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LASER-ASSISTED COPPER OXIDATION

The paper proposes a method for copper sheet oxidation by using a laser beam. The thickness of the oxide layer increases with temperature growth; therefore, the proper parameters of the experiment such as pulse power, frequency and the speed of the beam were adjusted. High power diode laser was used in the investigations. The topography of the oxidised copper sheets was determined using atomic force microscopy (AFM) and scanning electron microscopy with EDS analyses. Optical parameters of the deposited layer were characterised by spectrophotometry. Both roughness and thickness of the investigated samples were measured using the confocal laser scanning microscope. The technological recommendations for the laser micro-machining technology to obtain copper sheet oxidation by using the high power laser beam were selected.

Keywords: Cu, CuO, Cu_2O, laser micro-processing

1. Introduction

Metal oxides are a wide group of materials used in chemistry [1], catalysis [2], sensors production [3], electronics [4] or photovoltaics [5,6]. Most promising oxides are inexpensive and easy to fabricate, such as copper oxide which occurs in two stable forms: cuprous oxide (Cu_2O) and cupric oxide (CuO). Both of these materials are p-type semiconductors with different bandgap energy which is 2.1 eV for Cu_2O and 1.2 eV for CuO [7]. What is more, Cu_2O crystallises in a cubic structure and appears as red colour solid, while CuO is a monoclinic crystal system and black colour powder. Nevertheless, due to the low price, lack of toxicity and easiness of manufacturing both materials are very popular in many industries. In photovoltaics, copper oxide is most often used to create a heterojunction solar cell. This means that its bandgap energy must be strictly defined to properly match the other elements of the junction [8-10]. Therefore, it is very crucial to control the parameters of the selected CuO_x production method, which may be thermal oxidation [11], magnetron sputtering [12], or ALD [13]. The use of a laser beam to obtain metal oxides [10,14] and a non-metal oxide [15] is also known. In this research, we suggest using a laser pulse to produce copper oxide in a fully controllable, fast, easy and inexpensive way. The advantage of this solution is the fact that copper oxide is located on a copper sheet, which can be used as a rear electrode in the production of a full photovoltaic structure.

2. Material for research and methodology

In this study, the initial material was a commercial electrolytic tough pitch (ETP) R220 copper metal foil with a thickness of 300 mm. The total area of each sample was 25±0.3 cm^2. Oxides were fabricated on copper foil by thermal oxidation using Rofin-Sinar Laser GmbH in ambient conditions.

The following investigations were performed in this work:

- Selection of laser treatment parameters using high power diode laser (HPDL). The trials of the laser processing were carried out using an experimental stand equipped with a mentioned laser having a rectangular beam with the top-hat intensity distribution in the slow-axis direction and a near Gaussian in the fast-axis direction.
- The topography of oxidised copper sheets was observed using:
  - the atomic force microscope (Park Systems XE 100) in the non-contact mode.
  - Zeiss Supra 35 scanning electron microscope (SEM)
- Microchemical analysis of chosen oxidised copper sheets was performed using the scanning electron microscope equipped with an energy dispersive X-ray (EDS) spectrometer.
- Both thickness and roughness of oxidised copper sheets were measured using Zeiss confocal laser scanning microscope 5 (CLSM). The profile of contact was determined based on three medium measurements.

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- Diffraction records were made on X-ray diffractometer produced by a Bruker D8 ADVANCE at using filtered Cu Kα radiation (λ = 0.154056 nm) at room temperature. Conditions records were as follows: voltage – 40 kV, current – 40 mA, angular range 2Θ – from 15° – up to 120°, step Δ2Θ – 0.05°, counting time – 3 s.

3. Selection of laser treatment parameters

Figure 1 presents a system for laser treatment of the investigated samples. Table 1 presents the general device data. To obtain the oxidised copper sheet, six batches of samples for testing were prepared by using laser micro-treatment (Table 2).

Fig. 1. Laser-treatment processing: a) a view of experimental stand equipped with a 2.0 kW continuous wave high power direct laser, b) ceramic table with deposited sample before the process, c) sample after the process (example)

TABLE 1

Technical specifications of HPDL laser source

Manufacturer	Rofin-Sinar Laser GmbH
Wavelength of the laser radiation, nm	808÷940±5
Maximum output power, W	2000
Range of laser power, W	100÷2000
Focal length, mm	82
Laser beam spot size, mm	1.5×6.6
Range of laser power intensity, W/mm^2	10.1÷202.0

TABLE 2

Conditions of laser processing testing samples (where: grey colour means samples selected for further investigations)

Sample number	Number of samples made in series	Laser beam [W]	Warm-up time [s]	Focal length [mm]
1	1	200	12	155
	2	400		
	3	800		
	4	1200		
2	1	1200	10	
3	1	1200	14	
4	1	800	20	
5	1	800	16	
	2		20	
6	1	800	17	

4. Results and discussion

Figure 2 presents the real image of samples after laser treatment. In case of samples no 1 and 6, oxidation of copper was obtained with the following parameters: laser power 1200 W (sample no. 1) and 800 W (sample no. 6) and warm-up times of 12 sec (sample no. 1) and 10 sec (sample no. 6). In the case of sample no. 2, the treatment was done on the part of its surface only.

Fig. 2. A view of experimental samples used during the laser process, where were applied the following no samples a) 1, b) 2, c) 6 (examples). The numbering of samples corresponds to the numbering provided in Table 2

P-type semiconductor properties were confirmed for all tasted samples by using a thermocouple. The thickness of the investigated copper oxide layers was determined by checking the height profile of the three-dimensional surface topography measured using the confocal laser scanning microscope (Fig. 2). It was found that the thickness of copper oxide layers was up to10 µm.

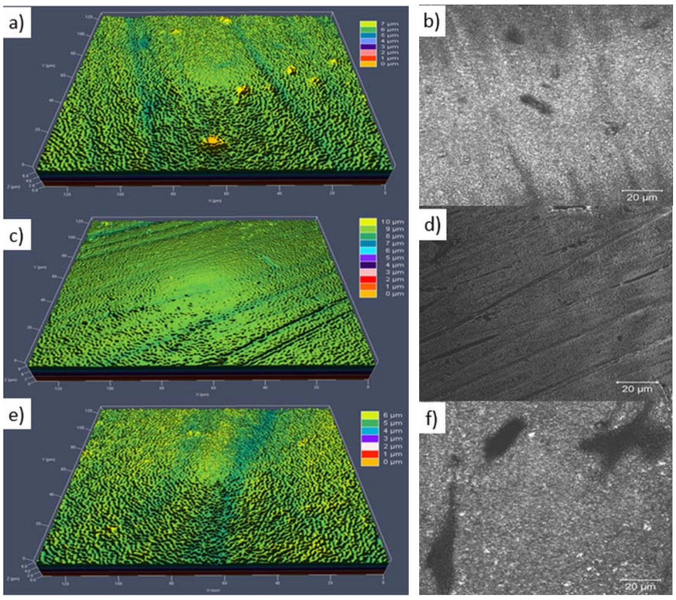

Fig. 3. Three- and two-dimensional surface topography (CLSM) of oxidised copper sheets: a, b) sample no. 1, b) sample no. 2 and c) sample no. 6 according to the numbering provided in Table 2

SEM micrographs of the obtained layers are shown in Figure 4. After laser treatment with the laser beam of 200 W and warm-up time 12 sec, as well as 1200 W and warm-up time 10 sec, a homogenous surface seems to cover the substrate. While for 800 W and a warm-up time of 17 sec the surface porosity increasing is observed.

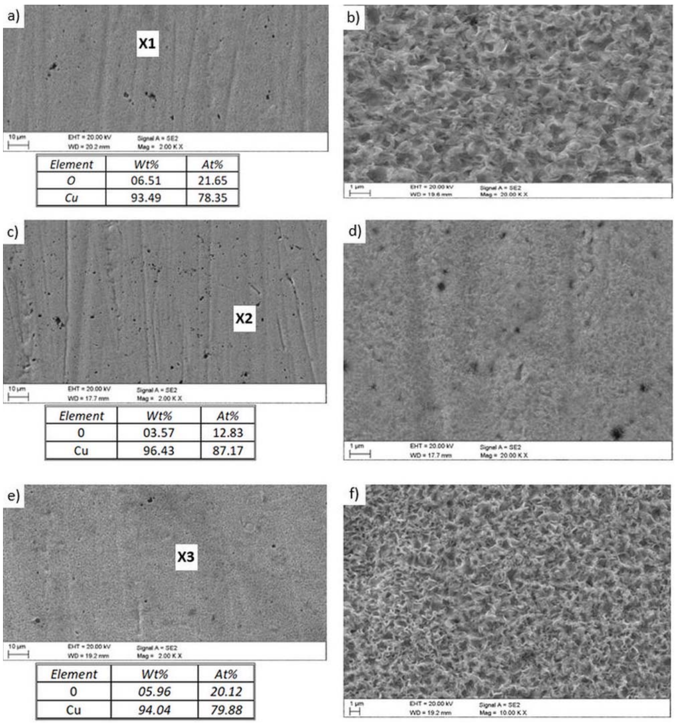

Fig. 4. Surface topography of layer oxidised copper sheets: a, b) sample no. 1; b, c) sample no. 2 and c, d) sample no. 6 according to the numbering provided in table 2 (SEM). g) X1, h) X2, i) X3. Tables of superficial distribution of elements from the micro-area a, c and e

Figure 5 presents the reflection coefficient from the oxidised copper sheet. The highest reflection was observed for sample 2 which is 76% for wavelength 1000 nm, while for samples 1 and 6 the same course of reflection curve was noticed, and the coefficient value for 1000 nm is 70%. This is the result of the high homogeneity of both layers. It should be mentioned that layer 2 was not completely uniform, as evidenced by the appearance of reference colours at its edges.

Table 3 presents the results of the haze factor calculation for the tested samples, which is in the range from 60 to 90%. The highest haze is characterised for sample 6, which is 89%, which indicates its low glossy while for sample 2 it is 61%. The results suggest a high roughness of the substrates. High roughness can be an advantage when producing full photovoltaic structures. It can be a natural texture that can lead to light trapping and, consequently, an increase in quantum efficiency.

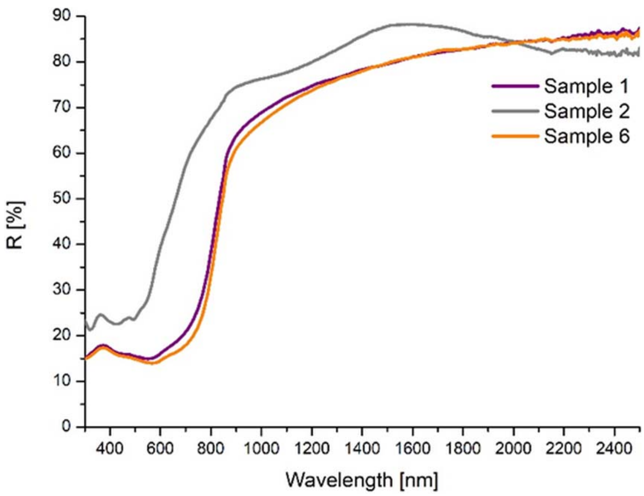

Fig. 5. Spectral reflection of chosen oxidised copper sheets in the wavelength range 300 to 2500 nm

TABLE 3

Results of measurements of the calculated haze ratio "Haze" of the tested samples

No	Sample number	Thickness [nm]	Coefficient of Haze Z [%]
1	1	160	87
2	2	110	61
3	6	66	89

Structure of investigated copper oxide layers (sample 1, 2 and 6) was determined by using the atomic force microscopy (Fig. 6). The porous structure is presented in Figure 6a when the fine-grained structure was observed in figure 6b, c.

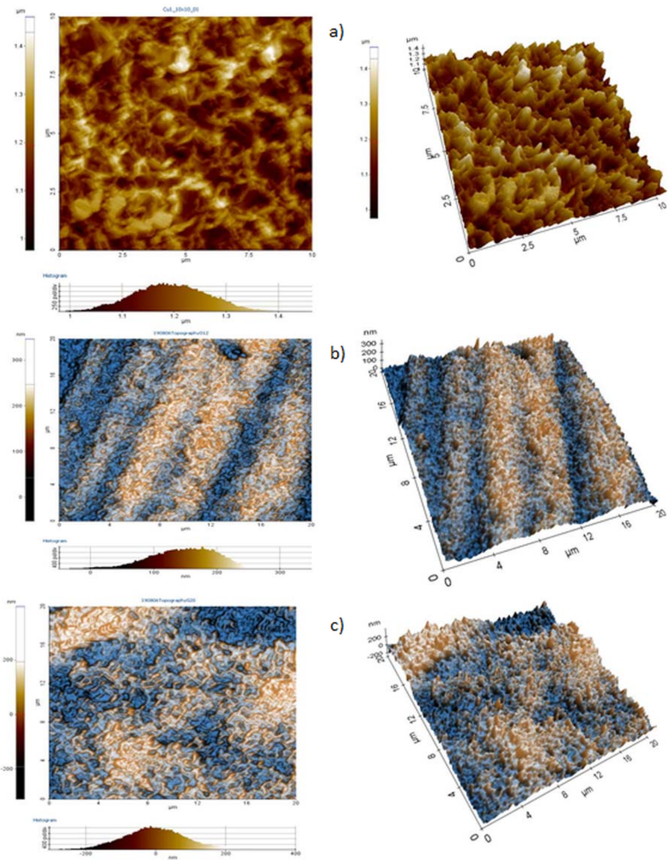

Fig. 6. Surface topography (AFM) of oxidised copper sheets: a, b) sample no. 1, b) sample no. 2 and c) sample no. 6 according to the numbering provided in Table 2

Figure 7 presents the X-ray diffraction of samples 1 and 6; sample 2 is not shown due to the high inhomogeneity of the layer where only small CuO and Cu_2O peaks were detected.

For samples 1 and 6, the following phases have been identified (Fig. 7): cubic Cu (green triangle), cubic Cu_2O (purple

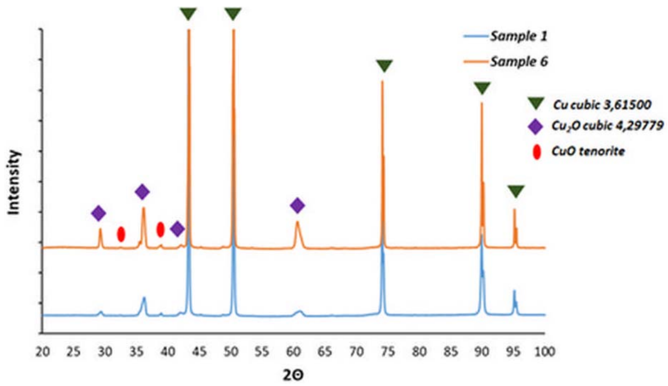

Fig. 7. Diffraction (a, c) and phase analysis results of investigated sample 1 and 6

diamond) and CuO (red circle). The measurement confirmed that the obtained layer is a mixture of monoclinic Cu_2O which stands as a major phase and cubic CuO minor phase. What is more, both of the investigated layers have the same phase composition, not differing from each other. Also, a changed Cu_2O phase lattice parameter was observed compared to used standard (a = 4.2650 Å for the standard and a = 4.29779 Å for the investigated samples).

5. Summary

The results of preliminary tests for the development of micro laser treatment are presented in Figure 8. The proposed method of laser-assisted copper oxidation allows obtaining copper oxides in an easy, fast and repeatable way. It is also possible to produce a single copper oxide phase by adjusting process parameters as laser beam power and warm-up time. Authors believe that results presented in this paper will add to the existing state of knowledge concerning the engineering of photovoltaic cells and technology of their manufacturing.

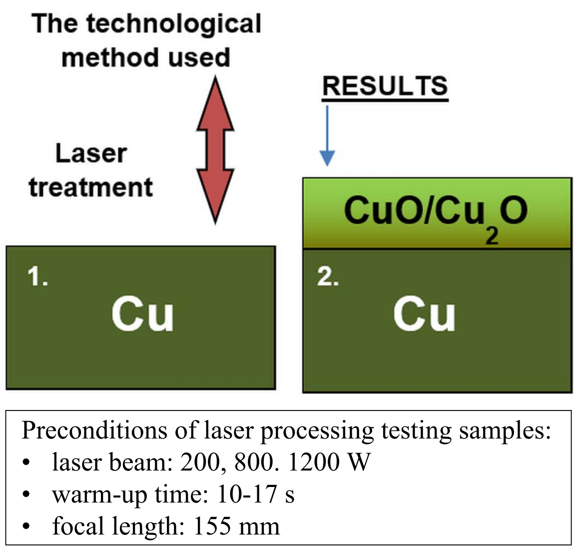

Fig. 8. Selection of laser processing parameters manufactured on the Cu substrate

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