

## Radiation Damage and Amorphization Mechanisms in Xe<sup>+</sup> Irradiated CuInSe<sub>2</sub> Single Crystals

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**Keywords:** CuInSe<sub>2</sub>, Radiation Damage, RBS/Channelling, Xe Implantation

### ABSTRACT

The damage evolution in ion bombarded CuInSe<sub>2</sub> single crystal has been studied using the RBS/channelling analysis with 2MeV He<sup>+</sup> ions. 40keV Xe<sup>+</sup> ions were implanted with fluences in the range from 10<sup>13</sup> to 10<sup>16</sup> cm<sup>-2</sup> and an ion current density of 1.9μA/cm<sup>2</sup> at room temperature. It was found that the radiation accumulation follows a linear function in a double logarithmic plot with slope m=1.5. The saturation level of the damage was achieved at a fluence of about 10<sup>15</sup> cm<sup>-2</sup>. A heterogeneous mechanism of the damage accumulation in the CuInSe<sub>2</sub> crystal irradiated with ions with mass equal to or greater than xenon mass is suggested.

### INTRODUCTION

Ternary compound CuInSe<sub>2</sub> (CIS) is a semiconductor material with chalcopyrite structure and is used as an exceptionally efficient absorber layer in thin-film solar cells. The efficiency achieved to date for the CIS based solar cells has been reported to be in excess of 17% [1]. One of the most important properties of these cells (which could find applications in space) is very high resistance to radiation - the best among known materials used for absorber layers [2,3]. The classical approach to the consideration of the radiation hardness property involves studying of the fluence dependence of the accumulation of radiation damage and amorphization processes. One of the first characterisations of radiation damage following implantation with various ions, made with the Raman technique [4], showed that implantation fluences at which amorphization was observed usually exceeded the theoretical (TRIM [5] predicted) values by 2-3 orders of magnitude.

### EXPERIMENTAL

The sample used for the study was p-type conducting CIS single crystal with dimensions 2x1cm<sup>2</sup>, and thickness 2mm. It was cut from the middle part of the ingot grown by the vertical Bridgman technique from a near stoichiometric charge [6]. The sample was mechanically polished with different grade diamond pastes and finished in a vibrating bath with 0.05μm alumina slurry. Polished sample was etched in 0.1% Br in methanol solution for 1min and annealed in vacuum for 30s at 300°C to remove a selenium layer left at the surface due to the etch [7]. The orientation of the crystal surface was found to be within 5° from the (112) plane. The prepared surface was irradiated at room temperature with 40keV Xe<sup>+</sup> to fluences: 10<sup>13</sup>, 3x10<sup>13</sup>, 10<sup>14</sup>, 3x10<sup>14</sup>, 10<sup>15</sup> and 3x10<sup>15</sup>. Different fluences were implanted into different stripes of 3mm width. One stripe was left undamaged for reference. The ion current density was 1.9μA/cm<sup>2</sup>. Rutherford

Backscattering/channelling (RBS/C) measurements were carried out using 2MeV He<sup>+</sup> ions in the normal incident beam geometry and with 168° backscattering angle. The energy resolution of the analysis was about 25keV. The homogeneity of the lattice quality was established by taking the aligned spectra at various points on the surface prior to implantation. The dechannelling parameter  $\chi_{\min} = Y_{\min}/Y_{\text{rin}}$  (where  $Y_{\min}$  is the minimum backscattering yield in the aligned spectra and  $Y_{\text{rin}}$  is backscattering yield in the random spectrum) was found to be  $6.2 \pm 0.2\%$ . The RBS aligned spectra were taken along the  $\langle 221 \rangle$  axial channel straight after the implantation. RBS aligned and random spectra for fluences in the range  $10^{14} - 3 \times 10^{15} \text{ cm}^{-2}$  along with one from virgin area are shown in Fig. 1. The sample was kept at room temperature for 8 months. The measurements were repeated to establish whether any annealing process had taken place at room temperature.

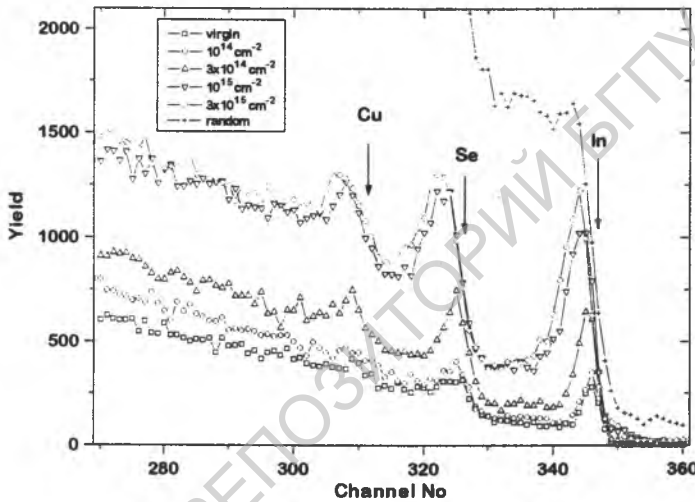


Fig. 1. Effect of 40keV Xe<sup>+</sup> irradiation on RBS aligned spectra from CuInSe<sub>2</sub> crystal.

## CALCULATION PROCEDURE

A model to explain dechannelling in multinary crystal lattices with a thin near-surface layer containing atoms displaced from lattice sites has been developed. This model gives a quantitative interpretation for the changes which occur in the RBS aligned spectra following damage in the near-surface layer. The model was used to calculate concentration depth profiles for indium atoms displaced from the lattice sites as a result of 10 keV hydrogen implantation into CuInSe<sub>2</sub> single crystals [8]. The aligned spectra of ternary compounds can be considered in terms of an overlay of the three separated aligned RBS spectra for each of the atomic species. The spectra are shifted in the energy scale according to the element mass. The high energy part of the spectra just before the surface peak was approximated to be linear. Parameters of this part of the spectrum were calculated from a mean square fit (regression line) of the experimental yield of the aligned spectrum. For other lines the parameters were calculated assuming that the slope coefficients of the lines and minimum values of the aligned yields ( $Y_{\text{aCu}}$ ,  $Y_{\text{aIn}}$ ,  $Y_{\text{aSe}}$ ) are proportional to the Rutherford scattering cross sections of the corresponding atomic species. The random yields corresponding to different

elements ( $Y_{rCu}$ ,  $Y_{rIn}$ ,  $Y_{rSe}$ ) were derived using the same approach. As a result three normalised functions  $\chi(x) = Y_a/Y_r$  (where  $x$  is the channel number) for the three elements can be calculated. After this procedure the energy scales were converted into depth using a standard technique [9]. Separated and normalised aligned spectra for the three elements from virgin and  $Xe^+$  implanted areas of the CIS crystal have been obtained. The difference between the energy losses for channelling and non-channelling ions was not taken into account. The depth available for the analysis depends on the difference in masses, type of ion used for the RBS probe and its energy. In the case of a 2 MeV  $He^+$  analysing beam in  $CuInSe_2$  the mass separated depth analysis can be achieved up to approximately 100nm. The depth concentration profiles for each sublattice were derived using the iterative calculation approach [10]. The derived concentration depth profiles of scattering centres for the three sublattices are shown in Fig.2 (a).

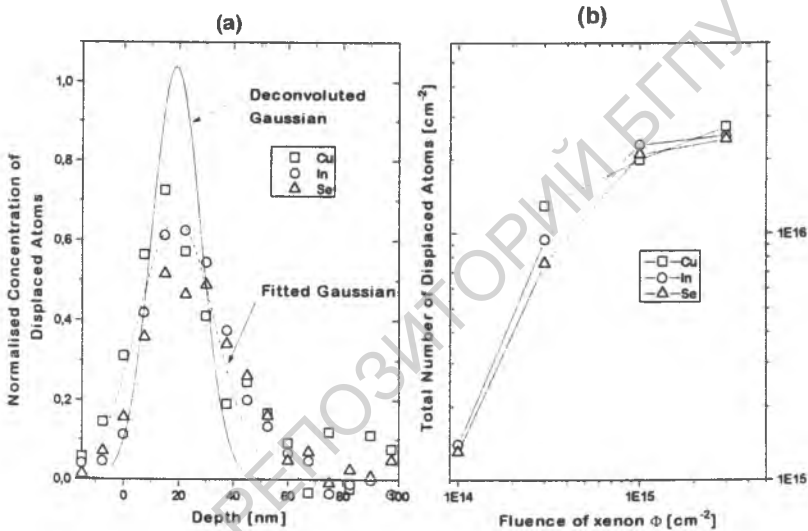


Fig.2. (a) - concentration of displaced atoms depth profiles with fitted and deconvoluted Gaussian curves for  $CuInSe_2$  implanted with  $10^{15} \text{ cm}^{-2} Xe^+$ ; (b) - the total number of displaced atoms accumulated in the near surface layer following  $Xe^+$  implantation.

The resolution of the spectrometer is measured to be 5 channels or in terms of depth for indium near surface layer it is  $2\sigma=38\text{nm}$ . The shape of the concentration profiles is close to a Gaussian curve with  $2\sigma=40\text{nm}$ , very close to the resolution. This implies that the shape has been considerably modified. The deconvoluted concentration profile along with the fitted Gaussian curve are shown in Fig.2(a). We still can not evaluate the depth location of the maximum because of the poor depth resolution but we can judge the maximum volume concentration of the damage. For a more accurate calculation of the concentration of the displaced atoms it is necessary to know the dechannelling cross-section which depends on the nature of the defects and the exact locations of the interstitial atoms in the lattice. Without this additional information derived values can be used only as a first order estimation of the concentration depth profiles and for relative comparison of the amount of accumulated damage. All the calculation procedures were integrated into a computer programme written in TURBO PASCAL.

## RESULTS AND DISCUSSION

Irradiation of the crystal with fluences up to  $10^{14}$   $\text{cm}^{-2}$  was found not to affect the aligned spectrum. For fluences larger than  $10^{14}$   $\text{cm}^{-2}$  three distinguishable peaks related to defects in the indium, selenium and copper sublattices appeared in the aligned spectra. Such peaks suggest that dechannelling in the damage layers mostly occurred due to direct scattering processes. The model described above has been employed to derive the number of displaced atoms and to estimate the maximum concentrations after the implantations. The distributions of displaced atoms for all the elements for the implantation fluences from  $10^{14}$  to  $3 \times 10^{15}$   $\text{cm}^{-2}$  were found to be similar within the accuracy of the experiment. It confirms a suggestion that during irradiation all the sublattices of compounds are damaged to the same degree [11]. The amount of the indium sublattice related damage has also been estimated with the RUMP programme. Indium related peaks of the simulated random spectra for CIS films were fitted to the peaks of the experimental aligned RBS spectra following the procedure of Mader [12]. From the RUMP calculation the increase in the number of displaced atoms as a function of implantation dose was obtained. This was achieved by calculating the increase in the thickness of a film which produced a similar indium related peak in the aligned spectrum. The results are shown in Table 1. The good agreement with the numbers derived using the model described above suggests that the model can be used for such evaluations. The amount of xenon incorporated into the near surface layer was also estimated for higher doses using the RUMP programme [13]. The results are shown in Table 1. The discrepancy between the amount of xenon detected and the fluence at  $3 \times 10^{15}$   $\text{cm}^{-2}$  can be ascribed to significant sputtering taking place in the case of xenon irradiation. The presence of a considerable fraction of xenon atoms suggests the existence of clusters of xenon atoms or even of small gas bubbles. Such defects has been established [14] to cause direct scattering observed in the aligned spectra.

Table 1. Fluence of xenon implanted into CIS crystal, doses of xenon and total numbers of displaced atoms derived from RBS/c spectra versus.

Fluence of $\text{Xe}^+$ [ $\text{cm}^{-2}$ ]	$10^{14}$	$3 \times 10^{14}$	$10^{15}$	$3 \times 10^{15}$
RUMP derived Dose $\text{Xe}^+$ [ $\text{cm}^{-2}$ ]			$10^{15}$	$1.5 \times 10^{15}$
RUMP derived number of In displaced atoms [ $\text{cm}^{-2}$ ]	$10^{15}$	$8 \times 10^{15}$	$1.9 \times 10^{16}$	$2.6 \times 10^{16}$
The programme calculated number of displaced atoms of In [ $\text{cm}^{-2}$ ]	$1.3 \times 10^{15}$	$9.1 \times 10^{15}$	$2.3 \times 10^{16}$	$2.8 \times 10^{16}$

The total numbers of displaced atoms derived for all the sublattices as a function the implanted xenon fluence are shown in Fig.2 (b). The curves show a saturation behaviour at a fluence of  $10^{15}$   $\text{cm}^{-2}$ . The maximum concentration of the atoms displaced due to implantation at this dose is very close to the atomic densities of the elements. Therefore it may be concluded that at this dose the crystal/amorphous phase transition has occurred. CIS crystals irradiated with  $10^{16}$   $\text{cm}^{-2}$  of 40keV

xenon have been characterised with TEM and SIMS analysis [15]. SIMS measurements of the xenon depth distribution showed a good agreement with the TRIM simulated data (the mean range is 16nm, the straggling is 7.2nm). The implanted layer was found to contain a high density of stacking faults and microtwins but not amorphous material. This fact was explained as a result of self healing during the implantation or, possibly, as solid-state recrystallization due to TEM specimen preparation. Therefore we can not confidently conclude that amorphization detected in terms of RBS/C actually takes place. Amorphous zones in CIS have been observed after a  $10^{17}$  cm<sup>-2</sup> dose of 40 keV oxygen, but unlike xenon, oxygen creates chemical bonds with CIS and with maximum volume concentration of 4% can already form secondary phases such as In<sub>2</sub>O<sub>3</sub> which may prevent healing process. The number of displacements created by one ion of xenon according to a TRIM calculation, without taking in account annealing processes is 1111. The derived value of the remnant damage for a  $3 \times 10^{14}$  cm<sup>-2</sup> xenon fluence is only 126 in the present work, almost 9 times smaller. This discrepancy may be explained as in terms of damage annealing taking place during implantation. In order to estimate the temperature in the area of the collision cascades during the thermal spike stage we calculated  $\Theta$  - the average energy deposited per target atom [16] has been estimated to be about 1eV/at assuming 84 as the mean mass in the compound. It was found that the effective thermal spike temperature could reach 11000K over a period of  $5 \times 10^{-12}$  s.

The radiation damage accumulation within range from  $10^{14}$  to  $3 \times 10^{14}$  cm<sup>-2</sup> was observed to follow a linear function described by  $m = \Delta \log \Sigma_d / \Delta \log \Phi = 1.5$ . Where  $\Sigma_d$  is the total number of displaced atoms following irradiation with fluence  $\Phi$ . According to the approaches [17,18] on damage production in semiconductors the experimental data suggest a heterogeneous mechanism of the crystal/amorphous phase transition of the CuInSe<sub>2</sub> crystal irradiated with Xe<sup>+</sup>.

We can compare CIS, silicon and GaAs radiation hardnesses. The amorphization of silicon implanted with 40keV Sb<sup>+</sup> ions, which is only 10% lighter than xenon, was observed after dose  $2 \times 10^{14}$  cm<sup>-2</sup> [19]. In the case of GaAs implanted with 80keV ions of Sb<sup>+</sup> amorphization was observed [20] after dose  $2 \times 10^{13}$  cm<sup>-2</sup> more than two order of magnitude lower than in the case of CIS. The origins of such extraordinary radiation tolerance of the CIS crystal lattice possibly are related to the high concentration of point intrinsic defects. These defects which are mostly vacancies and antisite defects, could reach concentrations of up 10% of the atomic density [21]. High quality CIS crystals are usually copper deficient therefore they should contain a substantial concentration of copper vacancies. The collision cascade simulation showed [22] that the presence of stoichiometric vacancies in semiconductor and insulators can hamper focusing processes decreasing the damaging effect of the collision. Also a role in the healing process must be related to the partly ionic nature of the bonds formed by copper atoms.

## CONCLUSION

- Xenon ions implantation into CIS crystals produces severe damage to the lattice.
- All three sublattices were found to be damaged to the same degree.
- The measured dose of xenon atoms in the samples considerably differs from the irradiating fluence possibly due to sputtering process.
- The rate of damage for the linear part of the dose dependence curve is about one order of magnitude lower than the theoretical prediction. This is clear evidence of the radiation hardness of the material and the existence of effective annealing processes of the point defects during the irradiation due to high temperature in the post collision thermal spikes.
- The defect layer is located at a depth which is in good agreement with TRIM prediction. This agreement allows to draw the conclusion that remnant defects, left after the recombination during

implantation, are not mobile at room temperature. The statement is confirmed by the fact that after 8 months at room temperature there is no evidence of annealing of the damage.

- The dose dependence curve reaches a saturation at a fluence of  $10^{15} \text{ cm}^{-2}$ , the displaced atom concentration maximum achieves 100% at the same fluence. We can therefore conclude from the RBS/C data that the crystal/amorphous transition has occurred at this fluence.

#### ACKNOWLEDGEMENT

The authors gratefully acknowledge Dr V Vishniakov for the help with implantation of xenon and Professor G Carter for the discussion.

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