1. Katarzyna UNGEHEUER[1], 2. Konstanty W. MARSZALEK[1], 3. Marzena MITURA-NOWAK[2], 4. Zbigniew. KAKOL[1]

AGH University of Science and Technology, Krakow (1),
The Henryk Niewodniczanski Institute of Nuclear Physics Polish Academy of Sciences, Krakow (2)
ORCID: 1. 0000-0002-7945-5758; 2. 0000-0002-0564-5743; 3. 0000-0001-5124-8688; 4. 0000-0002-5978-8627

doi:10.15199/48.2022.09.60

Modification of semiconducting copper oxide thin films using ion implantation

***Abstract**. The article describes method of Cr^+ ion implantation with energy of 10 keV and 15 keV. This method can be used to modify thin film semiconductors. Simulations of implantation process were performed using the Stopping and Range of Ions in Matter software, taking into account different energies of the ion beam. The apparatus diagrams of ion implantation and magnetron sputtering processes are presented. Optical and structural properties of non-implanted and implanted Cu_4O_3 and CuO films were studied.*

***Streszczenie.** W artykule opisana została metoda implantacji jonami Cr+ o energii 10 keV i 15 keV, która może być stosowana do modyfikacji cienkich warstw półprzewodnikowych. Wykonano symulacje procesu implantacji z wykorzystaniem programu Stopping and Range of Ions in Matter uwzględniając różne energie wiązki jonów. Przedstawiono schematy aparatury implantatora oraz układu do rozpylania magnetronowego cienkich warstw. Optyczne i strukturalne właściwości nieimplantowanych i zaimplantowanych warstw Cu_4O_3 i CuO zostały zbadane.*
Modyfikacja cienkich warstw tlenków półprzewodzących za pomocą implantacji jonowej

Keywords: thin films, ion implantation, PV cell absorber.
Słowa kluczowe: cienkie warstwy, implantacja jonowa, absorbery fotowoltaiczne.

Introduction

Ion implantation is a method where an accelerated ion beam is directed onto a target material. The process causes modification of surface physical properties, structural properties of the material into some depth dependent on the ion species and its energy. The energies used in ion implantation are usually in range of 10 – 200 keV yet experiments with ions of high MeV order energy are performed [1]. The goal of ion implantation process is to induce changes in materials properties, including corrosion resistance [2] mechanical [3], electrical [4,5] or optical [6,7] properties. It is most often used to precisely dope semiconducting materials to produce electronic devices.

Ions that hit the material can interact with it in two ways: by inelastic collisions with electrons bound to target atoms (called electronic stopping) or elastic collisions with nuclei of implanted material atoms (called nuclear stopping) [8]. The second one is the origin of recoils cascades, where an atom of target material has enough energy to displace another atom, and this process repeats until all energy is lost. Most of energy coming from electronic stopping is dissipated as thermal energy. Other effects of implantation as presented in Figure 1 are creation of phonons and plasmons, excitation of electrons in the target material, thermally induced diffusion, and most importantly structural damage that often results in amorphization of implanted layer.

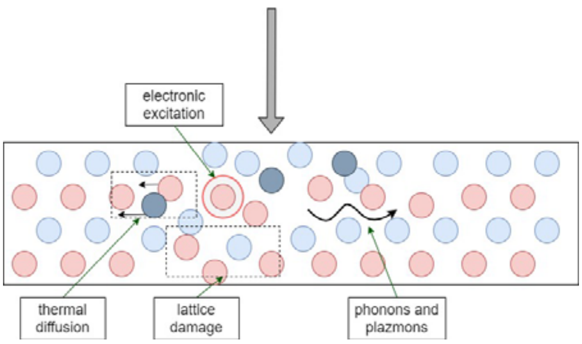

Fig.1. Diagram of interaction of ion beam with target material.

To retrieve the crystal structure irradiated materials are annealed. More importantly during annealing the dopant is uniformly distributed in the whole sample, and it is electrically activated as in amorphous form the electrical properties of modified material are far different from material with a chosen dopant in its structure. In this article we present the material only after the process of ion implantation.

It is possible to predict how the ions will influence the structure and how far they will penetrate the material. A software by Ziegler et al. Stopping and Range of Ions in Matter (SRIM)[9] is a tool that enables simulation of many energies and types of ions. And gives possibility to use any target, also multilayered. As input type and ratio of atoms, and the density of material, which is often different from the theoretical value, are determined.

Here we study copper oxides thin films. Copper can form three oxides: CuO, Cu_2O and Cu_4O_3, where the last one is a less stable form. All of them are p-type semiconductors and can be used in sensors, catalyst, PV cell solar absorbers [10].

In this work we deposited thin films of two copper oxides: CuO and Cu_4O_3 using magnetron sputtering method. Then we implanted them with Cr ions of 15 keV and 10 keV energy. Using SRIM software we simulated the range of ions and the recoil cascades in the material. Optical properties of non-implanted and implanted samples were studied using spectroscopic ellipsometry method. The X-Ray diffraction was used to determine deposited phase and determine the influence of implantation on structure of the oxides.

Deposition and implantation

Samples of thin layers of copper oxides were deposited by magnetron sputtering on glass and silicon substrates. Before deposition process the substrates were cleaned with warm water and soap, and then submerged in isopropanol ultrasonic bath for 20 minutes. The parameters of deposition process are presented in Table 1. The target used was Cu from Kurt J. Lesker of 99.95% purity.

Layers were implanted at the Institute of Nuclear Physics in Krakow. The CuO layers, 130 nm thick, were implanted with the energy of 15 keV and a dose of 5×10^{16}

ion/cm^2 and the energy of 10 keV with 1×10^{14} ion/cm^2, 5×10^{14} ion/cm^2, 1×10^{15} ion/cm^2 doses. Samples of Cu_4O_3, also approximately 130nm thick, were implanted with 15 keV ions and dose of 5×10^{16} ion/cm^2.

Table 1. Deposition parameters. T is temperature of heated substrate.

Parameter/ oxide	O_2 flow [sccm]	Ar flow [sccm]	P [W]	Pressure [Pa]	T [°C]
CuO	30	-	50	2.00	150
Cu_4O_3	27	3	50	1.51	150

Measurements of optical properties were performed with J.A. Woollam M 2000 ellipsometer. CuO samples were also studied with spectrophotometry method using AvaLight-DH-S-BAL source and AvaSpec-ULS-RS-TEC detector in transmission mode [11]. Structural properties were studied with X-ray diffraction using PANalytical X'Pert PRO diffractometer, with Cu anode (0.154 nm radiation wavelength). The magnetron sputtering deposition setup is schematically presented in Figure 2. Using a rotary pump and turbomolecular pump it is possible to achieve pressure of 10^{-3} Pa. The apparatus has two deposition chambers, thus it is possible to carry on two independent processes. In this work we used only chamber B. The apparatus enables reactive deposition with control of reactive gas flow, in this case it was oxygen.

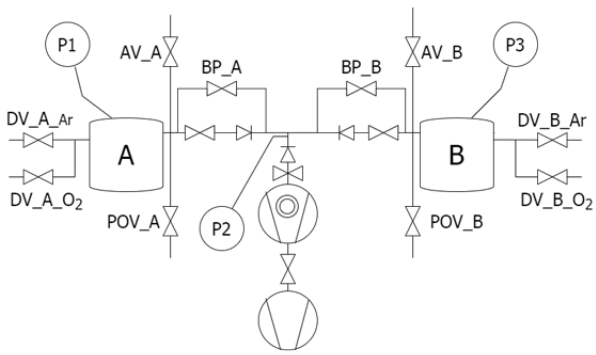

Fig. 2. Diagram of deposition apparatus. BP_ - bypass, P1-3 – vacuum probes, DV_A_Ar/O_2 – electromagnetic valves for dosing gases, A and B – deposition chambers.

In the implantation setup the most important element is the mass analyzer, which enables creation of a coherent beam consisting of one type of ion. Electromagnets bend the beam in a way to pass only desired ions, the analyzer can be seen in Figure 3. (a green box) along with ion source on the left. In the right part of Figure 3. the target chamber can be seen. A system of three diffusion pumps enables pressure levels of order 10^{-6} Pa in the target chamber and 10^{-3} Pa in the rest of the system. Two rotary pumps are used as fore vacuum pumps. A simple diagram of the whole system is presented in Figure 4

Fig. 3. Photographs of ion implantation apparatus. Left: ion source and mass analyzer, right: target chamber

Thanks to a system of vacuum locks it is possible to add material to source, exchange targets and carry out needed maintenance without airlocking the whole system. The target is placed in a carrier that is moving perpendicularly to the ion beam, thus executing scanning of the implanted material with the beam and achieving desired dose of implantation.

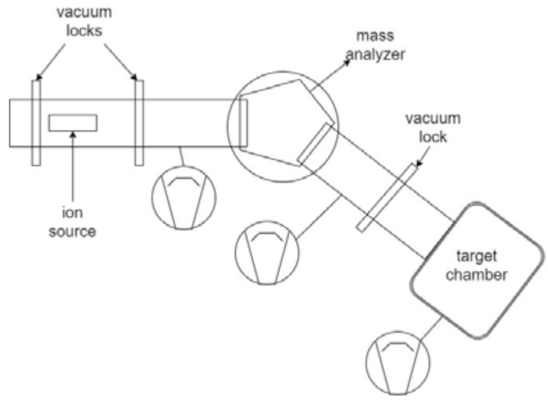

Fig. 4. Diagram of implantation apparatus.

Simulations

In this work we present results of simulation of copper oxides implanted with Cr ions. The software enables to input any of three copper oxides: CuO, Cu_2O, Cu_4O_3 and simulate the ion beam with two different energies: here 10 and 15 keV. All the simulations were performed for an ion beam perpendicular to the target surface and for 30 000 ions.

The density of target was set as 6,31 g/cm^3, 6,00 g/cm^3 and 5,84 g/cm^3 for three oxides CuO, Cu_2O and Cu_4O_3, respectively. Though this work focuses only on two of three oxides, the simulated ion range for all of them is presented in Fig. 4 to show that depending on density, and therefore the crystal structure of the material, the result will significantly differ.

The software includes calculation of many ion implantation parameters. It is possible to analyze the distribution of implanted ions as well as distribution of recoils – both O and Cu atoms. It can be noticed that depending on the chosen oxide, so its density and ratio of Cu and O ions, the range of implanted ions changes. In Figure 4 it can be seen that Cu_2O and Cu_4O_3 are easier to penetrate by ions than CuO, especially with 15 keV energy. Using lower energy of 10 keV causes ions to stay at positions closer to the surface of the target, the dispersion of implanted ions is smaller.

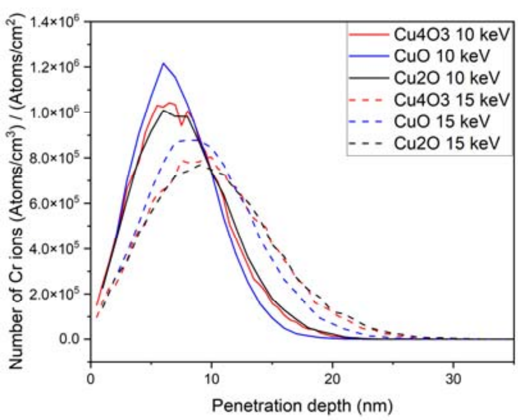

Fig. 4. Distribution of Cr ions implanted with 10 and 15 keV energy.

In Figure 5 trajectories of 30 000 ions implanted into Cu_4O_3 are presented. It can be seen that the process is chaotic. Though the beam enters the material in one point, the ions reach spots laterally to the beam, almost 20 nm away from the beam point of entrance.

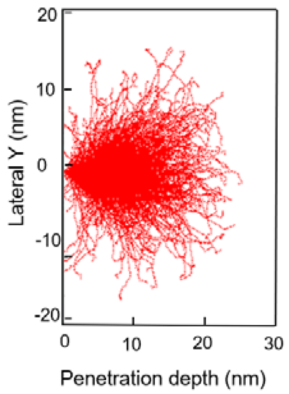

Fig. 5. Trajectories of Cr ions implanted into Cu_4O_3 with energy of 15 keV perpendicularly to the target surface

The final positions where the ions stop are distributed quite regularly as can be seen in Figure 6. Comparing this picture with Figure 5 we can say that an ion going through the material travels an irregular way. Some ions reach further in the structure than the others, this could be due to the channelling, where an ion inserts between two crystal planes and is directed between them without losing much energy [8].

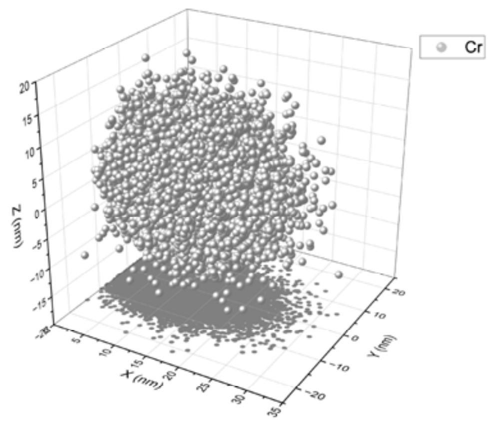

Fig.6. Final position of Cr ions in Cu_4O_3

An interesting results that the SRIM software provides is the recoils that occur during implantation (Fig. 7).

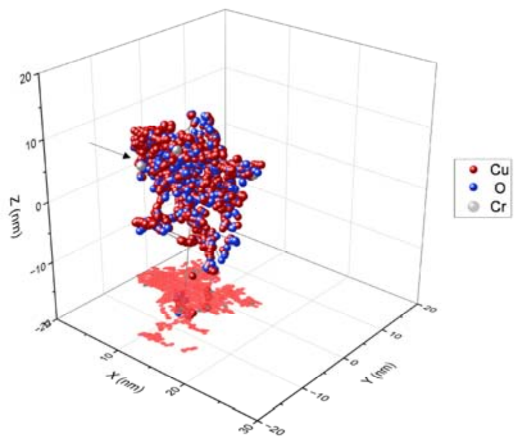

Fig. 7. Recoils created by the first 10 ions simulated

One ion that interacts with the atoms in the target's structure initiates a chain reaction of next excitations. Any atom excitation results with either deterioration of its position in the lattice, creation of vacancy or interstitial defect and if the atom has enough energy it passes it to its neighbours. In Figure 7 the recoils of Cu (red balls) and O (blue balls) of first 100 simulated Cr ions (grey balls) implanted with 15 keV into Cu_4O_3. In Figure 8 and Figure 9 simulations for 100 and 1000 ions are presented, respectively. This visualization shows that even 10 atoms cause many more atoms to deteriorate and disrupt the crystal structure of implanted oxide. With more simulated ions the damage done to the material is more profound. Considering that during the implantation the beam is scanned over the surface of the sample, the scale of changes in the material near the surface is meaningful and can lead to amorphization.

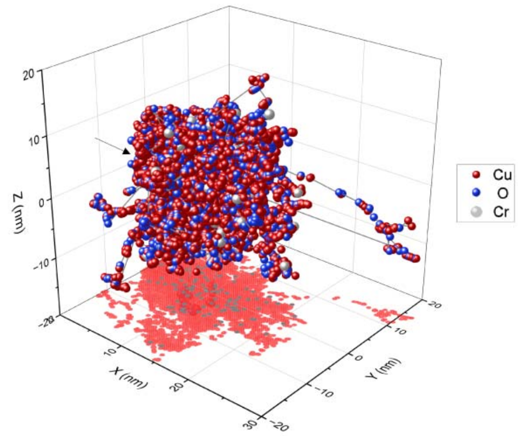

Fig. 8. Recoils for 100 ions

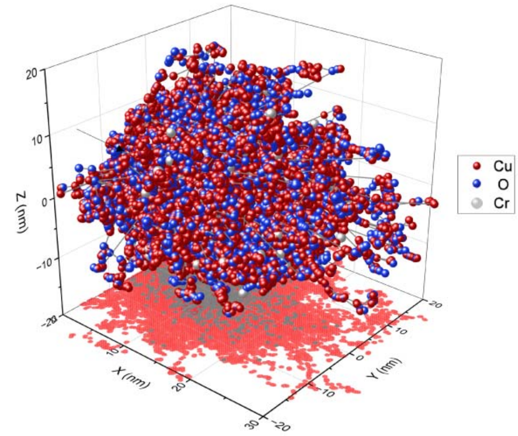

Fig. 9. Recoils from 1000 ions

Results

XRD results, which for CuO can be found in [11] and results for Cu_4O_3 show that the implantation decreased intensity of any oxide-origin peaks and increased their broadening. This means that the size of crystallites was smaller, and that the crystal structure was damaged. In case of Cu_4O_3 the oxide disintegrated into Cu.

Measurements with SE give information about optical properties of oxides. Figure 10 and Figure 11 show refractive index, extinction coefficient and absorption coefficient of implanted and non-implanted oxides. For both materials the implantation changed the n characteristic. Implantation of Cu_4O_3 and CuO with energy of 15 keV ions resulted with increased absorption for higher wavelengths. Implantation of CuO with 10 keV energy ions shows scarce influence on optical properties.

Looking at spectrophotometry measurements of absorbance, the implantation with 10 keV energy ions has negative effect on the parameters. Increasing the ion dose, reduces the absorbance of thin film. Results are presented in Fig. 12 (adapted from [11]).

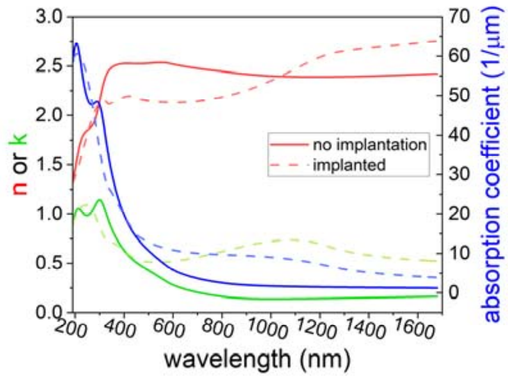

Fig. 10. Optical properties of implanted and non-implanted Cu_4O_3

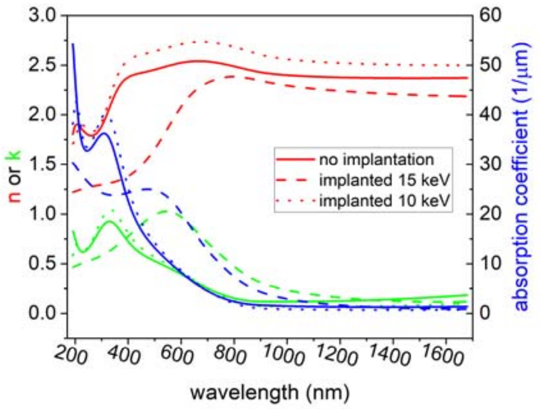

Fig. 11. Optical properties of implanted and non-implanted CuO

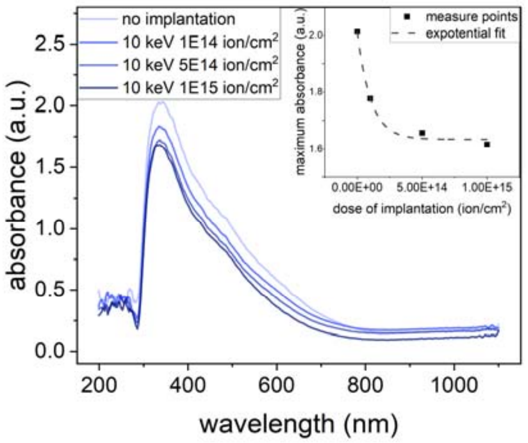

Fig. 12. Absorbance of CuO thin films implanted with 10 keV Cr ions of different dose

Conclusions

The ion implantation with Cr ions has influence on optical and structural properties of thin film copper oxides. SE results show that higher energy implantation should have positive influence on absorption of thin films, while implantation with lower energy could have the opposite effect, as absorbance measurements show.

Simulations of ion implantation process can give insight into processes going during implantation and allow to predict the depth range of ions and damage distribution, which enables design of complicated semiconductor devices.

The authors would like to thank AGH UST project no. for financial support.

***Authors**: Katarzyna Ungeheuer MSc Eng., AGH University of Science and Technology, Mickiewicza ave. 20, 30-059 Krakow, e-mail: ungeheue@agh.edu.pl; dr hab. Konstanty W. Marszalek Eng., prof. AGH, AGH University of Science and Technology, Mickiewicza ave. 20, 30-059 Krakow, e-mail: marszale@agh.edu.pl; PhD Marzena Mitura-Nowak, The Henryk Niewodniczanski Institute of Nuclear Physics Polish Academy of Sciences, Niezapominajek st. 8, 31-342 Krakow, e-mail: Marzena.mitura-nowak@ifj.edu.pl; prof. dr hab. inż. Zbigniew Kakol, AGH University of Science and Technology, Mickiewicza ave. 20, 30-059 Krakow, e-mail: kakol@agh.edu.pl*

REFERENCES

[1] S. Shi, D. Gao, B. Xia, D. Xue, *Argon ion irradiation induced phase transition and room temperature ferromagnetism in the CuO thin film*, J. Phys. D: Appl. Phys. 49 (2016) 055003 (5pp)

[2] Wei X., Ma J., Ma S., Liu P., Qing H., Zhao Q., *Enhanced anti-corrosion and biocompatibility of a functionalized layer formed on ZK60 Mg alloy via hydroxyl (OH-) ion implantation*, Colloids and Surfaces B: Biointerfaces 216, (2022), 112533

[3] Wei D., Li F., Li S., Wang S., Ding F., Tian T., Zhang P., Yao Z., *Effect of Cr ion implantation on surface morphology, lattice deformation, nanomechanical and fatigue behavior of TC18 alloy*, Applied Surface Science 506 (2020), 145023

[4] Kaur M., Gautam S., Goyal N., *Ion-implantation and photovoltaics efficiency: A review*, Materials Letters 309 (2022) 131356

[5] Williams J.S., *Ion implantation of semiconductors*, Materials Science and Engineering A253 (1998) 8–15

[6] Hariwal R. V., Malik H.K., Negi A., Asokan K., *Favourable tuning of optical absorbance, bandgap and surface roughness of ZnO thin films by C ion implantation at the critical angle*, Applied Surface Science Advances 7 (2022) 100189

[7] Liu F., Liu T., Yao Y., Liu Y., Kong W., Cheng L., Bao Y., Gu J., Wang S., Bu M., Huang H., *Lattice structures and optical properties of Ce:LYSO crystal waveguides with implanted C, Si and Cu ions*, Journal of Luminescence 242 (2022) 118559

[8] Pearton S.J., *Ion implantation in GaAs*, Solid State Phenomena Vol. 1&2 (1988) pp. 247-280

[9] Ziegler, J.F.; Ziegler, M.D.; Biersack, J.P., *SRIM- The Stopping and Range of Ions in Matter*, NIMPB 268 (2010) 1818–1823

[10] Heinemann M., Eifert B., Heiliger C., *Band structure and phase stability of the copper oxides Cu_2O, CuO, and Cu_4O_3*, PHYSICAL REVIEW B 87 (2013) 115111

[11] Ungeheuer K., Marszalek K.W., Mitura-Nowak M., Perzanowski M., Jelen P., Marszalek M., Sitarz M., *Influence of Cr Ion Implantation on Physical Properties of CuO Thin Films,* Int. J. Mol. Sci. 2022, 23, 4541