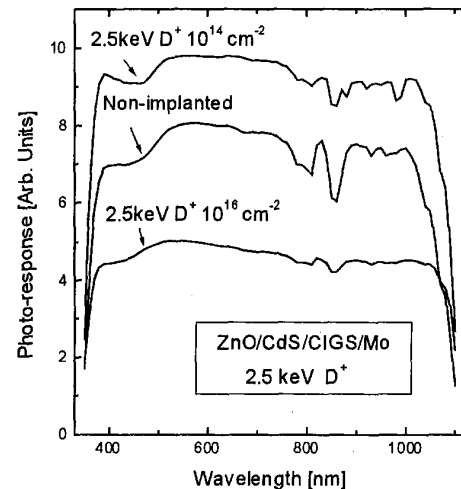


Fig.2. Effect of 2.5keV  $D^+$  implantation on photo-response of the ZnO/CdS/CIGS PV devices.

IH1, IH2, IH3), generated by implantation reduced dramatically relative to the dominant band. These peaks remained noticeable only in the PL spectra from the area implanted with  $10^{16} \text{ cm}^{-2}$  - the highest applied doses. The relative intensities of the dominant band from the implanted and non-implanted areas has also been changed: after annealing the intensity becomes higher for the non-implanted areas. Annealing led to a considerable increase in the  $j$ -shift, generated by excitation intensity rise, from both implanted and non-implanted areas. New values of the  $j$ -shift are shown in Table 1. The dominant band after annealing appeared at 1.085eV for non-implanted material. For implanted areas the dominant peak was found at energy lower than straight after implantation by 7meV. Normalised PL spectra measured from non-implanted and implanted (at  $10^{16} \text{ cm}^{-2}$ ) areas before and after annealing are shown in Fig.3. The increase in PL intensity following anneal made possible measurements of the temperature dependence of the dominant band

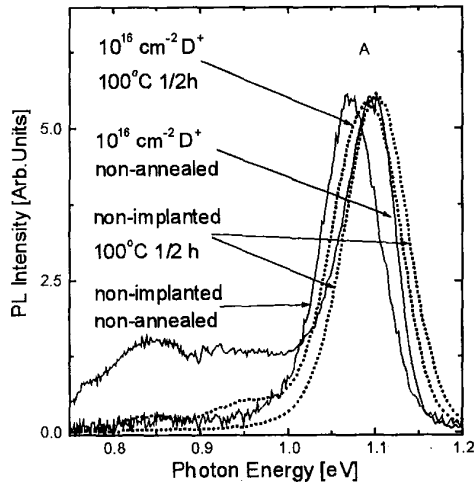


Fig.3. Normalised PL spectra from implanted and non-implanted areas before and after a 100°C anneal for ½ hr.

maximum position, as shown in Fig.4. Annealing also significantly increased photo-response from the device.

### Discussion

The PL spectra measured before and after D<sup>+</sup> implantation from CdS/CIGS hetero-structure are very similar to those observed from CIGS thin films implanted with D<sup>+</sup>, He<sup>+</sup> [3] and H<sup>+</sup> [4]. We have therefore used the tentative physical model proposed in [3, 4]. This model does not take into account effects of the electrical field due to the presence of the CdS/CIGS heterojunction although this may affect the healing of primary defects created during D<sup>+</sup> implantation, and the redistribution of implanted deuterium. In all cases the PL spectra from non-implanted material are dominated by a broad band near 1.1eV. This band is a usual feature in the PL spectra from In-excess CIGS material used for high efficient solar cells. Earlier PL studies of CIGS [6] and the excitation intensity measurements let us speculate that the dominant band originates from a band-tail recombination mechanism. Spatial potential fluctuations, generated by a large number of randomly distributed charged defects, create the band tails. In *p*-type CIGS at low temperature the holes are captured at deep states in the valence band tail, which act like acceptor levels [6]. The amplitude of potential fluctuation depends very much on the level of doping and compensation, which are governed by the excess of (In+Ga) over Cu. Such an excess determines the spectral position of the dominant band in PL spectra [7] and the *j*-shift magnitude. The higher the potential fluctuation amplitudes the greater the *j*-shift and the lower the peak energy. Although the CIGS films used in the experiments were not characterised prior to CdS deposition, measurement of similar, non-implanted CIGS thin films gave *j*-shifts below 14meV/decade [3]. In this work the *j*-shift after CdS deposition was found to be greater, at 23meV/decade. This can be explained by inter-diffusion of elements between CdS and CIGS. Diffusion of Cd into the CIGS layer and of Cu from the CdS/CIGS interface results in the creation of a graded interface region [8]. Cd atoms,

located in V<sub>Cu</sub>, can make this region more *n*-type and thus increase the level of compensation.

The implantation of deuterium generates a new band centred 24 meV higher than that of the dominant band prior to implantation. This effect can be attributed to a reduction in the amplitude of the potential fluctuations due to the passivation of charged defects by implanted deuterium. Implantation of deuterons can play a two-fold role: creating radiation damage and passivating existing defects. According to TRIM [9] calculations at 2.5keV one deuteron can create 8.6 vacancies in CIGS. But as deuterons pass through the CdS they lose a considerable part of their energy. With a mean penetration depth of about 50nm and straggling of 25nm, D<sup>+</sup> have their maximum concentration at the CdS-CIGS interface. In CIGS each deuterium ion can produce about 3 vacancies. At room temperature at least 98% of the structural radiation damage, created by 30keV Ar ions in CuInSe<sub>2</sub> single crystals, was found to be healed due to a very efficient repair mechanism [10]. Therefore we can expect that a significant fraction of the primary damage caused by deuterium implantation will be also healed as was observed for hydrogen implanted CuInSe<sub>2</sub> [11]. Some deuterium ions are trapped at the end of collision cascades but a considerable fraction diffuses much deeper than the mean penetration depth without displacing any lattice atoms. This diffusing population is expected to passivate intrinsic defects improving the structural, optical and electrical parameters of the material. After a low dose of D<sup>+</sup> bands at 1.07eV and 1.1eV co-exist together, whilst higher doses leave only the 1.1eV band.

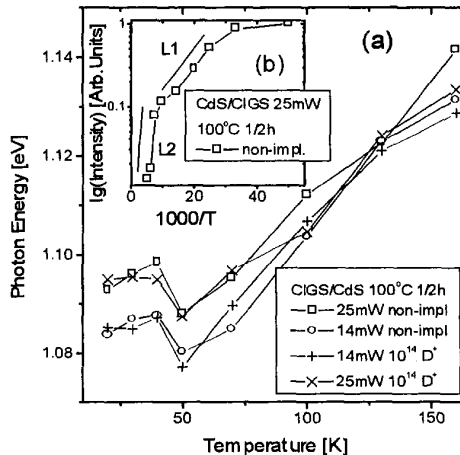


Fig.4. Temperature dependence of the A-band position in the PL spectra from non-implanted and implanted with 10<sup>14</sup> cm<sup>-2</sup> of D<sup>+</sup> CdS/CIGS area after 100°C half an hour annealing. The inset shows the Arrhenius plot of the PL intensity for non-implanted areas.

The *j*-shift of this new band was found to be reduced significantly down to 11 meV/decade. Such a reduction is also consistent with the passivation effects of charged defects by incorporated deuterium. Similar effects were observed after implantation of hydrogen into CIGS thin films without CdS layer [4] although the dominant band after implantation was found at lower energies. This difference can be related to the absence of cadmium

doping. Judging by the measured  $j$ -shift the level of compensation in bare CIGS is considerably lower than that in CIGS/CdS structures. It seems reasonable to speculate that, in bare CIGS, hydrogen could change the recombination mechanism from the band-tail to DAP whereas the presence of Cd in CIGS/CdS increases the population of charged defects making such a change difficult. Implantation of  $D^+$  reduced the height of the potential fluctuations in the band-tails. The appearance of the three low energy bands (IH1, IH2 and IH3) in the PL spectra were earlier reported for  $H^+$  [4],  $D^+$  and  $He^+$  [3] implanted CIGS thin films. The origin of these bands was attributed to intrinsic defects created after healing of the primary damage caused by energetic ions in collision cascades.

Low temperature annealing is a well-known technique to improve the PV device parameters. In our case such an annealing led to a considerable increase in intensity of the main PL band and photo-response. In early studies [12] this effect was attributed to a decrease in the density of non-radiative traps in the CdS/CIS interface. Recent reports [13] suggest a strong influence of Cd on the properties of CdS/CIGS hetero-junction. This suggestion is supported by considerable increase in  $j$ -shift, which implies a rise in the level of compensation following annealing. The reductions in  $j$ -shift shown in Table 1 indicate that the passivation effect of deuterium remains significant after annealing. This is now most pronounced for the highest dose whereas before the annealing its influence on the  $j$ -shift was already maximised at  $10^{14} \text{cm}^{-2}$ . This suggests a decrease in the deuterium population due to diffusion deeper into the bulk.

For non-implanted areas annealing led to the appearance of a new band at 1.085eV instead of one at 1.07eV. For implanted material annealing marginally changed the spectral position of the dominant band, which now can be found at 1.089eV. We can speculate that this change is due to an increase in the height of potential fluctuations caused by Cd. The non-linear PL temperature dependence after annealing, shown in Fig.4(a) for non-implanted and  $10^{14} \text{cm}^{-2}$   $D^+$  implanted areas, suggests that the main PL band after annealing consists of two transitions quenching at different temperatures. At low temperatures (up to 60K) one of these transitions, associated with L1 in Fig.4(b), increases the maximum emission energy with temperature rise  $h\nu_{\text{max}} \propto 3.2k_B T$  ( $k_B$  Boltzman constant, T-temperature). Such a behaviour at low temperatures can be assigned, for instance, to DAP recombination despite the high  $j$ -shift. At temperatures from 60K to 160K the gradual increase in the emission energy  $h\nu_{\text{max}} \propto 5.6k_B T$ , associated with L2 in Fig.4(b), can be explained in terms of the band-tail or band-band recombination models. Further work is needed to confirm the origins of these transitions. At first sight the two new peaks, which appeared (1) after implantation at 1.1eV and (2) after annealing in non-implanted areas at 1.089eV look similar, but their  $j$ -shift characteristics reveal differences. Implantation of  $D^+$  has reduced the compensation level whereas annealing has increased it.

Annealing reduced the PL intensity of the three IH bands. Due to the high mobility of intrinsic defects generated by ion implantation lattice damage, even  $100^\circ\text{C}$  can be sufficient to heal these defects.

In conclusion the implantation of  $D^+$  into CdS/CIGS structure reduces the  $j$ -shift of the dominant luminescence peak and increases the photo-response. It also generates three low energy bands similar to those observed after  $H^+$ ,  $D^+$ , and  $He^+$  implantation in CIGS films. Annealing increases the intensity of PL and also the  $j$ -shifts. These changes are interpreted in terms of radiation damage and passivation effects caused by deuterium and the doping effects of Cd. Further PL measurements will be required to confirm the origins of the observed effects.

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