

A PL study of CIGS thin films implanted with He and D ions

M.V. Yakushev^{a,*}, R.W. Martin^b, J. Krustok^c, H.W. Schock^d, R.D. Pilkington^a,
A.E. Hill^a, R.D. Tomlinson^a

^aPhysics Department, Salford University, Salford M5 4WT, UK

^bPhysics Department, Strathclyde University, 107 Rottenrow, Glasgow G4 0NG, UK

^cTallinn Technical University, Ehitajate tee 5, Tallinn 19086, Estonia

^dInstitut für Physikalische Elektronik, Universität Stuttgart, Pfaffenwaldring 47, D-70569, Stuttgart, Germany

Abstract

Cu(InGa)Se₂ thin films deposited on Mo coated soda-lime glass substrates by co-evaporation, were implanted with He⁺ and D⁺ (energies between 2.5 and 40 keV, doses from 10¹⁴ to 3 × 10¹⁵ cm⁻²) at room temperature. Implanted and non-implanted areas of the films were characterised using low temperature photoluminescence (PL). A single broad band (A1) at 1.1 eV dominated in the PL spectra from the non-implanted material. Also a long, low energy and low intensity tail with a well-defined band (A2) at 0.78 eV was detected. Implantation of either He or D reduced the band A1 intensity. Three high intensity low energy peaks IH1, IH2, and IH3 were observed in the PL spectra in both cases. One of the peaks (IH3) was detected at 0.78 eV. An increase in either dose or energy of implantation was found to increase the intensity of IH2 and IH3 normalised to that of A1. Similarities between the low energy bands observed after either He or D implantation suggests that all the three bands have intrinsic origins. It is speculated that the implanted ions accumulate in small bubbles or diffuse to the surface and grain boundaries. The characteristics of bands A2 and IH3 suggest that the defects responsible for the emission were present in the films before implantation. Lattice recovery processes leading to an overall reduction in the primary implant-related defect population could produce additional defects, which are associated with the low-energy PL peaks. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Thin films; Cu(InGa)Se₂; CIGS; Photoluminescence; Ion-implantation

1. Introduction

The ternary semiconducting compound CuInSe₂ (CIS) is of great interest because of its very successful application in the field of photovoltaics (PV). Currently Cu(InGa)Se₂ (CIGS) based PV devices hold the world record efficiency for solar energy conversion (18.8%) for thin film solar cells [1]. Also, the CIGS based solar cells are found to be extremely tolerant to ion radiation. This feature makes them candidates for use in space power systems. The origins of such an extraordinary radiation tolerance are not understood. Several studies concerned with radiation defects in CIS/CIGS single crystals and thin films have been made using Rutherford backscattering/channelling (RBS/C) [2,3], Raman [4–6], photoluminescence (PL) [7], positron annihilation techniques [8] and transmission electron microscopy (TEM) [9]. In these studies it was shown that the radiation hardness of this material exceeds that of III–V semiconductors such as GaAs by about two orders of magni-

tude. This result was attributed to the high mobility of defects in CIS at room temperature, which promote effective healing mechanisms. Such an explanation, based on high defect mobilities, was supported by theoretical calculations of the defect formation energies in CIS [10] and experimental evidence of significant copper interstitial mobility [11,12]. The electrical properties of CIS and therefore the performance of CIS based solar cells are governed by the interplay of a large number of intrinsic defects. Because of the multinary nature of the compound these defects are complex and are difficult to identify. One of the techniques successfully used for defect studies is PL. Although quite a number of papers have been published about photoluminescence in the ternaries these studies are mostly concerned with shallow PL bands. Much less is known about deep PL levels, which are very important for understanding the physical behaviour of these materials.

2. Experiment

CIGS thin films were deposited on Mo coated soda-lime glass substrates by co-evaporation [13]. The elemental

* Corresponding author. Tel.: +44-161-295-4222; fax: +44-161-295-5197.

E-mail address: m.yakushev@eee.salford.ac.uk (M.V. Yakushev)

composition measured with an EDX probe was found to be Cu 24.841, In 16.541, Ga 6.698, Se 51.919 at.%. The films were implanted with He⁺ and D⁺ using an ion implanter with magnetic separation. He ions were implanted at energies of 5, 10, 20 and 40 keV with a dose of $3 \times 10^{14} \text{ cm}^{-2}$ and at 10 keV with doses of 10^{14} and 10^{15} cm^{-2} . Deuterium ions were implanted at energies of 2.5, 5 and 10 keV with dose of $3 \times 10^{15} \text{ cm}^{-2}$ and with doses of 10^{14} , 3×10^{14} and 10^{15} cm^{-2} at 2.5 keV. The ion implantation was performed in vacuum (1.5×10^{-6} mbar) at room temperature. The ion current density during the implantation was $1.5 \mu\text{A}/\text{cm}^2$. Implantation was made into areas $2 \times 3 \text{ mm}$ so all the doses and energies of the same ion were implanted into one piece of the film $5 \times 12 \text{ mm}$, to facilitate reproducibility of the PL measurements. The intensity of PL from the sample implanted with helium was generally lower than from the one implanted with deuterium. Subsequently the helium-implanted sample was annealed in vacuum for half an hour at 100°C .

Implanted and non-implanted areas of the films were characterised with low temperature PL excited by an Ar ion laser with a beam wavelength of 488 nm. 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 temperatures from 10 to 300 K. The cold finger was mounted on a stage, which allowed two-dimensional parallel translations of the sample without changes in the optical adjustment. This made possible comparative measurements of the emission intensity from different areas of the same sample. Laser excitation power for the intensity dependencies was varied from 0.5 to 200 mW.

3. Results

A single broad band (A1) at 1.1 eV dominated the PL spectra from the non-implanted material. The intensity of this band varied by approximately 30% across each sample. Also a long tail of low intensity emission was detected in the low energy region of the PL spectra. The tail had usually one low intensity but well-defined peak (A2) centred at 0.78 eV.

Implantation of either D⁺ or He⁺ significantly changed the PL spectra: (1) intensity of band A1 was reduced for all the doses and energies used for implantation; (2) three prominent broad deep bands appeared at about 0.97 eV (IH1), 0.78 eV (IH3) and 0.88 eV (IH2). Band IH3 usually was well defined after any implantation. Bands IH2 and IH1 in many cases merged together in a flat feature between IH2 and A1. Although it was sometimes difficult to establish the positions of the bands IH1, IH2 it seems that IH1, IH2 and IH3 bands appear after implantation of either D⁺ or He⁺ and do not change their positions with changes in either dose or energy. Implantation of deuterium generally left the intensity of band A1 still high enough to detect, whereas helium ions reduced this peak after the lowest doses and energies used for the implantation. An increase in dose for both D and He resulted in an attenuation of the peak A1 and the three implantation-induced peaks. PL spectra from the samples implanted with different doses of D⁺ and He⁺ are shown in Fig. 1a,b, respectively.

For D⁺ implantation it was possible to calculate changes in intensities of bands IH3 and IH2 normalised to that of A1. This simple calculation showed that the attenuation of the intensity of band A1 is faster than that of IH2 and IH3. The dynamics of attenuation of the normalised intensities with

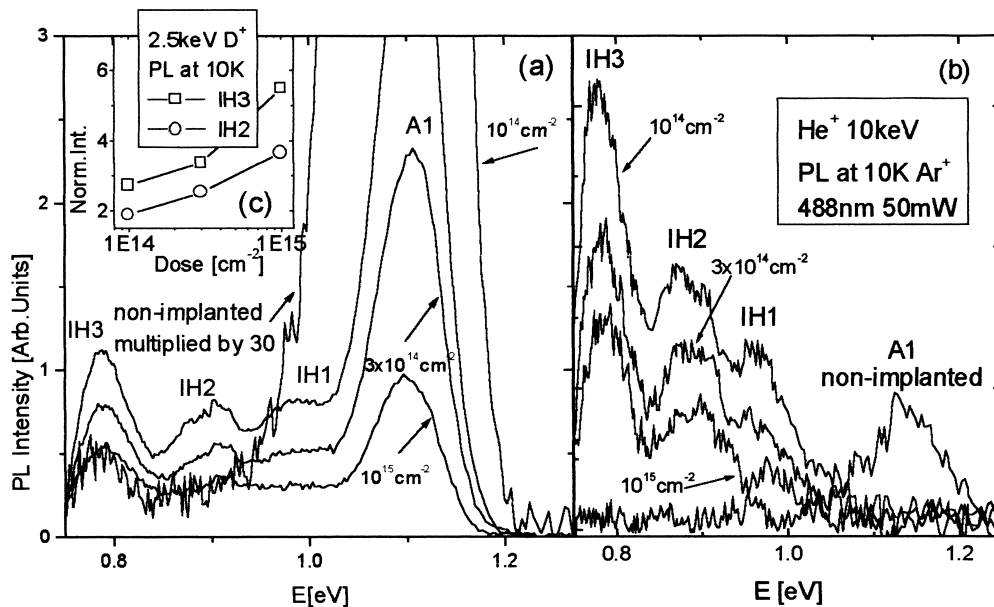


Fig. 1. PL spectra from CIGS thin films implanted with different doses of (a) D at 2.5 keV and (b) He at 10 keV. PL was measured at 10 K and excitation laser intensity 50 mW. Intensity of bands IH2 and IH3 normalised to that of A1 for D-implanted sample is shown in (c).

D^+ dose increase is shown in Fig. 1c. Increase in energy of either D^+ or He^+ was also followed by a decrease in the intensity of all the four peaks. Changes in the PL spectra from the samples implanted with D^+ and He^+ are shown in Fig. 2a,b, respectively. Changes in intensity of bands IH3 and IH2 normalised to that of A1 versus energy of D^+ are shown in Fig. 2c.

The attenuation of the intensity of band A1 is also faster than that of IH2 and IH3. Thus despite an overall reduction in the intensities of all the bands, the normalised values for bands IH2 and IH3 are growing with either dose or energy increase. Implantation of high-energy ions creates multiple radiation defects. Some of them work like non-radiative traps causing the observed decrease in the band intensities. If we assume that these non-radiative traps affect bands IH and A1 equally then normalising the intensities as shown in Figs. 1c and 2c will represent the growth of the population of the defects responsible for these bands.

Because of the difficulties in resolving bands IH1 and IH2 the analysis presented below was made only for bands IH3 and A1. Increase in either the dose or energy of implantation did not affect the position of IH3 whereas A1 was found to shift towards lower energy following either an increase in dose or in energy of the D^+ implantation. Annealing of the helium-implanted sample in vacuum for 0.5 h at 100°C resulted in a considerable increase of intensity for all the bands enabling the temperature dependencies of the PL spectra to be measured from 10 to 240 K. These PL spectra are shown in Fig. 3a. It is clear that band A1 is gradually shifting toward higher energies whereas IH3 shows no shift at all. Changes in the energy shifts of these bands are shown in Fig. 3b. The intensity of both bands decline with temperature rise, band A1 disappears faster. Emission associated

with band IH3 was observed to be quite intense up to room temperature.

PL spectra were taken with different excitation intensities from both D^+ and He^+ implanted samples. Band A1 was found to have a considerable blue shift with increase in the excitation intensity for both implants whereas for band IH3 the blue shift was very small. Regression lines were fitted into the blue shift-laser intensity data arrays plotted on the semi-logarithmic scale. Gradients of these lines represent the j -shift of the peaks: the blue shift per decade of increase in the excitation intensity. Estimated blue j -shifts are shown in Table 1.

4. Discussion

The band gaps for CuInSe_2 and CuGaSe_2 at 4.2 K were measured to be 1.0459 and 1.7305 eV, respectively [14]. Assuming a linear change of the band gap energy with $\text{Ga}/(\text{In} + \text{Ga})$ ratio an estimate of 1.243 eV can be derived for our samples. The wide emission band A1 observed at 1.1 eV in the PL spectra from non-implanted areas of CIGS films is an usual feature in the PL spectra from such material. It is attributed to donor–acceptor pair (DAP) recombination [15]. The blue shift with an increase in the excitation power is taken as evidence of this recombination mechanism. An increase in the laser intensity should favour closer DAP recombination, increasing energy of emitted photons $h\nu$. Increase in temperature also results in a blue shift because the carriers released thermally from their original sites redistribute to the sites with shorter distances where the probability of the recombination is higher. The temperature and excitation intensity behaviour of the observed band A1

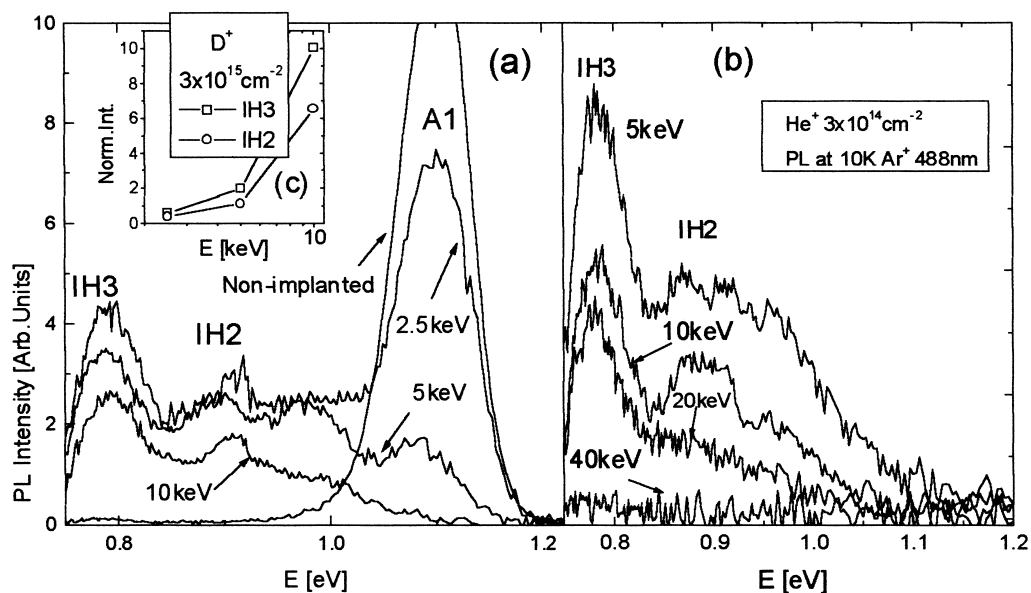


Fig. 2. PL spectra from CIGS thin films implanted with different energies of (a) D^+ , dose $3 \times 10^{15} \text{ cm}^{-2}$ and (b) He^+ , dose $3 \times 10^{14} \text{ cm}^{-2}$. PL was measured at 10 K and laser excitation intensity 50 mW. Intensity of bands IH2 and IH3 normalised to that of A1 for D^+ implanted sample (c).

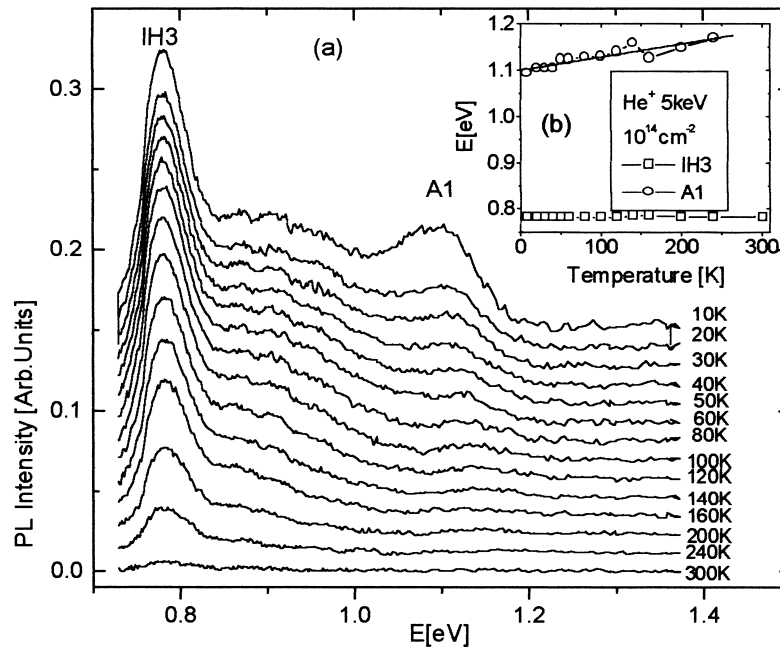


Fig. 3. Temperature dependence of the PL spectra from the (a) He implanted CIGS thin-film and (b) energy position of bands A1 and IH3.

seems to be consistent with the above considerations. At first sight band A1 could be attributed to the DAP recombination. But some details do not match the model: (a) the high rate of the blue shift for band A1, increasing significantly after implantation of either D or He, are not easily explained by models of DAP transitions [16]. Inconsistency in the interpretation of the PL data from CIGS thin films has already been observed [17]; (b) red shifts of band A1 with increasing deuteron implantation dose and energy also can be taken as evidence of an increase in the level of compensation. This shift could be the result of an effective reduction of the band gap following introduction of additional defects during ion implantation. The DAP model has been constructed for a low level of doping and compensation and can not directly be applied to CIGS which is known to be highly doped and compensated, especially after ion implantation. The electrical properties of CIS are governed by the interplay of a large number of intrinsic defects, which act as donors and acceptors. Ion implantation must increase the population of these defects increasing the level of compensation. The primary defects (vacancies and interstitial atoms) created in collision cascades along the ion tracks recombine and because of the multinary nature of the compound can create multiple defect clusters and antisite defects which are believed to be intrinsic dopants. Theore-

tical calculations of depth profiles and the rate of vacancy creation by one ion has been made for both D^+ and He^+ employing a TRIM programme [18]. The results are shown in Table 2.

Recently a new approach has been developed to understanding the nature of broad asymmetrical bands in PL spectra from chalcopyrites [19]. This approach is based on the theory of PL from highly doped and highly compensated semiconductors [20]. Oppositely charged defects related to donors and acceptors are randomly distributed and create spatial fluctuations of electrostatic potential in the crystal. When the concentration of these defects is high the fluctuations also become high. They convert the well-defined energy levels to a band. In highly doped semiconductors the state of the electron is defined not by the field of a particular impurity but by the collective electrostatic potential of all impurities in the semiconductor. These spatial potential fluctuations create the band tails. In p-type semiconductors at low temperature the holes are captured at deep states in the valence band tail, which act like acceptor levels. The tails can also considerably reduce the effective energy

Table 1
The blue j -shifts of the PL bands for non-implanted, D^+ and He^+ implanted CIGS

Bandy-shift (meV)	Non-implanted	2.5 keV D^+ ($3 \times 10^{15} \text{ cm}^{-2}$)	5 keV He^+ (10^{14} cm^{-2})
A1	14	33	29

Table 2
The mean penetration depths R , straggling ΔR and numbers of vacancies created by one D^+ and He^+ . Calculations made using TRIM programme.

E (keV)	D^+			He^+		
	R (nm)	ΔR (nm)	Vac/ion	R (nm)	ΔR (nm)	Vac/ion
2.5	39	20	8.6			
5	71	32	15.5	50	26	58.5
10	127	52	24	83	44	94.5
20				150	69	140

bandgap and introduce three possible recombination mechanisms: band-tail, tail-acceptor and tail-tail. It is possible that in our case the tails play an essential role in recombination. To clarify this suggestion more temperature dependent analysis of the PL spectra must be done at lower excitation intensities. In the present experiments excessive laser power could locally increase the temperature in the sample because of the low thermo-conductivity of the film and the glass substrate.

Besides the band A1, three other bands IH1, IH2 and IH3 were observed in the PL spectra after ion implantation. All the three bands were detected after either chemically active D or passive He implantation. Because of this fact it is speculated that these bands are associated with intrinsic defect generation and not to defect passivation or extrinsic doping effects. Data acquired for bands IH3 and A2 suggest that they should be of the same nature. These two bands were found at 0.78 eV. The low intensity of band A2 makes PL measurements difficult but the similarities in the temperature and intensity dependencies between the bands measured in the implanted and non-implanted material suggests that they have a common origin—(a) the fact that band IH3 becomes prominent in the PL spectra following implantation of either D or He suggests that it is rather related to radiation damage created by energetic ions than the extrinsic doping; (b) the energy position of either band A2 or IH3 does not depend on temperature and (c) a very small or zero blue shift at all has been observed for both bands following a change in the excitation power.

The defect associated with band IH3 seems to be intrinsic. Ion irradiation of CIGS thin films with keV energies significantly increases the population of this defect. The projectile energy was high enough to create point defects in collision cascades along the ion tracks. Implantation of a heavy ion like Xe^+ creates a collision cascade. Movement of the lattice atoms in the cascade can be interpreted as a local increase in temperature - the thermal spike [21]. An estimation of the spike parameters was done for a 40 keV Xe ion in a CIS single crystal [2]. The temperature was calculated to reach 11,000 K over a period of 5×10^{-12} s. Although D and He are much lighter than Xe, irradiation with these ions introduces significant energy into the lattice. This will enhance diffusion and lattice recovery processes leading to an overall reduction in the primary implant-related defect population. This process may also produce additional defects, which could be associated with the low energy PL peaks. Recently deep PL bands in CuInS_2 and CuGaSe_2 were discovered and the deep donor-deep acceptor model was proposed for these bands [22]. It was also shown that the interstitial intrinsic defect must be involved. Such an interstitial defect could also be involved in IH3 band.

Electrically neutral atoms could very quickly diffuse to the grain boundaries or to the surface and this process will be enhanced by the irradiation. Also the implanted ions could accumulate in small gas bubbles causing only non-radiative recombination.

The effects of deuterium implantation should be analogous to the implantation of hydrogen. As D is a heavy isotope of hydrogen we can expect relatively more radiation damage to be created during the implantation. Implantation of 5 keV hydrogen into CIS single crystals [23] was found to increase the DAP band. This increase was associated with passivation of non-radiative traps. The implantation also induced a low energy tail without any distinguishable peak. Implantation of 100 eV hydrogen into CIGS thin-films also resulted in an increase of the DAP peak intensity and a high intensity broad band which consisted of several merged peaks at energies from 0.81 to 1 eV has been observed [24]. Because low energy hydrogen can not create any point defects in a collision cascade the increase in the DAP peak intensity supports the suggestion that passivation is occurring under these conditions. The deep band was ascribed to the presence of hydrogen in interstitial positions. There is no direct evidence for defect passivation in D-implanted films, and we suggest that damage-induced defects dominate in the case of D. Implantation of 7 keV He ions in CIS single crystals [8] also did not induce any distinguished low energy bands in the PL spectra. Apart from the usual DAP band the PL spectrum from non-implanted crystal exhibited a flat low energy tail. The effect of implantation was a gradual reduction in intensity of both the DAP emission and the tail. It is not clear why ion irradiation induced deep levels only in CIGS thin films. A possible explanation is associated with the presence of numerous grain boundaries in thin films and the proximity of the surface. More experiments must be done to answer these questions.

5. Conclusions

Significant new features have been observed in the PL spectra obtained from He and D ion-implanted CIGS thin films. These observations have been discussed and are related to shifts in the intrinsic defect populations. These features have not been observed in H or He-implanted CIS single crystals.

Acknowledgements

The research was supported by EPSRC (GR/L 62757) and INTAS-96-No 634.

References

- [1] M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Nuofi, *Prog. Photovoltaics* (1999).
- [2] M.V. Yakushev, I.S. Tashlykov, R.D. Tomlinson, A.E. Hill, R.D. Pilkington, *Mater. Sci. Forum* 248/249 (1997) 171.
- [3] M.V. Yakushev, G. Lippold, A.E. Hill, R.D. Pilkington, R.D. Tomlinson, *Cryst. Res. Technol.* S31 (1996) 357.

- [4] G. Lippold, M.V. Yakushev, R.D. Tomlinson, A.E. Hill, W. Grill, *Cryst. Res. Technol.* S31 (1996) 381.
- [5] K. Weinert, G. Lippold, M.V. Yakushev, R.D. Tomlinson, R. Klenk, V. Nadenau, *Proc. 2nd World Conf. PV Sol. Energy Conv.*, Vienna, 1998, pp. 3679–3682.
- [6] G. Lippold, K. Weinert, M.V. Yakushev, R.D. Pilkington, K. Otte, *Soc. Proc. V* (1999) 540.
- [7] A. Polity, R. KrauseRehberg, T.E.M. Staab, M.J. Puska, J. Klais, H.J. Molle, B.K. Meyer, *J. Appl. Phys.* 83 (1998) 71.
- [8] M.V. Yakushev, F. Urguhart, R.W. Martin, C.A. Faunce, A.E. Hill, R.D. Pilkington, R.D. Tomlinson, *Inst. Phys. Conf. Ser.* 152 (1998) 437.
- [9] C.A. Mullan, C.J. Kiely, M.V. Yakushev, M. Imanieh, R.D. Tomlinson, A. Rockett, *Philos. Mag. A* 73 (4) (1996) 1131.
- [10] S.-H. Wei, S.B. Zhang, A. Zunger, *Inst. Phys. Conf. Ser.* 152 (1998) 765.
- [11] D. Cahen, L. Chernyak, *Adv. Mater.* 9 (1997) 861.
- [12] V. Nadazdy, M. Yakushev, E.D. Djebbar, A.E. Hill, R.D. Tomlinson, *J. Appl. Phys.* 84 (8) (1998) 4322.
- [13] B. Dimmler, E. Gross, R. Menner, et al., 25th PVSC, May 1996, Washington, DC, pp. 757–762.
- [14] A.V. Mudri, I.V. Bodnar, V.F. Gremenok, I.A. Victorov, A.I. Patuk, I.A. Shakin, *Sol. Energy Mater. Sol. Cells.* 53 (1998) 247.
- [15] K. Kushiya, Y. Ohtake, A. Yamada, M. Konagai, *Proc. 12th Euro. PV Sol. Energy Conf.*, Amsterdam, 1994, pp. 1580–1583.
- [16] E. Zacks, A. Halperin, *Phys. Rev. B* 6 (1972) 3072.
- [17] I. Dirnstorfer, Mt. Hofmann, M.D. Lampert, F. Karg, B.K. Meyer, *Inst. Phys. Conf. Ser. B* 152 (1997) 233.
- [18] J.P. Biersack, L.G. Haggmark, *Nucl. Instrum. Methods* 174 (1980) 257.
- [19] J. Krustok, H. Collan, M. Yakushev, K. Hjelt, *Physica Scripta* T79 (1999) 179.
- [20] A.P. Levanyuk, V.V. Osipov, *Sov. Phys. Usp.* 24 (1981) 187.
- [21] R. Kelly, A. Miotello, *Nucl. Instrum. Methods B* 122 (1997) 374.
- [22] J. Krustok, J.H. Schon, H. Collan, M. Yakushev, J. Madasson, E. Bucher, *J. Appl. Phys.* 86 (1) (1999) 364.
- [23] R.W. Martin, F. Urguhart, M. Yakushev, et al., *Inst. Phys. Conf. Ser.* No. 155, 1997, pp. 973–976.
- [24] M.V. Yakushev, R.W. Martin, G. Lippold, et al., *Proc. 14th Euro. PV Sol. Energy Conf.*, Barcelona 2 (1997) 2147.