ANALYSIS OF DEPTH PROFILES OF DEFECTS FORMED IN CuInSe₂ THIN FILMS AFTER IMPLANTATION WITH Ar⁺ IONS

Ch.E. SABZALIYEVA[1], N.N. MURSAKULOV[1,2], Kh.M. GULIYEVA[1], N.N. ABDULZADE[1]

[1]*Institute of Physics of the Ministry of Science and Education, H. Javid ave. 131,*
AZ-1073, Baku, Azerbaijan
[2]*Institute of Radiation Problems of the Ministry of Science and Education*
AZ 1143, B. Vahabzade Ave., 9, Baku, Azerbaijan.
E-mail: ch.sabzaliyeva@mail.ru   tel.: +994 538 04 96

Of particular interest is ion implantation of chalcopyrite semiconductor materials CuInSe₂ with high conversion efficiency, used as absorber layers in solar cells. CuInSe₂ sample was implanted with 30 keV Ar⁺ ions at room temperature with an ion current density of 3 μA/cm² and a radiation dose ranging from 10^{12} to $3 \cdot 10^{16}$ ions/cm⁻². After $3 \cdot 10^{15}$ cm⁻², the total damage is calculated to be $3 \cdot 10^{16}$cm⁻², suggesting that only 10 out of 525 created defects per implanted Ar ion were left unhealed.

INTRODUCTION

In recent years, interest in the study of radiation physics of solids has increased significantly. The main reason for this is the search for new types of materials that donʾt lose their ability to work in high radiation conditions. These materials are used in nuclear technology, space rockets, and the development of detector systems [1]. The lack of sufficient quantities of these new types of materials does not allow for the implementation of large projects. One of the important issues in radiation physics of solids is the study of the effect of various types of radiation on the surface structure of polycrystals and monocrystals.

Chalcopyrite solar cells show high tolerance to irradiation with high-energy electrons or ions, but the origin of this is not well understood. One type of interaction of the surface of a solid with accelerated ions (1-100 keV) is ion implantation [2,3].

The ternary compound CuInSe₂ is a semiconductor with a chalcopyrite structure and a band gap of approximately 1 eV. Making drastic changes in the properties of CuInSe₂, obtaining solid solutions and new phases based on it are among the development directions of photoelectric converters created based on these materials. Considering that chalcopyrite is a cheap material, this fact is of great interest. CuInSe₂ semiconductor materials have high conversion efficiency for photovoltaic devices and a (21.8% for laboratory size thin-film cells) are used as absorber layers for solar cells [4]. CuInSe₂ - based solar cells are also resistant to high-energy ion and electron radiation. Rutherford backscattering is an experimental method that provides information about the elemental structure and chemical composition of a substance. Rutherford backscattering spectroscopy is a type of ion scattering spectroscopy that is based on the analysis of the energy spectra of He⁺ ions (alpha particles) or protons with energies of~(1–3) MeV

scattered in the opposite direction from a sample [5-6]. Rutherford backscattering spectroscopy, like ion scattering spectroscopy, provides information about the chemical composition and crystallinity of a sample, as well as the surface structure of a crystalline sample, according to the energy spectra of the scattered alpha particles depending on the distance from the sample surface (or a certain depth). Combining RBS with the ion channeling effect (RBS/C) by aligning the beam of high energy positive ions with low index axes of the lattice provides information on the near surface depth profile of the concentration of structural defects in the lattice. The well-known energy loss rate (dE/dx) for most materials allows us to move from the energy scale to the depth scale. This is a one-time energy loss in the act of scattering, the amount of which is determined by the mass of the scattering atom [7]. The mechanism of the method is that when the ion beam (alpha particles or protons) is directed along the main directions of symmetry of single crystals, ions that avoid direct collisions with surface atoms can penetrate deep into the crystal (up to hundreds of nm) and move along the channels formed by the atomic rows. By comparing the spectra obtained when the ion beam is directed along the channeling directions and in directions different from them, one can obtain information about the crystalline perfection of the sample under study. From the analysis of the intensity of the surface peak, which is the result of direct collisions of ions with surface atoms, one can obtain information about the structure of the surface, for example, about the presence of reconstructions, relaxations and absorbances [8-9]. From the reflections falling on other energy channels, it is possible to determine the chemical composition. The main feature of the method is to obtain the above information about the sample using high-energy ions that penetrate deep into the solid and are scattered

back from atoms located deep inside. In this process, the main results are determined by the energy lost by the ion. The scattering cross section is found from the law of conservation of momentum during scattering. Due to the complicated phase diagram, it is difficult to grow $CuInSe_2$ crystals with high structural quality [10-11].

In this study, we have used the Rutherford backscattering technique to study the depth concentrations of defects formed by different doses of 30 KeV Ar ion beam in the Cu, In and Se sublattices of a high-structure quality $CuInSe_2$ single crystal.

EXPERIMENT

From a practical point of view, implantation of $CuInSe_2$ thin layers, which are used as absorber layers in solar cells, with Ar^+ and Xe^+ ions is of great importance.

A single crystal of p-type $CuInSe_2$ with dimensions of 2×1 cm and a thickness of 2 mm was grown by the vertical Bridgman method and cut from the middle of the ingot. The sample was mechanically polished with diamond paste. The polished sample was etched in 0.1% bromine methanol solution for 1 min and then heat - treated in vacuum at 300° C to remove the remaining selenium layer on the surface. The orientati on of the crystal was determined using X-ray diffraction patterns before implantation. The sample surface was determined to be within 5° of the (112) plane. After the sample surface was brought to the specified condition, the sample was implanted with 30 keV Ar^+ ions at room temperature with an ion current density of 3 mkA/cm^2 and a radiation dose ranging from 10^{12} to 3×10^{16} ions/cm^{-2}. To avoid channeling during implantation, the argon ion beam was positioned approximately 3° from the (221) plane axis used for Rutherford backscattering during implantation. One area was kept unimplanted to be used as a reference (etalon) site [12-13].

RESULTS AND DISCUSSION

The RBS spectra of ternary compounds can be considered as the sum of three separated RBS products corresponding to three atomic species. Each product is shifted in energy scale according to the element mass. In our work, we separate these three products from the overall matched spectrum of $CuInSe_2$. The Rutherford backscattering method was used to obtain depth profiles of the n_{Cu}, n_{In}, and n_{Se} scattering centers in the Cu, In, and Se sublattices, respectively. [14]. The In and Se profiles are shown in Figs. 1(a) and 1(b), respectively. It can be seen from Figure 1 that the concentration profiles of both In and Se consist of two peaks, (P1) a narrow peak at the surface and (P2) a wider peak at a depth of 40 nm. In the In profiles with lower scattering, the shape of these peaks is well described by Gaussian curves. An example of a Gaussian curve corresponding to the depth profile of In atoms after implantation at a dose of 3×10^{16} ions/cm^{-2} is shown in Figure 1(a). The width of this P1 peak is close to the depth resolution. This means that its shape has changed significantly due to the lack of resolution. Therefore, we propose to explain the P1 peak as a result of the presence of a thin "amorphous" layer. This layer may retain some symmetry, but He^+ ions do not channel within it. The height of this P1 peak does not reach the random value because of a lack of depth resolution. The calculated dependence of the accumulated defects due to P1 on the area of the P1 peak for each dose is shown in Figure 2. It grows almost linearly, without any saturation phenomenon. The second peak (P2) appears in the aligned spectra at a depth of 40 nm after implantation at doses above 1.5×10^{15} ions/cm^{-2}.
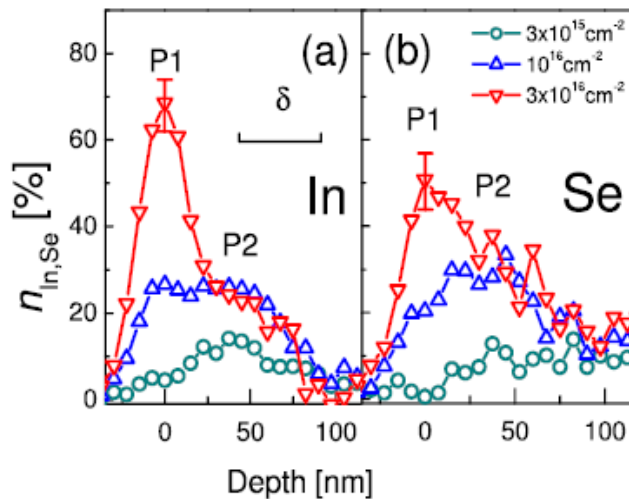

Fig. 1. Depth profiles of n(d) concentrations of scattering centers in the (a) In and (b) Se sublattices after 30 keV Ar^+ implantation.

The intensity of the peak increases with increasing dose and shows saturation at doses above 10^{16} ions/cm^{-2} [15]. The higher resolution for RBS due to indium allows the resolution of the P1 and P2 peaks in the depth profiles of indium, whereas for selenium these peaks merge [16].
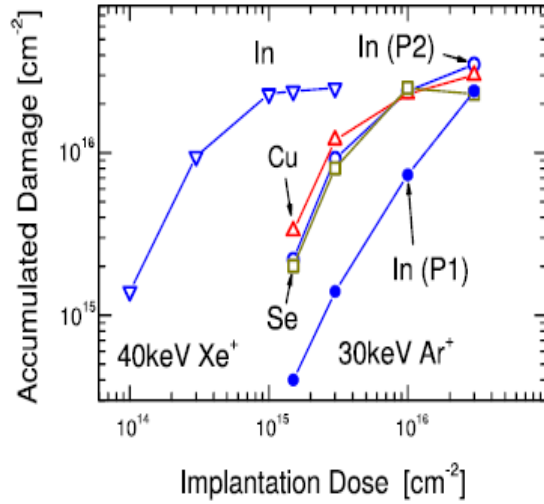
Fig.2. Damage accumulated in Cu, In, and Se sublattices after implantation of CuInSe₂ with 40 keV Xe⁺ and 30 keV Ar⁺ ions.
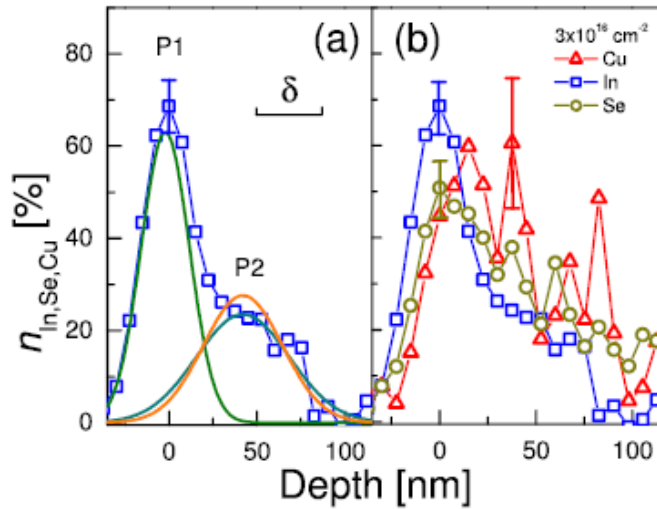

Fig.3. (a) Depth profiles of the In scattering centers after implantation with Ar⁺ ions at a dose of 3×10^{16} ion/cm² (with fitted Gaussians); (b) concentration depth profiles n(d) of the Cu, In, and Se scattering centers after implantation with Ar⁺ ions at a dose of 3×10^{16} ion/cm² (b).

The P2 peaks for different doses of Ar⁺ ions are well fitted by Gaussian curves. From Figure 1(a) we see that the deconvolution of this curve leads to a slightly reduced estimate of the full width at half maximum (FWHM) WP2 = 45 nm. The calculated dependences of the accumulated defects related to P2 on the area of the P2 peak for each dose and element are shown in Figure 3. The accumulated damage for all three elements saturate at doses above 3×10^{15} ions/cm². The P1 peak can be attributed to the effect of dominant scattering. Using Auger electron spectroscopy, selenium deficiency was detected after sputtering of CuInSe₂ single crystals with 5 keV Ar⁺ ions. X - ray photoelectron spectroscopy of CuInSe₂ single crystals sputtered using 0.5 keV Ar⁺ ions revealed the presence of an indium layer with a copper deficient surface of CuInSe₂ (the ordered vacancy compound CuIn₃Se₅ and the binary phase In₂Se₃) under this layer. The concentration depth profiles and distribution of vacancies induced by irradiation of 30 keV Ar⁺ ions in CuInSe₂ were calculated using the TRIM program. The average penetration depth and the FWHM of the depth profiles for Ar⁺ ions were obtained as R_{Ar} = 27 nm and W_{Ar} = 30 nm, respectively. The calculated depth profiles of vacancies induced by irradiation are slightly smaller, approximately R_{Vac} = 16 nm and FWHM is W_{Vac} = 42 nm [17-18]. The maximum depth of defects is significantly smaller than the experimentally obtained value of R_{P2} = 40 nm. A physical model has been proposed to explain these results. This model is based on the assumption that point defects in CuInSe₂ have high mobility at room temperature. This assumption is supported by theoretical calculations of defect formation energies in CuInSe₂ and experimental evidence that the implanted copper atoms are very mobile. The mobility of the implanted copper atoms can be enhanced by thermal peaks generated by Ar⁺ ions. Theoretical estimates of the thermal effects of 30 keV Ar⁺ ions in CuInSe₂

predict that the temperature in the volume of the collision cascade can reach 1700 K within 10-11 seconds. We speculate that Ar-implantation can form small bubbles, stacking faults, and dislocation loops [19]. Scanning electron microscopy studies of $CuInSe_2$ crystals implanted with Xe^+ ions revealed high concentrations of stacking faults and dislocation loops [20-21]. According to TRIM calculations, each Ar^+ ion with an energy of 30 keV creates 525 vacancies and interstitial atoms. These defects should amorphize the surface at a distance between 6 nm and 24 nm after a dose of 10^{15} ions/cm^{-2}. However, the first signs of damage are observed in the corresponding aligned spectrum after a dose of 1.5×10^{15} ions/cm^{-2}. This can be considered as evidence for the existence of effective recovery processes at room temperature in $CuInSe_2$. After implantation of 3×10^{15} ions/cm^{-2}, the total defects were calculated to be 3×10^{16} cm^{-3}, which indicates that only 10 out of 525 defects created by each implanted Ar^+ ion remained unrecovered. At first sight, it seems remarkable that 98% of the damage can be self annealed at room temperature. But a more

accurate consideration of this effect gives even more interesting results. At this dose, only 10% was calculated to be in the P1 peak, which is associated with dominant scattering, while the rest was found in the P2 peak, which is deeper than the depth predicted by TRIM for unrecovered defects, and this can probably be explained by packing defects and dislocation loops. This indicates that more than 98% of the initial defects recombined and formed defects [22-23].

CONCLUSIONS

Implantation of 30 keV Ar^+ ions into a $CuInSe_2$ single crystal creates two defect layers on the surface, due to sputtering dominated by Se and Cu atoms, and in the implanted Ar layer, probably due to packing defects and dislocation loops. It was found that the way to reduce the implantation of Ar^+ ions into $CuInGa(Se,S)_2$ layers during magnetron sputtering is to make the gas discharge voltage and the seat temperature as small as possible.

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[1] *M. Ye.* Electrical Transport Properties and Band Structure of $CuInSe_2$ under High Pressure. M. Ye, R. Tang, Sh. Ma, Q. Tao, X. Wang, Y. Li, and P. Zhu. The Journal of Physical Chemistry. -C 2019, -v. 123, -p. 20757-20761.

[2] *S.J. Yoon.* Structural and Optical properties of Chemically Deposited $CuInSe_2$ Thin Film in Acidic Medium. S. J. Yoon, L. İseul, K. S. Hyung, L. J. Kee, L. H. Young, L. W., H. Sung-Hwan. Journal of Naoscience and Nanotechnology. -2012, -v. 12. № 5. -p. 4313-4316.

[3] *R.A. Young.* The Rietveld Method. R.A. Young. - Oxford: Oxford University Press, - 1993. -p. 290- 298.

[4] *A.V. Mudry, A.V. Korotki, E.P. Zaretskaya, V.B. Zaretskaya, N.N. Mursakulov, N.N.Abdulzade, Ch.E. Sabzaliyeva.* Growth and optical properties of Cu(In,Ga)Se$_2$ thin films on flexible metallic foils. Azerbaijan Journal of Physics volume XVI, Number 2 Series: En June 2010. p.408-413.

[5] *J.L. Shay and J.H. Wernick.* Ternary Chalcopyrite Semiconductors-Growth, Electronic Properties, and Applications (Pergamon, New York, 1975).

[6] *P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier, and M. Powalla.* Phys. Status Solidi R 9, 28 (2015).

[7] *S.J. Yoon.* Structural and Optical properties of Chemically Deposited $CuInSe_2$ Thin Film in Acidic Medium. S. J. Yoon, L. İseul, K. S. Hyung, L.J. Kee, L. H. Young, L. W., H. Sung-Hwan. Journal of Naoscience and Nanotechnology. -2012, v. 12. № 5. -p. 4313-4316.

[8] *R.A. Young.* The Rietveld Method. R.A. Young. - Oxford: Oxford University Press, - 1993. -p. 290- 298.

[9] *W.K. Chu, J.W. Mayer, and M.A. Nicolet.* Backscattering Spectrometr (Academic, New York/San Francisco/London, 1978).

[10] *T. Haalboom, F. G€odecke, M. Ernst, Ruble, R. Herberholz, and H.W. Schock,* The 11th International Conference Ternary and Multinary Compounds, Institute of Physics, Salford, UK (1997), p. 249.

[11] *M. Yakushev, A. Zegadi, H. Neumann, P.A. Jones, A. E. Hill, R.D. Pilkington, M.A. Slifkin, and R.D. Tomlinson,* Cryst. Res. Technol. 29,427, 1994.

[12] *R.D. Tomlinson.* Sol. Cells 16, 17, 1986.

[13] *M.V. Yakushev, G. Lippold, A.E. Hill, R.D. Pilkington, and R.D. Tomlinson.* J. Mater. Sci.: Mater. Electron. 7, 155, 1996.

[14] *M. Kulik.* Effect of ion implantation on optical properties of near surfaces layers on Kr+ implanted GaAs: SE and RBS investigation. M. Kulik, E. B Asgerov, A. P Kobzev, M. Latek. "Fizikanın müasir problemləri" IX Respublika konfransı. Bakı, -2015, -p. 511-512.

[15] *T.P. Massopust, P.J. Ireland, L.L. Kazmerski, and K.J. Bachmann.* J. Vac. Sci. Technol., A 2, 1123, 1984.

[16] *K. Otte, G. Lippold, D. Hirsch, A. Schindler, and F. Bigl.* Thin Solid Films 361–362, 498, 2000.

[17] *D. Cahen and L. Chernyak.* Adv. Mater. 9, 861, 1997.

[18] *V. Nadazdy, M. Yakushev, E. D. Djebbar, A.E. Hill, and R. D.Tomlinson.* J. Appl. Phys. 84, 4322, 1998.

[19] *P. Sigmund.* Appl. Phys. Lett. 25, 169, 1974.

[20] *C.A. Mullan, C.J. Kiely, M.V. Yakushev, M. Imanieh, R.D. Tomlinson, and A. Rockett.* Philos. Mag. A 73, 1131, 1996.

[21] *J.A. Hinks and S. E. Donnelly.* Philos. Mag. 91, 517, 2011.

[22] *S.E. Donnelly, J.A. Hinks, P.D. Edmondson, R. D. Pilkington, M.Yakushev, and R. C. Birtcher.* Nucl. Instrum. Methods B 242, 686, 2006.

[23] *C. Stephan, S. Schorr, M. Tovar, and H.-W. Schock.* Appl. Phys. Lett. 98,091906, 2011.