JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics

FINAL REPORT ON THE START PROGRAMME

Influence of the thermal treatment and irradiation on CuO nanostructured samples for photovoltaic applications

Supervisor:
Dr. Aleksandr Sergeyevich Doroshkevich

Student:
M. Sc. Silvia María Fortuné Fábregas, Cuba
University of Havana

Participation period:
July 09 – September 02,
Summer Session 2023

Dubna, 2023

Abstract

The characterization of the copper (II) oxide (CuO) samples is a key point in the development of a photovoltaic device based on CuO nanostructures with a novel architecture and by low cost techniques. The CuO layer plays an important role because is the support and the absorbent material of the solar radiation in the solar cell. This layer will be on a novel device with an inverted and a branched architecture based on elongated CuO nanostructures. The obtained nanostructures already were studied by SEM, Raman and IR spectroscopy. To investigate the structure, thermal history and defects; X-rays Diffraction (XRD), Differential Scanning Calorimetry (DSC) and Positron Annihilation by Doppler Broadening Spectroscopy (PAS-DBS) were used. The results indicate the presence of a recrystallization process in the CuO nanostructured layers modified by a sequential thermal treatment and the recovering of the CuO layers after the irradiation procedure.

Content

1. Introduction

The relevance of the study. The solar cells can be classified in three different types or generations according to the absorbent materials, the dimensions, the synthesis techniques and the designs. The first generation is formed by the silicon solar cells, the second by the thin film solar cells and the third type by the emergent or nanostructured solar cells. In fact, now a days, the photovoltaic devices with higher efficiency are the silicon solar cells. The thin film solar cells use less raw materials than silicon solar cells and other materials. Among the nanostructured solar cells are the most promising devices because allows the use of even less material and a great variety of architectures, materials, synthesis techniques with a lower cost than its predecessors. Furthermore, this new devices shows efficiency records at a higher rate than the other types of solar cells. The nanostructured solar cells have a great potential due to the use of quantum effects, radial junctions, novel designs and materials flexibility that allows a reduction in the inversion and production costs. In this research, we are aiming for the use of non-toxic, abundant and stable materials easy to obtain by low cost techniques in a novel architecture based on copper (II) oxide (CuO). The use of an excellent absorber of the solar radiation and a sustainable material as the CuO in elongated nanostructures, allow us to improve the absorption of the radiation, reduce the reflection loses and increase the carriers transport by a radial junction. This approach is excellent for defect rich materials like CuO. The improvement of the electric and optic characteristics of the absorber material is crucial because this material define the photophysics and transport properties of the device [1], for that reason its modification by annealing or irradiation is very important during the fabrication process. The standard thermal treatment of CuO nanostructured layers was already studied [2–5], but in this research the heat treatment will be sequential and an irradiation procedure will be studied, in order to study the structural changes that take place in the CuO layer leading to its recrystallization.

In this research was performed a study about the influence of the sequential thermal treatment (STT) and the irradiation in nanostructured samples for photovoltaic applications.

The scientific tasks are:

1. study of the temperature influence of on the samples structure
2. study of the irradiation influence of on the samples structure

3. analyze the defects formation and evolution in the thermally treated CuO layers
4. understand the thermodynamic behavior of the CuO samples
5. study the origin of the recrystallization process that affects the CuO layer

In order to perform the previous scientific tasks, thermodynamic, structural and spectral characterizations techniques will be used to study the influence of the temperature and the irradiation in the nanostructured CuO layer.

Degree of knowledge of the problem. The CuO is part of the family of copper oxides, a group of well-known sustainable p-type semiconductors. This semiconductor material has gain more attention in this recent years due to its magnetic, catalytic and optics properties on supercapacitors, sensors, catalyzers, arsenic removal and solar cells [6]. In the literature exist a variety of studies of the CuO heat treatment [2–5], but the recrystallization process is not a common behavior of the nanostructured CuO layer. The modification of the CuO layer by the temperature is very important because this semiconductor layer will be on a low cost solar cell. Besides, the CuO layer structural properties could be enhanced with a controlled irradiation without damaging its lattice.

The aim of the study is to investigate the structural changes that takes place in the CuO layer under thermal treatment and under irradiation.

In order to accomplish this study the CuO samples were treated with two different routes with a sequentially thermal treatment (STT) and with irradiation.

The object of the study are the CuO samples with a sequential thermal treatment and the CuO irradiated samples. The samples were modified by two different routes thermally treated from 200 to 500 °C and another samples were irradiated from $3.13 \cdot 10^{13}$ to $3.38 \cdot 10^{17}$ part/cm^2.

Research methods or characterization techniques the characterizations techniques used to study the influence of the temperature on the CuO nanostructured layer are X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and Positron Annihilation Spectroscopy (PAS).

Practical significance of the research results. The results will be used in the fabrication of a nanostructured solar cell based on CuO elongated nanostructures by low cost methods.

2. Methods

In this section will be presented the CuO nanostructured layers synthesis, modification by thermal treatment and the irradiation procedure. Besides, will be provided a brief description of the characterization techniques that will be used in this research.

2.1. Synthesis of CuO thermally treated samples

2.1.1. CuO nanostructures seeding process

The CuO nanostructures were grown on soda lime glass substrates, properly cleaned using ultrasonic baths with ethanol (10 minutes), 1M of KOH (10 minutes) and distilled water (20 minutes) [7], respectively. Previous to the nanostructure growing, a seeding process was followed. First, some drops of precursor solution of 5 mM of copper (II) acetate ($CuAc_2$) in ethanol was deposited on the substrate surface and then, a thin layer of it was formed applying the spin-coating method (s-CuO samples). The spin-coating, consist in rotating the solution-covered substrate at 2000 rpm, during 20 seconds and repeat the process 4 times. Then the samples were annealed in air at 250 °C for 30 minutes to form the CuO seeds layer from the $CuAc_2$ decomposition.

2.1.2. CuO elongated nanostructures synthesis

The CuO nanostructures were grown by Chemical Bath Deposition (CBD) placing the CuO seeded substrate upside down in an equimolar aqueous solution of 25 mM of copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Merck GR for analysis) and hexamethylenetetramine (HMT, Sigma-Aldrich ACS reagent grade ≥ 99.0 %). The samples were afterwards heated at 90 °C for 4 hours. The resulting nanostructures were thoroughly rinsed with distilled water and ethanol, and dried using a nitrogen stream [8].

2.1.3. CuO nanostructures thermal treatment

The previous samples were selected for a cumulative thermal treatment from 200 to 500 °C in air during 1 hour in each cycle. To perform this, the as grown samples are introduced in the oven and taken at 200 °C during 1 hour after which one sample is retired. This sample is labeled 200 °C. The rest are kept in the oven and taken into 300 °C for another hour after which a second sample labeled 200 + 300 °C is extracted. The process is repeated until the last sample has received the 4 thermal treatments 200, 300, 400 and 500 °C (Figure 1). This cumulative process would increase the crystalline quality of the samples in a continuous process.

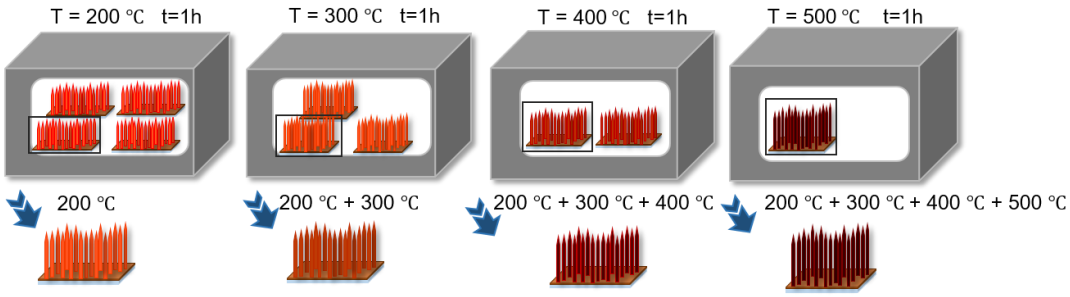

Figure 1: CuO sequential thermal treatment process.

2.2. Irradiation of the CuO samples

Ion irradiation is the implantation of high speed energetic particles on the surface of an object according to the incident particle energy. The irradiation objective is to produce the alteration of structural, optic, mechanical, electrical, magnetic and thermal properties of the material. This technique can be used to enhance the nanostructures properties, contrary to the common belief that irradiation only destroys the material lattice producing its amorphization [9].

The CuO samples obtained by spin coating were irradiated with $^{+}$He particles. The accelerator was operated with an energy of 1.0 MeV and a current of 0.5 μA. The CuO as grown sample was placed on the Aluminum sample holder and then, into a steal 316l irradiation chamber (Figure 2). After the irradiation, 5 samples were produced, those samples have different irradiation doses from 3.13 $\cdot 10^{13}$ to 3.38$\cdot 10^{17}$ part/cm^2 (Table 1). Those samples were studied by DSC and XRD to investigate the structural changes that take place in the CuO layer and compared it with the thermal treatment results.

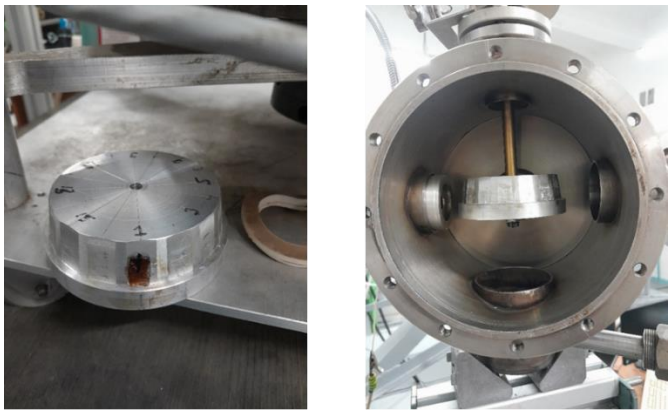

Figure 2: Sample holder and irradiation chamber at the EG-5 laboratory.

Sample name	Doses (part/cm^2)	time (s)
CuO reference	0	0
CuO_10	$3.13 \cdot 10^{13}$	10
CuO_100	$3.13 \cdot 10^{14}$	100
CuO_1000	$3.13 \cdot 10^{15}$	1000
CuO_5000	$3.13 \cdot 10^{16}$	5000
CuO_3h	$3.38 \cdot 10^{17}$	10 800

Table 1: Irradiated samples parameters.

2.3. X-Rays Diffraction (XRD)

X ray diffraction is a versatile and not destructive characterization technique to study the crystalline structure of materials. This technique allows identify phase, structures and preferential orientation. XRD also provide information about the crystallite size and the lattice stress. The diffraction pattern is obtained if the diffracted beam by the crystalline planes of the sample satisfies the Bragg's Law:

$$n\lambda = 2\, d\, sin\, \theta$$

Where n is an integer known as the order of reflection, d the interplanar distance, θ the angle of incidence and λ the wavelength of the X-ray incident beam. The diffraction pattern is the graphical representation of counts on the detector and the diffraction angle. The most important components in a diffraction pattern are the maximum position expressed byθ, 2θ, d, $1/d$ and the maximums intensity and its profile.

The maximums position is established by the planes (*hkl*, Miller indexes) that satisfies the Bragg's Law. This component allow the calculation of the unit cell dimensions. The position depends of the radiation wavelength, instrumental factors, sample alignment and axial divergence of the beam.

The intensity is a function of the periodicity of the scattering centers. Through the intensity of the diffraction maximums the atomic parameters and the preferential orientation of the crystalline planes of the sample can be obtained. The intensity depends of the temperature (because the atoms aren't fixed in the lattice), polarization, absorption (attenuation while the radiation travels through the sample) and the structure (unit cell content) of the unit cell.

The shape of the maximums is represented by the peak-shape function. The peak shape function depends on crystalline structure and the convolution of different functions. This parameter depends of the monochromaticity, the beam divergence and slit width. Moreover, this parameter is

influenced by the specimen microstructure (crystallinity, disorder and defects). For that reason is possible to calculate the crystallite size and study the microstrains [10].

The XRD patterns were obtained with an X-ray diffractometer PAN analytical EMPYREAN using Co $K\alpha$ λ = 1.78892 nm (40 mA, 40 kV) in the Joint Institute of Nuclear Research (JINR) in Dubna, Russian Federation.

2.4. Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) is the most used thermal method due to its simplicity, availability and rapidity. In this technique the sample and the reference are placed in special containers on the measurement equipment. The heaters rise the temperature at a determined rate, or keep the sample at a fixed temperature. The DSC measures the energy differences and is a quantitative technique [11]. The DSC measurements can be performed according to three different instruments types, DSC compensated power, DSC heat flux and DSC modulated instruments. The measurements were performed using a DSC heat flux. A DSC heat flux is an instrument that measures the heat flux difference between the sample and the reference, while the sample temperature is constantly changing. In DSC by heat flux the total heat flux $\frac{dH}{dt}$ is

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)$$

Where H is the enthalpy in $J\ mol^{-1}$, C_p is the specific heat capacity per *mol* in $J\ K^{-1}mol^{-1}$ and $f(T, t)$ in the sample kinetic response in $J\ mol^{-1}$. Then, the heat flux is the contribution of the specific heat capacity term and the kinetic response. In DSC when the heat flux increases the kinetic process is exothermic and a reduction in the flux indicate an endothermic process [11].

The DSC measurements were carry out in the JINR with a DSC NETZSCH DSC 204F1 Phoenix type DSC heat flux. The heating rate was 10 °C/min from 26-600 °C and the sample weight was 38 mg.

2.5. Positron Annihilation by Doppler Broadening Spectroscopy (PAS-DBS)

Positron Annihilation Spectroscopy (PAS) is a characterization technique based on the change in the energy of the annihilation gamma quantum. This technique is the only one that can identify atomic size vacancies and to characterizes its sizes, structure and concentration with a high degree of sensitivity (10^{-7}). Besides, this technique is not destructive or unlike XRD, sensitive to local

variations of the lattice constant. PAS is unique because makes possible to monitoring the defect formation and evolution in samples with a resolution that cannot be achieved with TEM (Transmission Electron Microscopy) [12].

The positron was predicted in 1928 by Paul Dirac and discovered four years later by Carl David Anderson in a cloud chamber. As an antiparticle, when a positron interacts with an electron, they annihilate each other emitting mostly two photons in opposite directions. Those photons can provide valuable information about the electron density and states at the annihilation site through the time, energy and angular spectra of the annihilation radiation. Considering the previous information exist three types of PAS: Positron Annihilation Lifetime Spectroscopy (PALS), Doppler Broadening Spectroscopy (DBS) and Angular Correlation of Annihilation Radiation (ACAR). In this research will be used DBS to detect vacancies and vacancies clusters.

The annihilation event at a defect produces a narrower spectrum at the 511 keV line in comparison with the annihilation of the positron with electron in the ideal structure. DBS uses a high energy resolution detector of high purity Germanium (Ge) detector (HPGe) to measure the energy of annihilation and record the 511 keV peak spectrum. Exist two main parameters in PAS, the line shape parameters S ad W. The parameter S by the Shape of the peak and W by Wing of the peak are known as the defect parameters and are used to characterize the peak (Figure 3). The parameter S indicate the positron annihilation fraction with low momentum valence electrons, this means that an increase in S suggest a rise in the amount of defects of this type. The other parameter W, designate the positron annihilation fraction with core electrons.

The technique DBS does not provide direct information about the size of defects. Besides, qualitative information about the change in defect structure can be predicted from the S-W graph [13].

The PAS measurements were obtained at the JINR with a high purity Germanium detector with a resolution of approximately 1.2 keV.

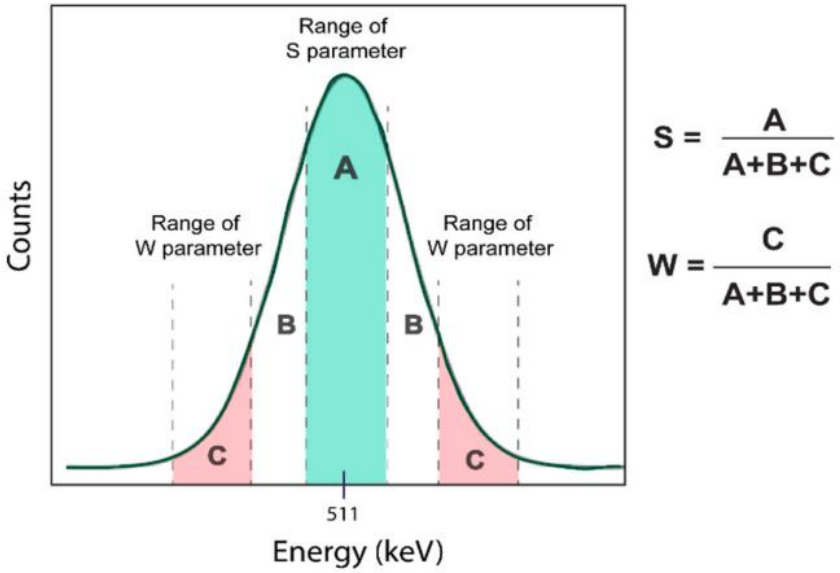

Figure 3: Definition of defect parameters S and W extracted from the 511 keV annihilation peak Image from [13].

3. Results

In this section will be presented the results and discussions about the thermodynamic, structural and spectral information extracted from the characterizations techniques described previously.

3.1. CuO thermally treated samples

X-Rays Diffraction

The diffractograms in Figure 4 confirm that the CuO samples with a sequential thermal treatment (STT) have a monoclinic structure type tenorite (PDF-2 2022 98-008-7124) [14]. The CuO nanostructured samples have a preferential orientation along the [001] direction. The (111) maximum shows an increase in its intensity starting at the reference sample until the sample with the thermal treatments at 200 and 300 °C (CuO 200+300 °C). Then, that maximum's intensity starts to decrease until the last sample. The relative intensity of the (002) maximum presents variations that could suggest a recrystallization process on the CuO nanostructured layer (Table 2).

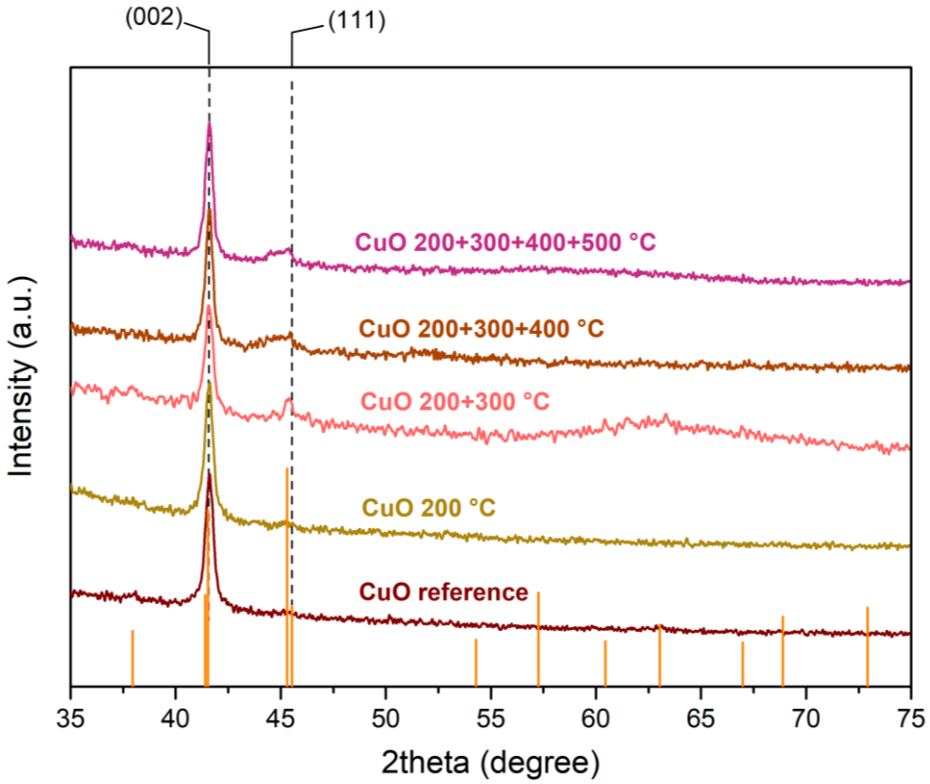

Figure 4: XRD patterns of CuO thermally treated samples.

Samples	Relative intensities (111)/(002)
CuO reference	0.197
CuO 200 °C	0.205
CuO 200+300 °C	0.432
CuO 200+300+400 °C	0.287
CuO 200+300+400+500 °C	0.269

Table 2: Relative intensity of maximum (002) at samples thermally treated.

The interplanar distance related to (002) plane (d_{002}) shows an interesting variation that supports the recrystallization hypothesis. The transition from the reference sample to the sample treated at 200 °C and the transition from CuO 200+300 °C to CuO 200+300+400 °C indicate a compression process in the CuO layer lattice. The other segments of the graph suggest an expansion process. The reason of this transitions must be the growth of bigger grains at expenses of the smaller ones, a recrystallization process.

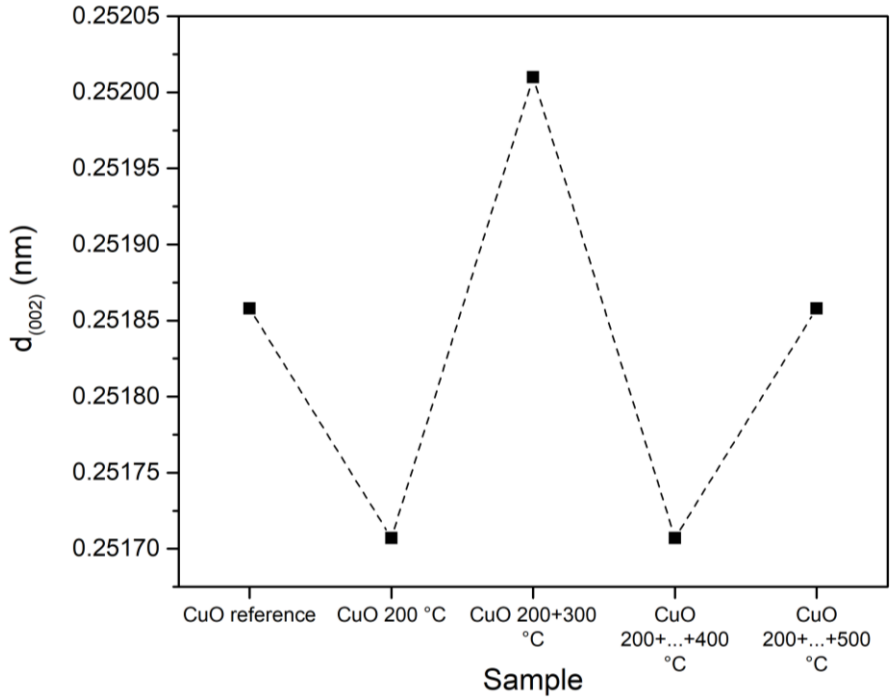

Figure 5: Interplanar distance at (002) (d_{002}) plane at different samples thermally treated.

In the Figure 5 the interplanar distance of the (002) plane for each sample doesn't show a remarkable deviation from the CuO reference interplanar distance value.

Differential Scanning Calorimetry

The DSC analysis presents the heating curve of the CuO reference sample from 26 to 600 °C. This graph indicate a weight loss around 350 °C. The reason of this loss could be a decomposition of $Cu_2(OH)_2CO_3$ [15]. The other event is around the 550 °C until 600 °C and could be related to the CuO nanostructures melting. Therefore, the temperature of the heat treatments must be kept under 600 °C to avoid damage to the CuO nanostructured thin layer.

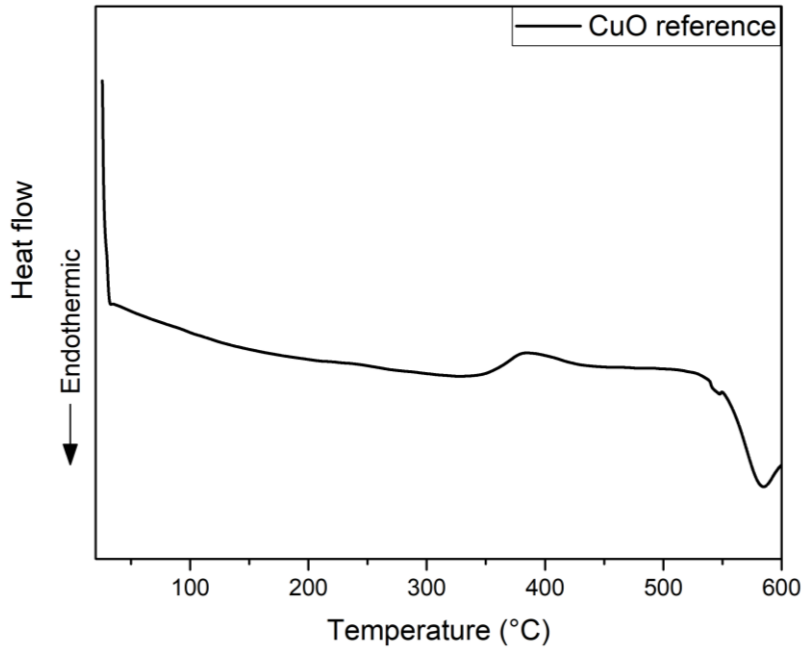

Figure 6: DSC curve for CuO as grown nanostructures.

Positron Annihilation by Doppler Broadening Spectroscopy

The S parameter in the PAS represents a fraction of positrons annihilating with low momentum valence electrons and vacancy type defects with their concentration. The S parameter decreases at 4 keV for the sample CuO reference and at 7 keV for CuO sample treated until 500 °C and then increases. This increase could suggest the presence of a different defect mechanism in those samples. The CuO nanostructured samples treated at 200 °C and until 400 °C show a decrease in the parameter S with the positrons penetration into the CuO layer. This is due to the introduction of interstitial O that compensates the Cu^{2+} in the CuO lattice, leading to the reduction of S. In the range 10-15 keV the samples treated until 300 and 400 °C shows a slight decrease in the parameter S. This could suggest the presence of a recrystallization process on those samples.

Apparently during recrystallization the Cu small vacancies combine to create vacancy clusters on the grain boundaries. Below 500 °C the positrons annihilates in simple vacancies and then in vacancy clusters.

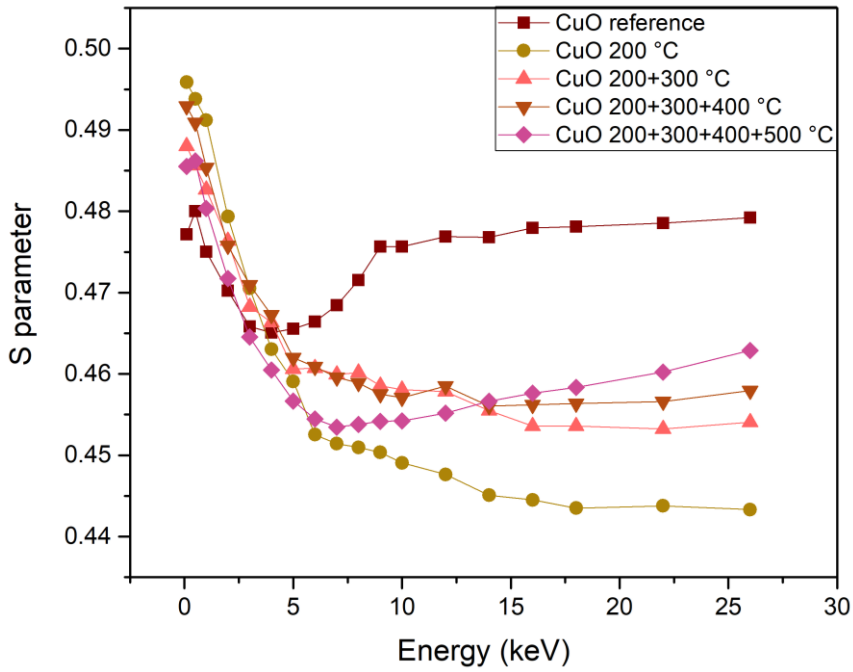

Figure 7: Dependence of the measured S parameter on the positron energy for the reference sample and the thermally treated samples.

3.2. Irradiated samples results

X-Rays Diffraction

The XRD of the CuO irradiated samples confirm that the CuO nanostructured layer still have a monoclinic structure. The layers also present a preferential orientation along [001] direction (Figure 8). The diffraction maximum at (111)(200) disappears when the CuO sample is irradiated during 5000 seconds.

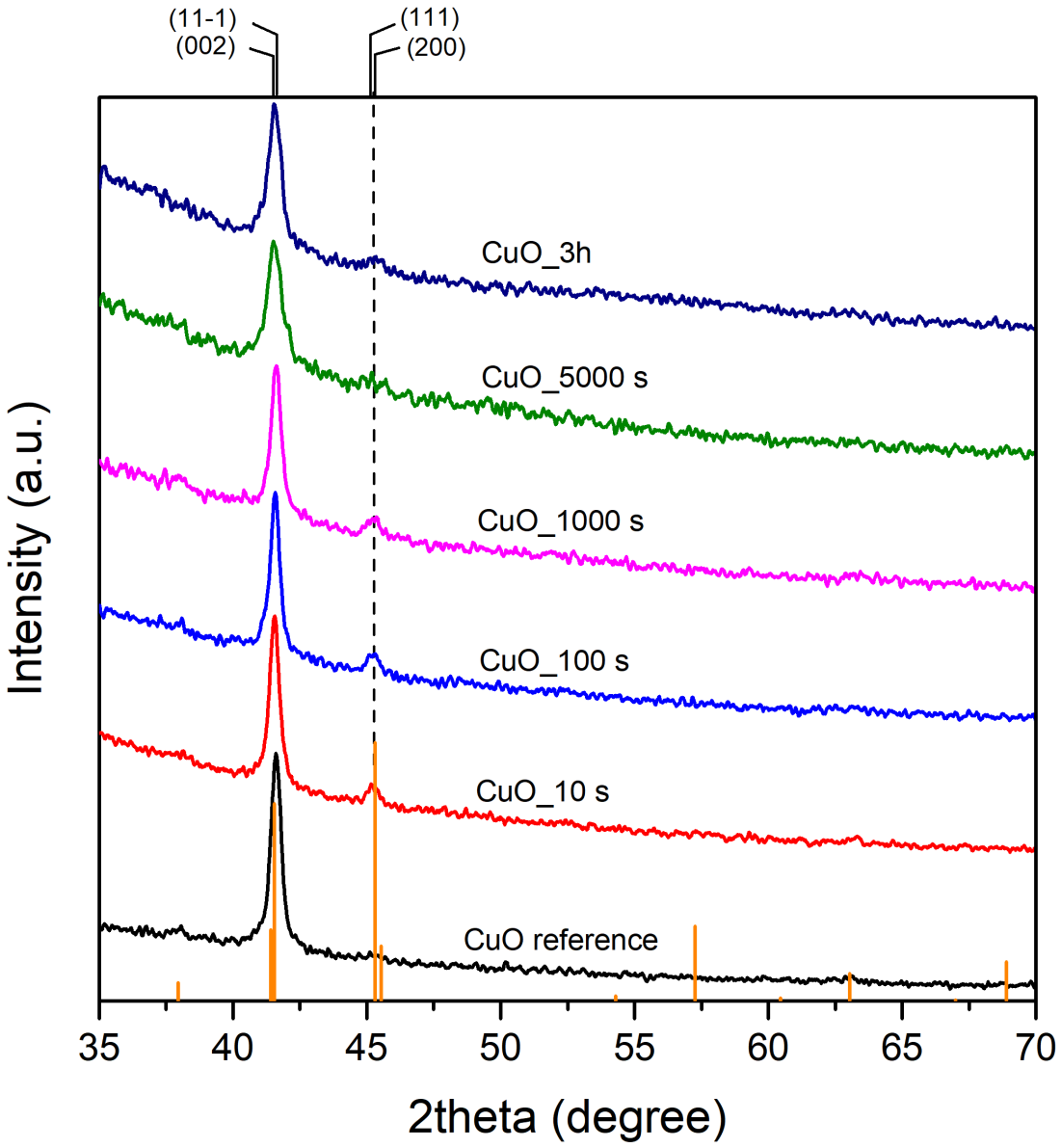

Figure 8: XRD patterns of CuO irradiated samples.

At the beginning was suggested that the decrease in intensity is related with the sample size decrease, but the last sample CuO_3h shows an increase on its intensity in comparison with previous samples. Therefore, the (002) peaks intensity changes are not related to the samples size, if not to the irradiation influence on the CuO layer. Moreover, the Full Width at Half Maximum (FWHM) at (002) shows an initial decrease and then at CuO sample irradiated during 1000 s increase it value suggesting a rearrangement of the CuO layer lattice after the irradiation procedure.

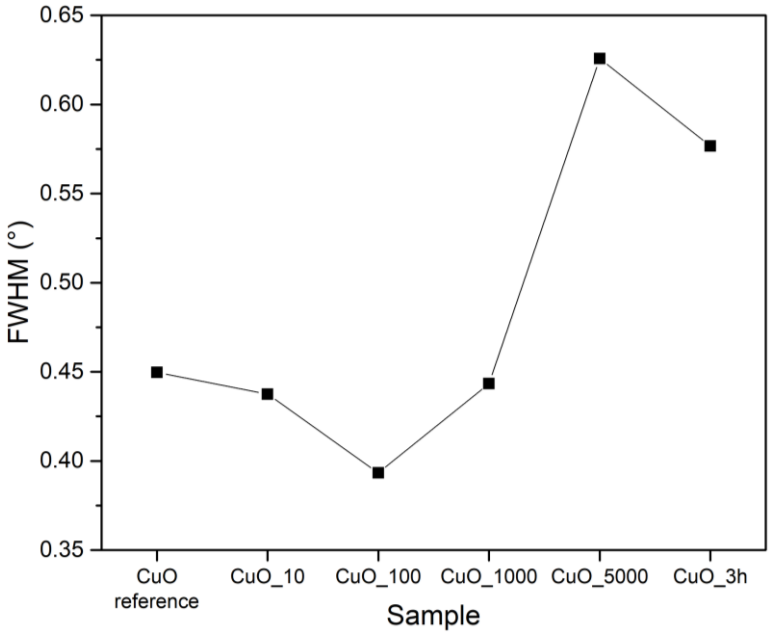

Figure 9: Full Width at Half Maximum (FWHM) at the (002) peak of CuO irradiated samples.

The red line represent the 2theta shifts of each sample in comparison to the CuO reference sample. The Figure 10a shows that from the sample irradiated during 10 s (CuO_10s) to the irradiated until 1000 s (CuO_1000s) the (002) maximum shows a right shift. This right shift indicate that in the sample lattice is taken place a compression. From sample CuO_1000s to CuO_5000s the sample lattice expands. This results may support the hypothesis of the CuO layer recovering after the irradiation treatment.

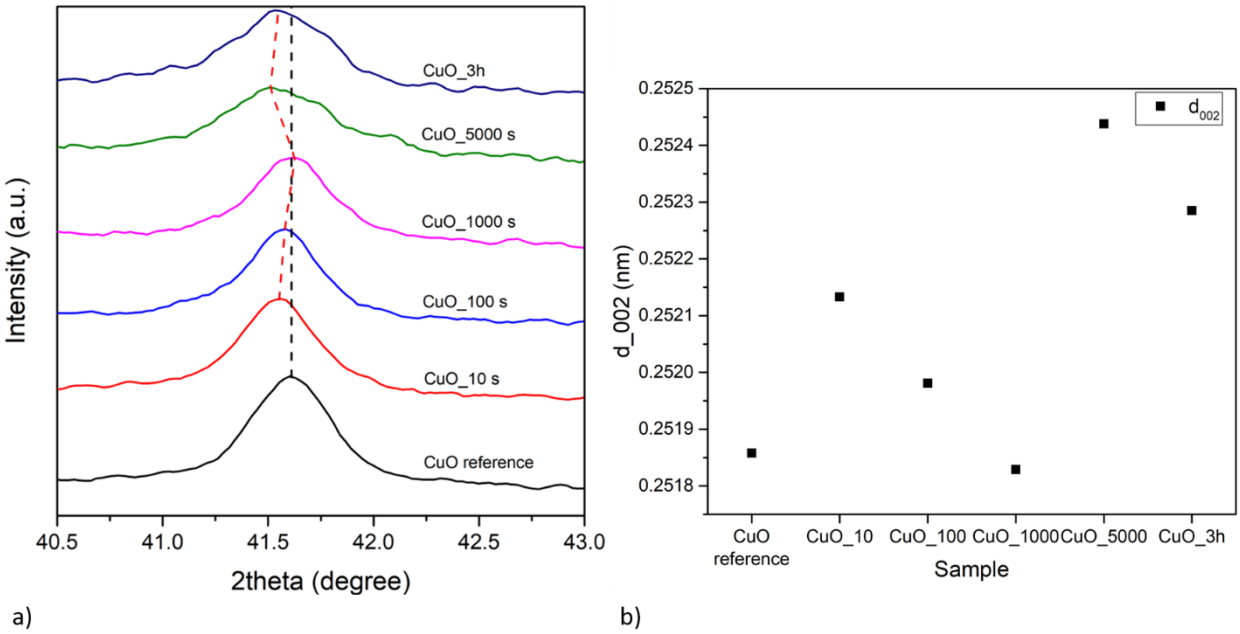

Figure 10: Normalized diffractograms of the (002) peaks for CuO irradiated nanostructured layers at different doses (a) and interplanar distance of each irradiated sample (b).

Differential Scanning Calorimetry

The DSC study shows the heating curve of the CuO irradiated sample from 26 to 600 °C. After the irradiation the sample doesn't presents the previous weight loss, but the endothermic event near 550 °C is still present.

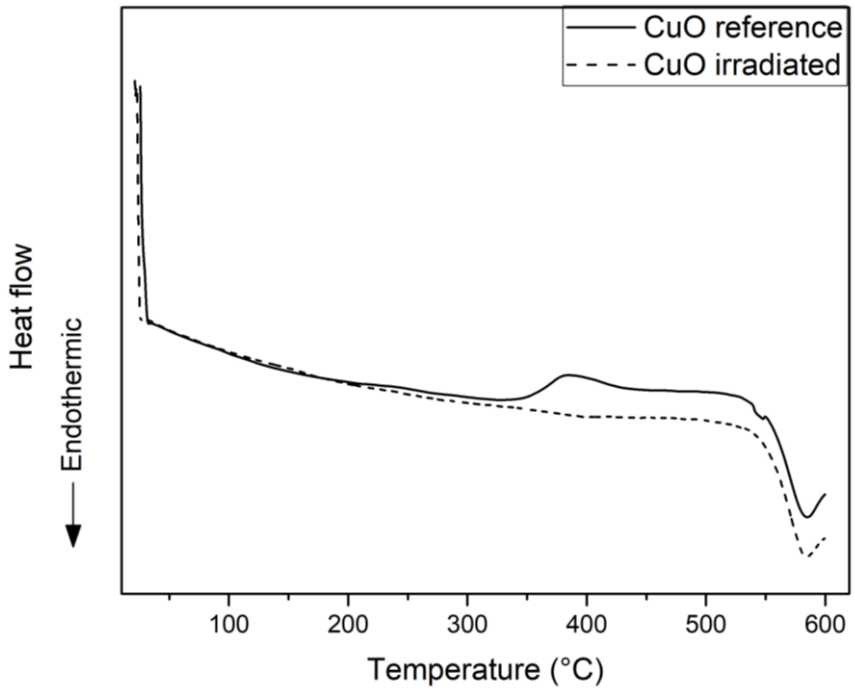

Figure 11: DSC curve for CuO as grown and irradiated CuO nanostructures.

4. Conclusions

The modification of CuO nanostructured layers by a sequential thermal treatment and by irradiation was studied in this Report. The first modification route was the heat treatment that induce a recrystallization process in the CuO nanostructured layers. The irradiation of the CuO layer produce remarkable structural changes without damage the CuO lattice. Besides, the irradiation results suggest that the CuO layers could recover from irradiation after certain doses. This is an important result, because suggest that the CuO can be irradiated without damage risk to enhance some of its properties.

5. Recommendations

Considering the previous results we propose this recommendations for future studies about CuO modification for photovoltaic applications:

- Defects analysis of CuO irradiated samples
- Electric studies of CuO irradiated samples
- Compositional analysis of CuO irradiated samples
- Morphological study of CuO irradiated samples by scanning electron microscopy (SEM)

6. References

[1] B.K. Meyer, A. Polity, D. Reppin, M. Becker, P. Hering, P.J. Klar, T. Sander, C. Reindl, J. Benz, M. Eickhoff, C. Heiliger, M. Heinemann, J. Blasing, A. Krost, S. Shokovets, C. Muller, C. Ronning, Binary copper oxide semiconductors: From materials towards devices, Phisica Status Solidi (B). 23 (2012) 1487–1509.

[2] Q. Zhang, K. Zhang, D. Xu, G. Yang, H. Huang, F. Nie, C. Liu, S. Yang, CuO nanostructures: Synthesis, characterization, growth mechanisms, fundamental properties and applications, Progress in Materials Science. 60 (2014) 208–337.

[3] T.H. Tran, V.T. Nguyen, Copper oxide nanomaterials prepared by solution methods, some properties, and potential applications : a brief review, International Scholarly Research Notices. 2014 (2014) 14.

[4] A.S. Zoolfakar, A. Rani, A.J. Morfa, A.P. O'Mullane, K. Kalantar-zadeh, Nanostructured copper oxide semiconductors: a perspective on materials, synthesis methods and applications, Journal of Materials Chemistry C. 2 (2014) 5247–5270.

[5] P. Sawicka-Chudy, E. Rybak-Wilusz, M. Cholewa, Review of the development of copper oxides with titanium dioxide thin-film solar cells, AIP Advances. 10 (2020) 010701-1–16.

[6] Y. Bin Zhang, J. Yin, L. Li, L.X. Zhang, L.J. Bie, Enhanced ethanol gas-sensing properties of flower-like p-CuO/n-ZnO heterojunction nanorods, Sensors and Actuators, B: Chemical. 202 (2014) 500–507.

[7] K.D. Malviya, H. Dotan, K.R. Yoon, I.-D. Kim, A. Rothschild, Rigorous substrate cleaning process for reproducible thin film hematite (α-Fe2O3) photoanodes, Journal of Materials Research. 31 (2016) 1565–1573.

[8] F. Wu, Q. Qiao, B. Bahrami, K. Chen, R. Pathak, Y. Tong, X. Li, T. Zhang, R. Jian, Solution-processed all-oxide bulk heterojunction solar cells based on CuO nanaorod array

and TiO2 nanocrystals, Nanotechnology. 29 (2018) 215403.

[9] R.M. Obodo, M. Asjadb, A.C. Nwanya, I. Ahmad, T. Zhaoc, A.B.C. Ekwealora, M. Maaza, F.I. Ezemaa, Evaluation of 8.0 MeV Carbon (C2+) irradiation effects on hydrothermally synthesized Co3O4-CuO-ZnO@GO electrodes for supercapacitor applications, Electroanalysis. 32 (2020) 2958--2968.

[10] V.K. Pecharsky, P.Y. Zavalij, Fundamentals of powder diffraction and structural characterization of materials, Segunda, Springer, 2008.

[11] D.A. Skoog, F.J. Holler, S.R. Crouch, Principios de análisis instrumental, Sexta, CENGAGE Learning, 2008.

[12] F.A. Selim, Positron annihilation spectroscopy of defects in nuclear and irradiated materials- a review, Materials Characterization. 174 (2021).

[13] F.A. Selim, Positron annihilation spectroscopy of defects in nuclear and irradiated materials- a review, Materials Characterization. 174 (2021) 110952.

[14] JCPDS - International Centre for Diffraction Data PCPDFWIN 2022 Chart 98-008-7124,.

[15] G. Zhu, H. Xu, Y. Xiao, Y. Liu, A. Yuan, X. Shen, Facile fabrication and enhanced sensing properties of hierarchically porous CuO architectures, ACS Applied Materials & Interfaces. 4 (2012) 744–751.

7. Acknowledgements

I want to thank to the organizers of the START Programme of the Joint Institute for Nuclear Research (JINR) for give me this opportunity. I want to acknowledge the hard work of Professor Dr. Aleksandr S. Doroshkevich, for receive me as a member of his research group, for its invitation and prepare all the conditions that made possible this Report during vacations time and the Cuban-Russian collaboration. I am very grateful of Phan Luong Tuan for its guidance and collaborative spirit even before my arrival to Dubna. I want to acknowledge the help of Luis Miguel Ledo Pereda, its attention and invaluable support as a mentor to me.

I want to recognize the all the colleagues I meet during my work at the EG-5 internship: the scientific team, the accelerator technical team, Dr. Samir Samadov, Dr. Tatiana Vershinina (FLNP), Dr. O. Ivanshina (FLNP). I also want to thank to all the scientific collaborators I meet here at the FLNP. I want to thank to Professor Otilia Culicov, Elena Karpova, Olga Reshetova and START Team for their attention. I also want to show gratitude to my beloved friend Unises Dumenigo at the International Relations Office of the University of Havana for her advice and

support. To Professor Edwin Pedrero, Professor Fernando Guzman and my supervisor Dr. Lidice Vaillant for their support.

I also want to express gratitude to the Cuban and Russian collaborators for the support and love I receive during my father illness and after his decease.