

A Photoluminescence Study of Hydrogen-Implanted $\text{Cu}(\text{InGa})\text{Se}_2$ Thin Films

To cite this article: Michael V Yakushev *et al* 2000 *Jpn. J. Appl. Phys.* **39** 320

View the [article online](#) for updates and enhancements.

Recent citations

- [Stimulated Emission of Thin \$\text{Cu}\(\text{InGa}\)\text{Se}_2\$ Films Irradiated by Protons](#)
I. E. Svitsiankou *et al*
- [A photoluminescence study of \$\text{CuInSe}_2\$ single crystals ion implanted with 5 keV hydrogen](#)
M V Yakushev *et al*

A Photoluminescence Study of Hydrogen-Implanted Cu(InGa)Se₂ Thin Films

Michael V YAKUSHEV^{1*}, Robert W MARTIN¹, Fiona URQUHART¹, Alexander V MUDRIY², Hans W SCHOCK³, Juri KRUSTOK⁴, Richard D PILKINGTON⁵, Arthur E HILL⁵ and Robert D TOMLINSON⁵

¹Department of Physics and Applied Physics, Strathclyde University, Glasgow, G4 0NG, UK

²Solid State and Semiconductor Physics Institute, Belarus Academy of Science, Minsk, 220072, Belarus

³Institut für Physikalische Elektronik, Universität Stuttgart, D-70569, Germany.

⁴Tallinn Technical University, Ehitajate tee 5, Tallinn, EE0026, Estonia

⁵Department of Physics, University of Salford, Salford, M5 4WT, UK

Cu(InGa)Se₂ (CIGS) thin films deposited on Mo-coated soda-lime glass substrates by co-evaporation, were implanted with H⁺ (2.5keV, doses from 10¹⁴ to 10¹⁷cm⁻²) at room temperature. Implanted and non-implanted areas of the films were characterised using photoluminescence (PL) at 10K. The PL spectra from non-implanted areas showed a broad band at 1.13eV (A1) and a long, low energy and low intensity tail with a well-defined band at 0.78eV. Implantation with up to 10¹⁵cm⁻² increased the intensity of band A1. Higher doses resulted in a reduction of the band intensity. Also three high intensity low energy peaks were observed in the PL spectra after implantation. One of the peaks was detected at 0.78eV. A high value of the blue shift for the excitation intensity dependence of band A1 before the implantation suggested recombination through conduction and valence band tail states. After implantation the blue shift was found to decrease, it is assumed that the implanted H passivates some of the charged defect states in the band tails.

KEYWORDS: Thin films, CIGS, PL, Hydrogen, Ion-Implantation.

1. Introduction

CIGS-based thin-film solar cells are very efficient devices, with efficiencies in excess of 18%¹. It is believed that further improvements in the performance of these devices could be achieved by passivating some of their numerous defects by hydrogen. The incorporation of hydrogen was found to improve the structural, electrical and optical parameters of CIS single crystals and CIGS thin films². The implantation of KeV H⁺ is of interest, because at these energies hydrogen can be delivered into CIGS substrates through a CdS layer. Studies of the defects created by energetic hydrogen ions could also help to understand the origins of the extraordinary radiation hardness by CIS-based devices.

2. Experiment

CIGS thin films were deposited on Mo coated soda-lime glass substrates by co-evaporation³. The elemental composition measured by EDX was found to be Cu-24.841, In-16.541, Ga-6.698, and Se-51.919 at.%. The films were implanted with 2.5keV H⁺ (doses from 10¹⁴ to 10¹⁵cm⁻²) at room temperature using an ion implanter employing magnetic separation. The ion current density was about 5μA/cm². Implanted and non-implanted areas of the films were characterised with PL excited by a 488 nm Ar⁺ laser. The PL emission was detected using a liquid nitrogen cooled Ge detector. All the experiments were performed in a closed-cycle He cryogenic system at 10K. The laser excitation power was varied from 1 to 100mW.

2. Results

A high intensity broad band (A1) at 1.13eV and a long tail of low intensity emissions in the low energy region were found in the PL spectra from the non-implanted material. The tail had a well-defined peak at 0.78 eV (A2). Implantation of hydrogen

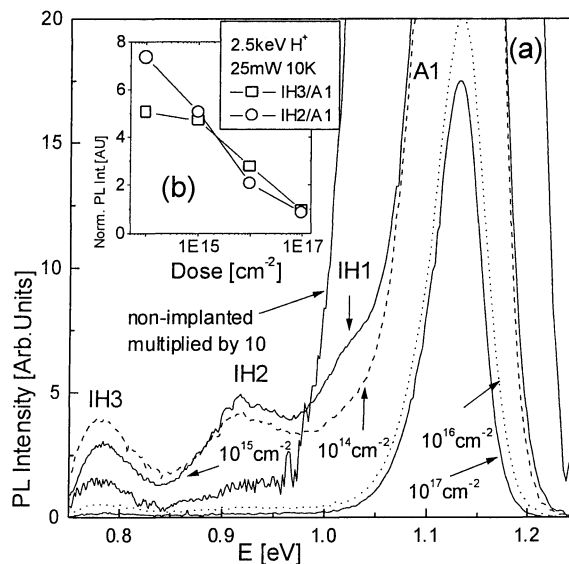


Fig.1. (a)- photoluminescence spectra taken (at 10K, 25mW laser power) from Cu(InGa)Se₂ thin films implanted with different doses of 2.5keV H⁺; (b) - Changes in intensity of bands IH2 and IH3 normalised to that of A1.

significantly changed the PL spectra, increasing the band A1 intensity after doses of up to 10¹⁵cm⁻². In the low energy

* EMAIL: michael.yakushev@strath.ac.uk

region the implantation produced three broad deep bands at about 1.02eV (IH1), 0.92eV (IH2) and 0.78eV (IH3). PL spectra from non-implanted and implanted areas are shown in Fig.1(a). Band IH3 was usually well defined after any dose. It achieved a maximum in intensity after 10^{15} cm^{-2} . Similarities between band A2 observed from non-implanted CIGS and band IH3 from implanted material suggest that both bands have the same intrinsic defect origins. Bands IH2 and IH1, which appeared after doses above 10^{15} cm^{-2} merged together in a flat feature between IH2 and A1. Also an increase in dose above 10^{15} cm^{-2} resulted in an attenuation of the peak A1 and all the three implantation-induced peaks. The dynamics of the attenuation in the intensity of peaks IH2 and IH3 normalised to that of A1 is shown in Fig.1(b). Increase in the dose did not affect the position of IH3 whereas band A1 had a red shift. The width of A1 reduced with dose increase. PL spectra were taken for different laser power values from non-implanted and implanted regions of the films. An increase in excitation power was followed by a blue shift (*j*-shift) of the A1 peak. The magnitudes of the blue shift of the A1 peak are shown in Table 1. The peaks IH1, IH2 and IH3 did not show any shift with change in excitation intensity.

Table 1. The blue *j*-shift [meV/decade] of A1 band for different doses [cm^{-2}] of 2.5keV hydrogen.

non-implanted	10^{14}	10^{15}	10^{16}	10^{17}
14	10	3	4	5

3. Discussion

High concentrations of oppositely charged intrinsic defects in CIGS create spatial fluctuations of electrostatic potential producing band tails. At low temperatures holes are captured at deep states in the valence band tail, which acts like an acceptor band ⁴⁾. Band A1, which showed a *j*-shift of 14meV/decade, measured from non-implanted areas of CIGS films can be ascribed to Band-Tail (BT) recombination. At low temperatures this mechanism dominates in highly doped and compensated CIGS ⁵⁾. The implantation of keV hydrogen ions can be described in terms of four processes: (1) creation of displacement defects (vacancies and interstitials) in ballistic cascades; (2) healing of these defects during and shortly after implantation; (3) chemical bonding of atomic hydrogen; (4) fast diffusion of hydrogen deep into the bulk. At 2.5keV hydrogen projectiles are stopped in the first 50nm from the surface ⁶⁾. During and immediately after the collision process a large fraction of the primary defects (up to 75%) heal due to high defect mobilities reported at room temperature²⁾. Chemically active hydrogen atoms also passivate both intrinsic and implantation-induced defects. H^+ implantation can therefore be considered in terms of two competitive processes: creation and passivation of defects. In our work H^+ implanted with a dose of 10^{14} cm^{-2} was found to increase the intensity of band A1. This effect was observed in H-implanted CIS single crystals and ascribed to a reduction in the population of non-radiative traps due to hydrogen passivation ⁷⁾. The observed reduction in the blue *j*-shift after H implantation can be attributed to passivation of charged defects in the band tail.

This process uncovers donor and acceptor levels, which were previously overlapped by the tails. The peak A1 can then be attributed to donor-acceptor pair recombination (DAP). This change in the emission mechanism also explains the observed red shift of band A1 and the reduction in its width following implantation. Hydrogen implantation produced three deep bands IH1, IH2 and IH3. These bands were also observed after implantation of CIGS thin films with D^+ and He^+ ⁸⁾ and were attributed to intrinsic defects created during and shortly after implantation. The only difference during H implantation seems to be the rate of change in the intensity of these peaks with increasing dose. Implantation of H with doses below 10^{15} cm^{-2} resulted in the growth of these peaks, whereas D and He ion implantation resulted only in an attenuation of their intensity after a minimum dose of 10^{14} cm^{-2} . The intensity of these peaks normalized to that of A1 increased with dose increase for D^+ and He^+ and reduced for H^+ . This can be explained by the difference in the projectile mass and the resulting increase in the number of vacancies produced by one ion (2.5 for H^+ , 8.6 for D^+ and 58 for He^+ ⁶⁾). H^+ creates the least number of defects and the effect of healing/passivation dominates. Deuterium is also expected to passivate defects but in this case the passivation effect is overshadowed by the high defect production rate. This increases the population of charged defects, which generate the band tails. The considerable increase observed in the blue *j*-shift after D^+ implantation⁸⁾ supports this proposal. Although the specific defects associated with bands IH are still unknown it is clear that they are intrinsic in origin and that low concentrations of these defects existed in CIGS before implantation. The observed similarities in the PL spectra after H, D or He ion implantation suggest that primary point defects (vacancies and interstitials), created in collision cascades, regardless of the chemical activity of the implanted atomic species are being transformed at room temperature into the same remnant intrinsic defects. We explain this behavior by the high mobility of the primary defects on a micro-scale. Hence the high radiation hardness of CIS/CIGS is due to a fast and dynamic recovery of the lattice following radiation damage.

Acknowledgement

This work has been funded by INTAS (grant n° 634), NATO (grant PST/CLG 974740) and EPSRC (grant GR/L 62757).

References

- 1) M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, and R. Nuofi: Prog. Photovoltaics, 7 (1999) 311.
- 2) M.V. Yakushev, G. Lippold, A.E. Hill, R.D. Pilkington and R.D. Tomlinson: Cryst. Res. Technol. 95 (1995) 357.
- 3) B. Dimmler, H.W. Schock: Prog. Photovoltaics, 4 (1996) 425.
- 4) A.P. Levanyuk, V.V. Osipov: Sov. Phys. Usp. 24 (1981) 187.
- 5) J. Krustok, H. Collan, M. Yakushev and K. Hjelt: Physica Scripta, T79 (1999) 179.
- 6) J.P. Biersack, L.G. Haggmark: Nucl. Instr. Meth. 174 (1980) 257.
- 7) R.W. Martin, F. Urguhart, M. Yakushev, C.A. Faunce, A.E. Hill, R.D. Pilkington, J.A. Van den Berg, D.A. Armour, R.D. Tomlinson: ISTMC-11, Inst. Phys. Conf. Ser. 152 (1997) 417.
- 8) M.V. Yakushev, R.D. Pilkington, A.E. Hill, R.D. Tomlinson, R.W. Martin, J. Krustok: Thin Solid Films. 362 (2000) 488.