

Effects of D⁺ implantation of CIGS thin films through a CdS layer

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Abstract

Cu(InGa)Se₂ thin films coated with a 30 nm CdS layer were implanted with doses of 10¹⁴–10¹⁶ cm⁻² of 2.5 keV D⁺ at room temperature. Implanted and non-implanted areas of the films were characterised using low-temperature photoluminescence (PL). A broad band (A) at 1.07 eV, attributed to the band-tail recombination, dominated the PL spectra from the non-implanted material. Implantation of D⁺ generated four new transitions in the PL spectra: 3 low-energy peaks; and a dominant peak at 1.10 eV. The blue shift of the 1.10 eV band with excitation power rise was shown to be only half that of band A. This was attributed to the passivating effects of D⁺ on the amplitude of the band-tail potential fluctuations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cu(InGa)Se₂ (CIGS)-based photovoltaic (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 the CdS layer directly into the interface region. Excess energy is then absorbed by polycrystalline CdS. In this case implantation of hydrogen could be done using a conventional ion implanter. In addition, a CIGS layer coated with CdS will be protected against any possible detrimental effects of exposure to the atmosphere. A

study of the effects of energetic ions in CdS/CIGS heterostructures may also help to understand the physics of radiation damage in CIGS and illuminate the origins of the remarkable high radiation hardness exhibited by CIGS-based photovoltaic (PV) devices. In this work, D⁺ ions were used for modeling H behaviour because depth profiling of deuterium can be done with much higher accuracy.

2. Experimental details

CuIn_xGa_{1-x}Se₂ thin films were deposited on Mo-coated soda-lime glass substrates by the co-evaporation technique, and coated with 30 nm of CdS using a standard chemical bath deposition process at Stuttgart. The CIGS is copper-deficient, with $x \approx 0.7$, giving a band-gap in the region of 1.25 eV [2]. The films were implanted with doses of 10¹⁴, 10¹⁵ and 10¹⁶ cm⁻² of 2.5 keV D⁺ (ion current = 1.5 μA cm⁻²) at room temper-

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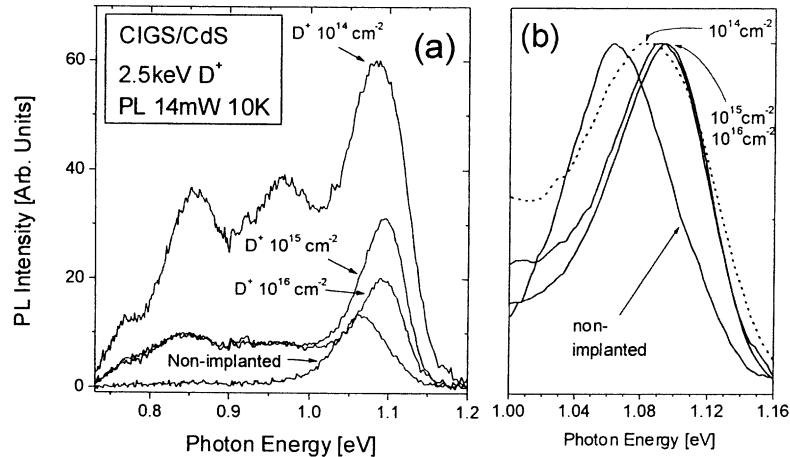


Fig. 1. (a) PL spectra from CdS/CIGS thin films implanted with different doses of 2.5 keV D^+ . PL was measured at 10 K and a laser power of 14 mW. (b) Detail of the dominant band in the same spectra, after normalisation and smoothing.

ature using an ion implanter with magnetic separation. Implanted and non-implanted areas of the films were characterised using photoluminescence (PL) excited by the 488-nm-line from an Ar ion laser, and detected using a cooled Ge detector. All the experiments were performed in a closed-cycle, He cryogenic system at temperatures of 10–300 K. The laser excitation power for the intensity dependencies was varied from 2.5 to 50 mW, focussed to a spot roughly 100 μm in diameter.

3. Results

PL spectra taken at 10 K are shown in Fig. 1. A single broad band (A) at 1.07 eV dominates the spectrum from non-implanted areas. Fig. 1a shows that D^+ implantation led to an increase in the intensity of the dominant band, reaching a maximum for the dose of 10^{14} cm^{-2} . The implantation also induced 3 broad, low-energy peaks IH1, IH2 and IH3, which achieve their maximum intensity after a dose of 10^{14} cm^{-2} .

Implantation of D^+ with a dose 10^{14} cm^{-2} increased the A band width, and shifted its centre to a higher energy, as seen in the normalised PL spectra in Fig. 1b. After higher D^+ doses the width of this band narrows again, becoming slightly narrower than in the non-implanted case. The dominant band is now centred at 1.10 eV, and the changes in shape following implantation are interpreted 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} cm^{-2} sample results from the merging of the two co-existing peaks. The PL

intensity from the sample before annealing was found to be quite low at temperatures above 30 K, limiting the use of temperature-dependent PL data, but useful information was gained from PL spectra taken at different laser excitation intensities. Increasing excitation intensity generated a significant blue shift (j -shift) of the A-band, as shown in Fig. 2 and Table 1. The j -shift of the dominant band was observed to be significantly reduced following D^+ implantation. The low-energy bands, generated by D^+ implantation, did not show any shift with excitation power change.

4. Discussion

The PL spectra measured before and after D^+ implantation from CdS/CIGS heterostructure are very similar to those observed from bare CIGS thin films implanted with He^+ , D^+ [3], and H^+ [4]. Therefore, we use 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 processes of healing of primary defects, created during D^+ implantation, and redistribution of implanted deuterium. In both cases, the PL spectra from the non-implanted material are dominated by a broad band at approximately 1.1 eV. This band is a usual feature in the PL spectra from In-excess CIGS material used for high efficient solar cells. In this work, the low PL intensity at temperatures above 30 K did not allow measurement of temperature dependencies in order to identify origins

Table 1

The blue j -shift of the dominant band with excitation intensity rise for non-implanted and D^+ -implanted CdS/CIGS

D^+ dose	Non-implanted	10^{14} cm^{-2}	10^{15} cm^{-2}	10^{16} cm^{-2}
j -shift [meV/decade]	23	11	12	10

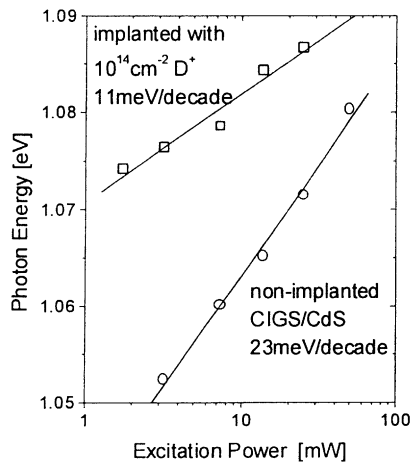


Fig. 2. The j -shift of the dominant peak energy with excitation power for the non-implanted and one-implanted region of the film.

of this band. Earlier PL studies [5], and excitation intensity measurements lead us to 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 [5]. The amplitude of potential fluctuations depends very much on the level of doping and compensation, which are governed by the excess of (In + Ga) over Cu. This excess determines the spectral position of the dominating band in PL spectra [6], and the j -shift magnitude. The higher the potential fluctuation amplitude the greater the j -shift. Although the CIGS films used in the experiments were not characterised before the CdS deposition, the j -shift in similar non-implanted CIGS thin films was measured to be below $14 \text{ meV decade}^{-1}$ [3]. In this work, the j -shift after CdS deposition was found to be greater, at $23 \text{ meV decade}^{-1}$. This can be attributed to inter-diffusion of elements between CdS and CIGS, given that the CdS layer seals the CIGS film, and protects it from the incorporation of oxygen and/or water from air [7]. Diffusion of Cd into the CIGS layer, as reported from earlier XPS measurements [8], results in the creation of a graded interface region. Cd atoms, located in V_{Cu} , make this region more n -type and therefore, more highly compensated.

The implantation of deuterium introduced a new dominant band, at an energy higher than that of band A by 30 meV. 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; to create radiation damage, and to passivate existing defects. According to TRIM calculations at 2.5 keV, one deuteron can create 8.6 vacancies in CIGS [9]. However, as the deuterons pass through the CdS,

they lose a considerable part of their energy. With a mean penetration depth of approximately 50 nm and straggling of 25 nm, D^+ have their maximum concentration at the CdS-CIGS interface. Each deuterium ion is now expected to create approximately 3 vacancies in CIGS. At room temperature at least 98% of the structural radiation damage, created by 30 keV Ar ions in CuInSe_2 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 also be healed as reported for hydrogen-implanted CuInSe_2 [11]. Some deuterium ions are expected to be trapped at the end of collision cascades but a considerable fraction diffuse 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^+ , two main PL bands co-exist, leaving only the higher energy band after higher doses. The j -shift of this new band was found to be reduced significantly down to $11 \text{ meV decade}^{-1}$. Such a reduction is also consistent with the passivation effects of charged defects by incorporated deuterium. This effect has been observed after implantation of hydrogen into CIGS thin films without a CdS layer [4], although the dominant band was found to shift towards lower energies. This difference can be related to the absence of cadmium doping. The appearance of three, low-energy bands (IH1, IH2 and IH3), in the PL spectra was earlier reported for D^+ , He^+ [3], and H^+ [4] 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.

In conclusion, the changes in the PL spectra after implantation of D^+ into CdS/CIGS structure are similar to those observed after H^+ , D^+ and He^+ implantation in CIGS films, and can be interpreted in terms of radiation damage and passivation effects. To establish the origins of these changes further PL measurements are proposed, with biases applied to Mo and CdS layers.

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References

- [1] M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Nuofi, Prog. Photovoltaics 7 (1999) 311.
- [2] A.V. Mudryi, I.V. Bodnar, V.F. Gremenok, I.A. Victorov, A.I. Patuk, I.A. Shakin, Sol. Energy Mater. Solar Cells 53 (1998) 247.

- [3] M.V. Yakushev, R.W. Martin, J. Krustok, H.W. Schock, R.D. Pilkington, A.E. Hill, R.D. Tomlinson, *Thin Solid Films* 361 (2000) 488.
- [4] M.V. Yakushev, R.W. Martin, F. Urquhart, A.V. Mudriy, H.W. Schock, J. Krustok, R.D. Pilkington, A.E. Hill, and R.D. Tomlinson. Proceedings of the 12th ICTMC, Taiwan, 2000. To be published in *Jap. J. Appl. Phys.*
- [5] J. Krustok, H. Collan, M.V. Yakushev, K. Hjelt, *Phys. Scr.* T79 (1999) 179.
- [6] I. Dirnstorfer, M. Wagner, D.M. Hofman, M.D. Lampert, F. Karg, B.K. Meyer, *Phys. Stat. Sol. (a)* 168 (1998) 163.
- [7] T.M. Friedmeier, D. Braunger, D. Hariskos, M. Kaiser, H.N. Wanka, H.W. Schock. Proceedings of the Twenty-Fifth IEEE PVSC, 1996, p. 845.
- [8] T. Nakada, A. Kunioka, *Appl. Phys. Lett.* 74 (1999) 2444.
- [9] J.P. Biersack, L.G. Haggmark, *Nucl. Instr. Meth.* 174 (1980) 257.
- [10] M.V. Yakushev, A.E. Hill, R.D. Pilkington, R.D. Tomlinson. Proceedings of the Sixteenth European P.V. Solar Cell Energy Conference, Glasgow, 2000.
- [11] M.V. Yakushev, G. Lippold, A.E. Hill, R.D. Pilkington, R.D. Tomlinson, *Cryst. Res. Technol.* 95 (1995) 357.