1. Katarzyna UNGEHEUER[1], 2. Amelia E. BOCIRNEA[2], 3. Denis A. PIKULSKI[3], 4. Konstanty W. MARSZAŁEK[1], 5. Aurelian C. GALCA[2], 6. Juliusz CHOJENKA[4], 7. Tamas FODOR[5], 8. Kalman VAD

AGH University of Krakow, Institute of Electronics, Krakow, Poland (1), National Institute of Materials Physics, Magurele, Romania (2), AGH University of Krakow, Faculty of Metal Engineering and Industrial Computer Science, Krakow,Poland (3), Polish Science Academy Institute of Nuclear Physics, Krakow Poland (4), Institute for Nuclear Research, Hungarian Academy of Sciences, Debrechen, Hungary (5)
ORCID: 1. 0000-0002-7945-5758; 2. 0000-0002-5397-4728, 3. 0009-0002-1488-8277, 4. 0000-0002-0564-5743, 5. 0000-0002-1914-4210, 6. 0000-0002-6719-0828, 7. 0000-0002-1428-7538, 8. 0000-0003-2512-9276

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Influence of proton irradiation on CuO thin films properties

Abstract. *Copper oxide (CuO) is a semiconductor material used in photovoltaics, sensors, and photocatalysis. In this study, the effect of proton radiation on thin layers of this oxide was investigated to simulate conditions in space. The irradiation did not significantly affect the material's structural or optical properties. However, the surface resistance of the layers increased, along with the amount of surface adsorbates and the uniformity of the surface changed. (**Wpływ promieniowania protonowego na właściwości cienkich warstw CuO**).*

Streszczenie*. Tlenek miedzi CuO to półprzewodnikowy materiał znajdujący zastosowanie w fotowoltaice, sensorach czy fotokatalizie. W tej pracy został zbadany wpływ promieniowania protonowego na cienkie warstwy tego tlenku, co miało na celu symulację warunków w przestrzeni kosmicznej. Napromieniowanie nie wpłynęło znacząco na właściwości strukturalne i optyczne materiału. Zwiększeniu uległ opór powierzchniowy warstw oraz ilość zanieczyszczeń na powierzchni, a także zmieniła się jej jednorodność.*

Keywords: copper oxide, space environment, proton irradiation, thin films.
Słowa kluczowe: tlenek miedzi, warunki kosmiczne, promieniowanie protonowe, cienkie warstwy.

Introduction

Copper oxides are semiconducting materials recognized for many years, with applications in various fields including photovoltaics, sensors and photocatalysis. CuO, known as cupric oxide is an intrinsic p-type semiconductor that crystallizes in monoclinic C2/c space group. It exhibits good conductivity, stability and high light absorption [1]. The energy band gap value for thin oxide is reported to be between 1 to 1.9 eV which depends mostly on deposition method. Typically, this value is around 1.5 eV which is a great value for photovoltaic energy conversion with about 30 % efficiency achievable according to Schockley-Quisser limit theory [2]. Different electronic and optoelectronic devices can use CuO as a functional layer and may, in the future, be applied in space applications - exploration or human settlements.

Each material used in the scape is exposed to a specific environment. In space the temperature ranges from -150°C to 150°C, and, most importantly, cosmic radiation is present [3]. Here, we focus on proton irradiation, which constitutes a major part of radiation in the region of low earth orbit and have an important influence on materials and electronic devices used in satellites or on the International Space Station. The protons and electrons are trapped in this region by Earth's magnetic field within the so-called Van Allen belts. The energy of protons there ranges from 0.1 to 400 MeV [4]. In this work we investigate how radiation with energy of 226.5 MeV will influence the properties of thin film CuO.

CuO thin films were deposited with reactive magnetron sputtering and characterised with various techniques to study their structural, optical, electrical and chemical properties as well as film homogeneity. The main focus was also to see how irradiation influenced pure CuO film, additionally, a chromium doped film was also studied.

Materials and methods

CuO was deposited with reactive magnetron sputtering as described in [5]. All samples were around 130 nm thick. Samples designated with # were deposited without heating of the substrate. The irradiation experiment was performed at the Institute of Nuclear Physics in Krakow using the C-235 cyclotron at the Gantry stage. The beam fluence was $1x10^{11}$ cm^{-2}, which corresponds to a few hundred years on low Earth orbit [3]. Some samples were doped with Cr via ion implantation method with different energies and doses: 10 keV and $3x10^{14}$ cm^{-2}, 10 keV and $1x10^{15}$ cm^{-2}, 15 keV $5x10^{16}$ cm^{-2}. Cr ion implantation of CuO is discussed in [5, 6]. The CuO# sample after implantation was annealed in air at 400°C for 6h and then irradiated with protons. This sample was primarily prepared to study surface homogeneity with spectroscopic ellipsometry. X-ray diffraction (XRD) was used to examine the crystal structure of the films. Philips X'PERT MPD diffractometer with a Cu anode was used for measurements, and peak identification was carried out using X'Pert HighScore software from PANalytical. The sheet resistance of the thin films was characterised with RM3000+ device from Jandel.

Homogeneity of samples was evaluated with mapping measurements using J.A. Woolam 2000M spectroscopic ellipsometer. Optical properties, specifically light absorption, was measured using spectrophotometry with an AvaLight-DH-SBAL source and an AvaSpec-ULS-RS-TEC detector.

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical properties of the surface. The setup included an analysis chamber equipped with a 150 mm hemispherical electron energy analyser (Phoibos). The analyser operated in fixed transmission mode (FAT) with a pass energy of 20 eV. The X-ray source was a monochromatized Al Kα, with an energy of 1486.6 eV , operating at 250 W power (12.5 kV × 20 mA). Charging effects were compensated using a flood gun (1V × 0.1 mA) and by applying a binding energy correction to the C 1s contamination core level at 286.4 eV. The XPS data was analysed using Igor Pro software.

Results and discussion

The diffractograms of as deposited CuO and irradiated with proton beam are presented in Figure 1. For both samples only peaks from CuO are present, no other copper oxides phases are detected. In the chosen range there are following peaks visible: (110) and two double peaks (-111)&(002) and (111)&(200) as identified with ICDD card #01-080-1268. The peaks' positions do not change after proton irradiation. Only the peaks intensity ratio slightly differs, the double peak(111)&(200) becomes more dominant.

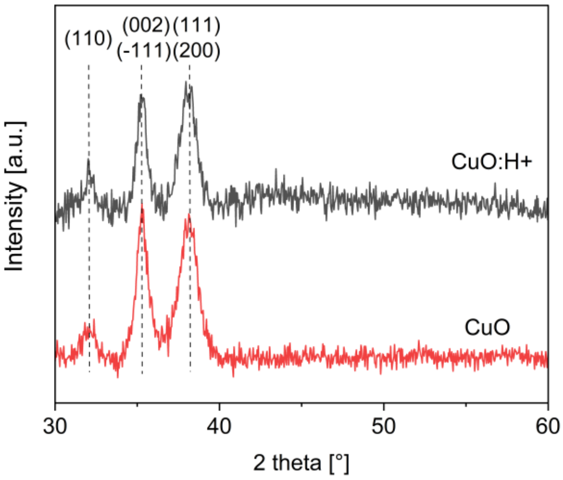

Fig.1. X-ray diffractograms of CuO as deposited and CuO:H+ irradiated with proton beam

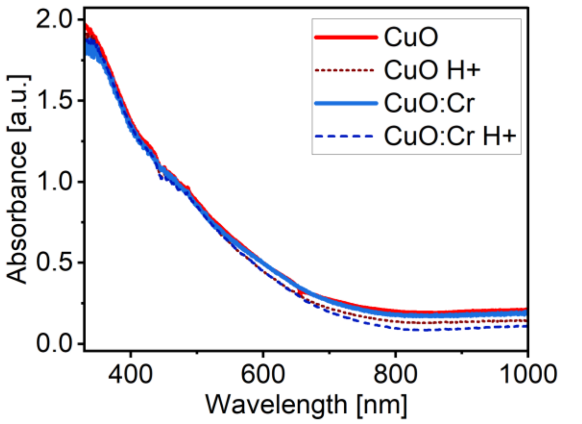

Fig.2. Light absorption of as deposited CuO, irradiated with protons and the sample implanted with Cr ions of 10 keV energy and $1x10^{15}$ cm^{-2}

The absorbance of the as-deposited CuO thin film,the irradiated film, the CuO doped with Cr via ion implantation, and irradiated, are shown in Figure 2. Both ion implantation and proton irradiation reduce the light absorption of CuO, with the second having stronger influence. The most significant change in absorbance is observed for wavelengths higher than 500 nm. The reduction of absorption by implantation can be reduced by annealing [7].

XPS was used to study how irradiation influenced the surface chemical properties. The signal depth for XPS is a few nm, depending on the studied element. Narrow scans of Cu 2p and O 1s lines are presented in Figure 3. The data was fitted with Voigt-function. All the components originating from the same element had the same broadening, both Lorentzian and Gaussian, in case of Cu 2p the 1/2 and 3/2 peak had different Lorenztian broadenings. The function used to calculate the background was Total Sum for Cu 2p spectra and Shirley for O 1s Shirley spectra.

Both samples show a Cu 2p signal characteristic for CuO with two strong peaks and shake-up satellites [8]. The only difference introduced by irradiation is slight decrease of signal intensity and widening of the main two peaks. There are clear differences for O 1s spectra. After irradiation, the components coming from surface Cu^{1+} and adsorbates have much stronger intensity, while the main O 1s signal coming from Cu^{2+} is weaker. Moreover there appears a signal at high binding energy around 536 eV, which originates from more organic adsorbates [9]. For the as-deposited CuO, the contributions were approximately 62% from the CuO lattice, 17.8% from Cu^{1+}, and 20.2% from adsorbates.

For irradiated sample, these contributions were as follows CuO – 48.8%, Cu^{1+} - 14.3%, and adsorbates – 36.9%. The calculations based on fitting provide quantitative proof that irradiation caused an increase in adsorbates and defects on the surface of CuO thin film.

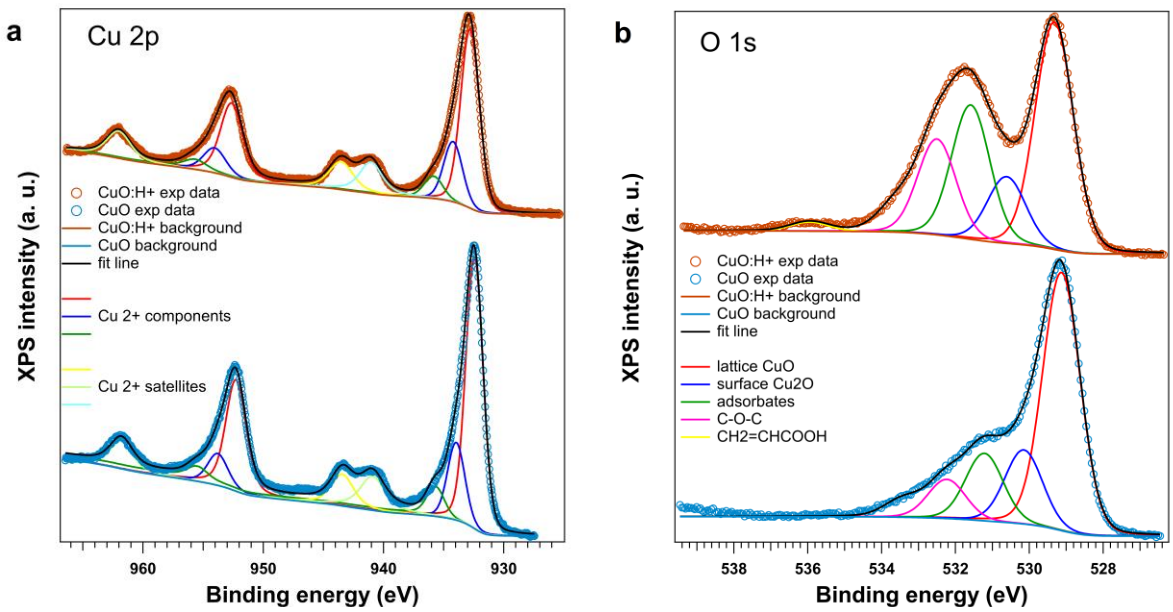

Fig.3. XPS narrow spectra of CuO as deposited and irradiated with proton beam CuO: H+ for a) Cu 2p line and b) O 1s line

Table 1. Sheet resistance of CuO samples

Sample	Sheet resistance [Ω/□]
CuO as deposited	$8.18 \times 10^5 \pm 196$
CuO irradiated	$1.00 \times 10^6 \pm 389$
CuO# as deposited	$9.04 \times 10^7 \pm 2.27 \times 10^5$
CuO# Cr (10 keV 3×10^{14})	$9.24 \times 10^7 \pm 6.00 \times 10^5$
CuO# Cr annealed	$1.41 \times 10^7 \pm 1.99 \times 10^5$
CuO# Cr annealed irradiated	$5.57 \times 10^7 \pm 4.87 \times 10^5$

Electrical properties were characterised by measuring the sheet resistance of the films. The results are presented in Table 1. Each measurement was repeated for 10 times in three different points on a sample. The irradiation increased sheet resistance of CuO film by around 20%. This is expected effect as irradiation should introduce defects to the film. The CuO# samples have much higher resistance which proves that heating of the substrate during deposition is a crucial aspect to achieve highly conductive films. Ion implantation of this film increased the resistance of this CuO film by around 3%, annealing caused decrease of resistance by around 85%, and then proton irradiation again increased the resistance approximately three times. It is expected that ion implantation decreases conductivity by introducing defects, and subsequent annealing should restore the crystal structure and activate the dopant, restoring the electrical conductivity as well [7].

The CuO# samples were characterised by mapping measurements using spectroscopic ellipsometry. The parameter presented on the maps (Figures 5 – 8) is the pseudo refractive index parameter $\langle n \rangle$ which is defined in Equations 1 and 2 [10].

To prove that doping with implantation was successful and introduced Cr into the CuO film a measurement with Secondary Neutral Mass Spectroscopy was performed at Institute for Nuclear Research in Hungary. A sample of 130 nm thickness deposited on Si and implanted with 15 keV energy and 5×10^{16} cm^{-2} dose of Cr ions was studied with this method. The resulting elemental distribution is presented in Figure 4. There is clearly visible Cr presence with a peak of Cr atoms amount at around 30 nm in depth.

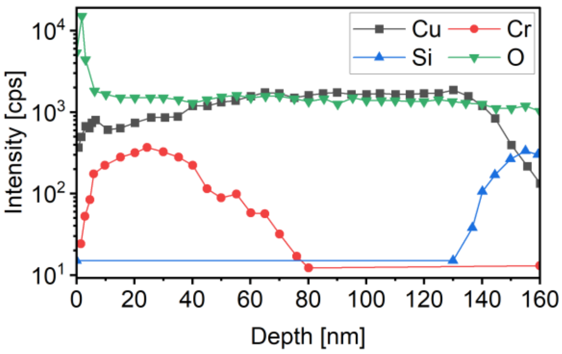

Fig.4. Secondary Neutral Mass Spectroscopy distribution of Cu, Si, Cr and O.

(1) $$\langle \tilde{n} \rangle^2 = (\langle n \rangle + i \langle k \rangle)^2 = \sin\varphi^2 \cdot \left[1 + \tan\varphi^2 \cdot \left(\frac{1-\rho}{1+\rho}\right)^2\right]$$

(2) $$\rho = \tan\Psi \cdot e^{i\Delta}$$

where $\tilde{n}$ – complex refractive index, n – refractive index, k - extinction coefficient, φ – angle of incidence, Ψ – amplitude ratio, and Δ – phase difference of polarised light [10]. The pseudo refractive index was calculated for wavelength of 333 nm.

The map of the as-deposited film (Fig. 5) shows uniformity, with exception of two points. The implanted sample has better homogeneity (Fig. 6). The value of pseudo refractive index is similar for these two samples. The sample after annealing (Fig. 7) exhibits comparable homogeneity but a higher value of the parameter, which indicates strong changes on the material after annealing. The sample after proton irradiation (Fig. 8)shows a strong gradient of $\langle n \rangle$ value, it seems that irradiation had profound influence on the implanted CuO film.

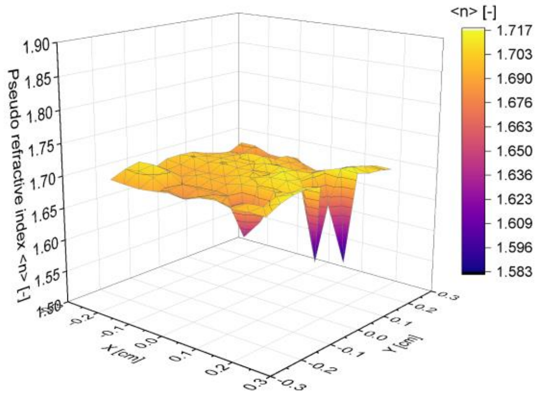

Fig. 5. Pseudo refractive index map for as deposited samples CuO#.

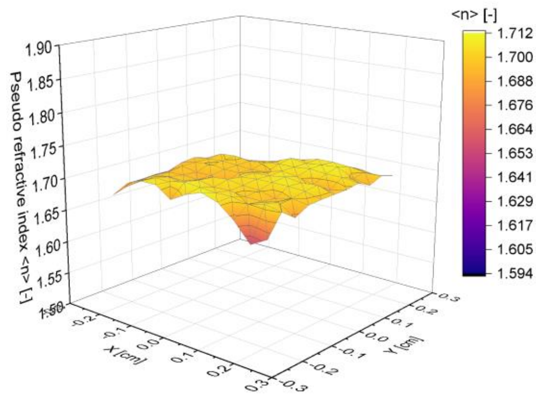

Fig. 6. Pseudo refractive index map for as deposited samples CuO# implanted with Cr ions of 10 keV energy and 3×10^{15} cm^{-2} dose.

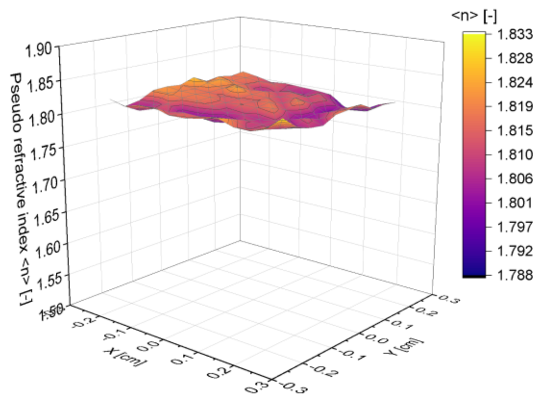

Fig. 7. Pseudo refractive index map for as deposited samples CuO# implanted with Cr ions and then annealed in air at 400°C for 6 hours.

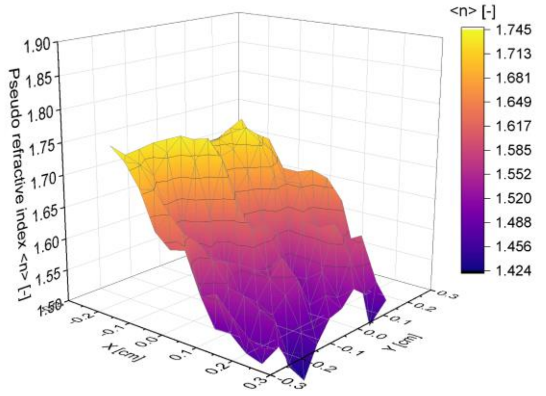

Fig. 8. Pseudo refractive index map for as deposited samples CuO# implanted with Cr ions, annealed and irradiated with protons.

Conclusions

Irradiation with protons at an energy of 226.5 MeV had a slight effect on the properties of the thin CuO layer. The crystal structure remained unchanged, while the surface resistance of CuO increased by approximately 20%. XPS analysis revealed that the surface of the irradiated sample exhibited a higher presence of adsorbates. Additionally, light absorption for low energies decreased for both the CuO layers and the implanted sample. Ion implantation reduced the layer's conductivity, while annealing increased it; irradiation also caused a reduction in conductivity. Although all samples displayed similar uniformity on pseudo refractive index $<n>$ maps, the implanted sample after irradiation showed a gradient in values.

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***Authors**: mgr inż. Katarzyna Ungeheuer, AGH University of Krakow, Faculty of Computer Science, Electronics and Telecommunications, Institute of Electronics, Mickiewicza ave. 30, 30-059 Kraków, e-mail: ungeheue@agh.edu.pl; dr. Amelia Elena Bocirnea, National Institute of Materials Physics, Atomistilor str. 405 A, Bucharest-Magurele, Romania, e-mail: amelia.bocirnea@infim.ro; mgr inż. Denis Alexander Pikulski, AGH Universiy of Krakow, Faculty of Metal Engineering and Industrial Computer Science, Mickiewicza ave. 30, 30-059 Kraków, e-mail: dapikulski@agh.edu.pl; dr hab. inż. prof. AGH, Konstanty Waldemar Marszałek, AGH University of Krakow, Faculty of Computer Science, Electronics and Telecommunications, Institute of Electronics, Mickiewicza ave. 30, 30-059 Kraków, e-mail: marszel@agh.edu.pl; dr. Aurelian Catalin Galca, National Institute of Materials Physics, Atomistilor str. 405 A, Bucharest-Magurele, Romania, e-mail: ac_galca@infim.ro; dr inż. Juliusz Chojenka, The Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences, Radzikowskiego str. 152, 31-342 Kraków, e-mail: juliusz.chojenka@ifj.edu.pl; dr. Tamás Fodor, HUN-REN Institute for Nuclear Research, Bem square 18/c, 4026 Debrecen, Hungary, e-mail: fodor.tamas@atomki.mta.hu; dr. Kálmán Vad, HUN-REN Institute for Nuclear Research, Bem square 18/c, 4026 Debrecen, Hungary, e-mail: vad.kalman@atomki.mta.hu*

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