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Synthesis of copper oxides films via anodic oxidation of copper foil followed by thermal reduction

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Abstract. Copper oxides films were successfully synthesized via anodic oxidation of copper foil at various conditions followed by thermal reduction of oxidized samples in inert nitrogen atmosphere. The morphology and phase composition of final and intermediate products were determined by scanning electron microscopy, X-ray diffraction and Raman spectroscopy techniques. Optimal synthetic conditions of Cu_2O films on copper foil surface were established.

1. Introduction

Quick growth of industrial activity in last decades compels manufactures to pay great attention to make a new way of energy supply with the decreasing of environment pollutants [1, 2]. Hydrogen generation via water splitting under sunlight on the surface of semiconductor photoelectrodes is one of the most promising way because it lets to produce fuel with the minimal environmental impact [3, 4]. Photo-electrochemical water splitting process often carries out in photo-electrochemical cells (PEC) which in most cases consist of three electrodes: working (semiconductor), counter (more often is platinum), and reference (silver chloride, saturated calomel etc) electrodes. During water decomposition process, semiconductor surface is illuminated and as a result electrons and holes are generated. Charge carriers induce oxidation/reduction reactions to produce oxygen and hydrogen (equations 1 – 3) [5, 6]:

$$\text{Oxidation: } H_2O + 2h^+ \rightarrow 2H^+ + {}^1\!/_2\, O_2 \quad (1)$$

$$\text{Reduction: } 2H^+ + 2\bar{e} \rightarrow H_2 \quad (2)$$

$$\text{The overall reaction is: } H_2O \xrightarrow{h\nu} H_2 + {}^1\!/_2\, O_2 \quad (3)$$

Among various semiconductor materials for PEC photoelectrodes, cuprous oxide (Cu_2O) is one of the most attractive materials because of its cheapness, environment safety, good value of band gap (2,0 – 2,2 eV) which provide absorbance of considerable part of solar spectrum [7-9]. In order to provide all necessary requirements imposed for semiconductor materials for PEC applications, a variety of Cu_2O structures (wires, cubes, polyhedral, flower-like structure, etc.) [10-13] and copper oxides

composites have been obtained by different techniques, such as hydrothermal, microwave-assisted hydrothermal, electrodeposition, chemical oxidation with thermal reduction, sputtering, etc. [9, 14-17].

Anodic oxidation is a surface treatment low-cost method, which can provide synthesis of different nanostructured materials on metals' surface. By this method shape, morphology and size of structures can be modulated by change of concentration, temperature, pH, etc. [18, 19]

In this work Cu_2O films on copper foil surface (ready effective photoelectrode for water splitting process) have been successfully synthesized via simple and cheap two step method. The first step was a galvanostatic anodic oxidation of copper foil in alkaline solution over a range of current densities in order to obtain $Cu(OH)_2$ wires. The second step was the thermal reduction of wires under inert atmosphere (N_2), as a result Cu_2O film covers up surface of copper foil.

2. Experimental

2.1. Materials

All chemical reagents used are analytical grade (Copper foil (Cu, 99.99% purity, 20x20x0.5 mm), sodium hydroxide (NaOH, Pure)). All solutions used in this research were prepared with deionized water.

2.2. Anodic oxidation followed by thermal reduction

Cuprous oxide films were fabricated via anodic oxidation of copper foil followed by thermal reduction of oxidized sample as shown in figure 1.

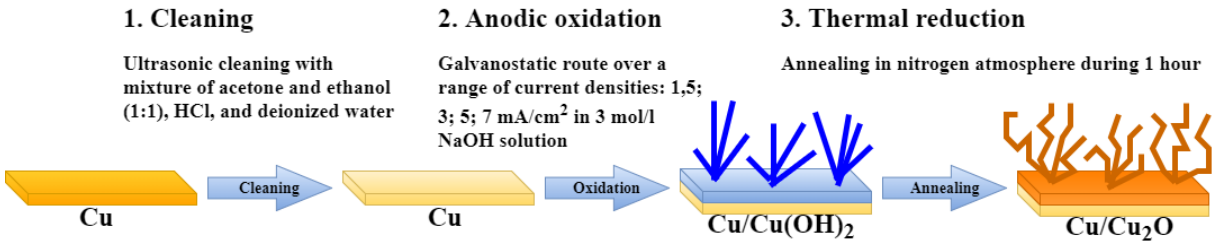

Figure 1. The synthesis scheme of Cu_2O films.

$Cu(OH)_2$ wires have been obtained according to methods, described in [9, 19]. Before the anodization process, a square copper plates had been ultrasonically cleaned in mixture of acetone and ethanol (1:1), HCl (10%) and deionized water. The anodic oxidation was performed with two-electrode cell (anode – copper plate, cathode – stainless steel net) in 3 mol/l NaOH solution over a range of current densities: 1,5; 3; 5; 7 mA/cm^2 with and without stirring for 30 or 10 minutes (two last samples). The obtained samples were extracted from the solution, rinsed with deionized water and ethanol, and dried in air. Thermal reduction was carried out for samples, obtained by anodization at 5 mA/cm^2 for 10 minutes without any stirring. Annealing was performed in tube furnace (Naberthem R 50/250/12) at various temperatures (200 – 600°C) in inert atmosphere (N_2) for 1 hour.

2.3. Characterization

Morphology of fabricated films was examined by scanning electron microscopy (SEM) with scanning electron microscope Supra 50 VP (LEO) operated at 5 – 20 kV. X-ray diffraction (XRD) patterns were obtained using X-ray diffractometer Rigaku D/MAX 2500, with $Cu_{K\alpha}$ radiation (λ = 1,54178Å) in the range of 2θ from 10^o to 80^o. The Raman spectra were recorded by Renishaw InVia system equipped with an Ar laser (514 nm, 20 mW, 10% of max power).

3. Results and discussion

3.1. SEM characterization

SEM images of samples, which were obtained by anodic oxidation at different conditions, are presented on figure 2.

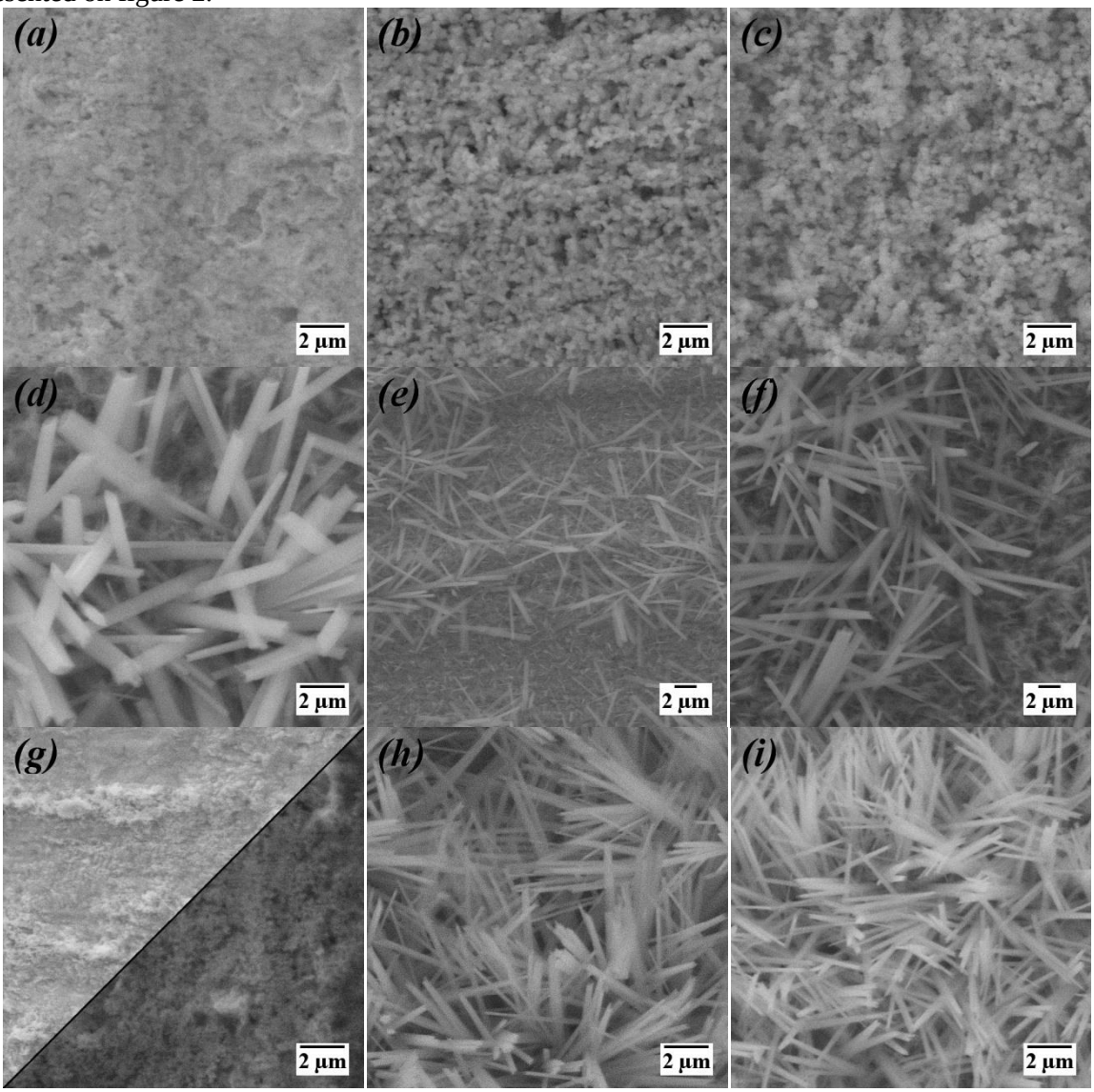

Figure 2. SEM images of copper plates after anodization at: (*a*) 1,5, (*b*) 3, (*c*) 5, (*d*) 7 mA/cm^2 with solution stirring during 30 minutes; (*e*) 1,5, (*f*) 3, (*g*) 5 (top) and 7 (bottom) mA/cm^2 without stirring during 30 minutes; (*h*) 5 mA/cm^2 during 10 minutes; (*i*) 7 mA/cm^2 during 5 minutes.

Anodic oxidation of copper foil leads to the formation of films on the substrates surfaces with different morphology. Anodization at 1,5 – 5 mA/cm^2 during 30 minutes with solution stirring (figure 2 *a* – *c*) follows the formation of dense films, while increasing of current density up to 7 mA/cm^2 (figure 2 *d*) leads to the growth of wires on the copper foil surface with a length (L) of 5 – 7 μm and thick (D) of about 600 – 900 nm.

Without stirring wires on the surface of copper foil start to grow even at 1,5 mA/cm^2 (figure 2 *e*) and the larger a value of current density is, the more wires form on the surface. Therefore, convection currents, which take place during solution stirring, allow to prevent wires growth on copper foil surface. When the current density reach the values 5 and 7 mA/cm^2 (30 minutes) the film tears off from substrate and a thin layer of anodization products stays on surface (figure 2 *g*). To protect the

films from separation at higher current densities the time of process was decreases to 10 and 5 minutes respectively. By applying these synthesis parameters, films with the largest density of wires on the surface have been obtained (figure 2 *h*, *i*). Wires with L = 3 – 5 μm and D = 200 – 400 nm have been formatted at current densities 1.5, 3 mA/cm^2 and 5 mA/cm^2 during 30 minutes anodization process. Increase of current density to 7 mA/cm^2 led to formation of wires reaching the length L ~ 9 μm and the same values of thickness.

SEM images of samples, which have been fabricated by thermal treatment of oxidized copper foil (5 mA/cm^2 10 minutes) at various temperatures of 200 – 600^{o}C in nitrogen atmosphere during 1 hour, are displayed in figure 3.

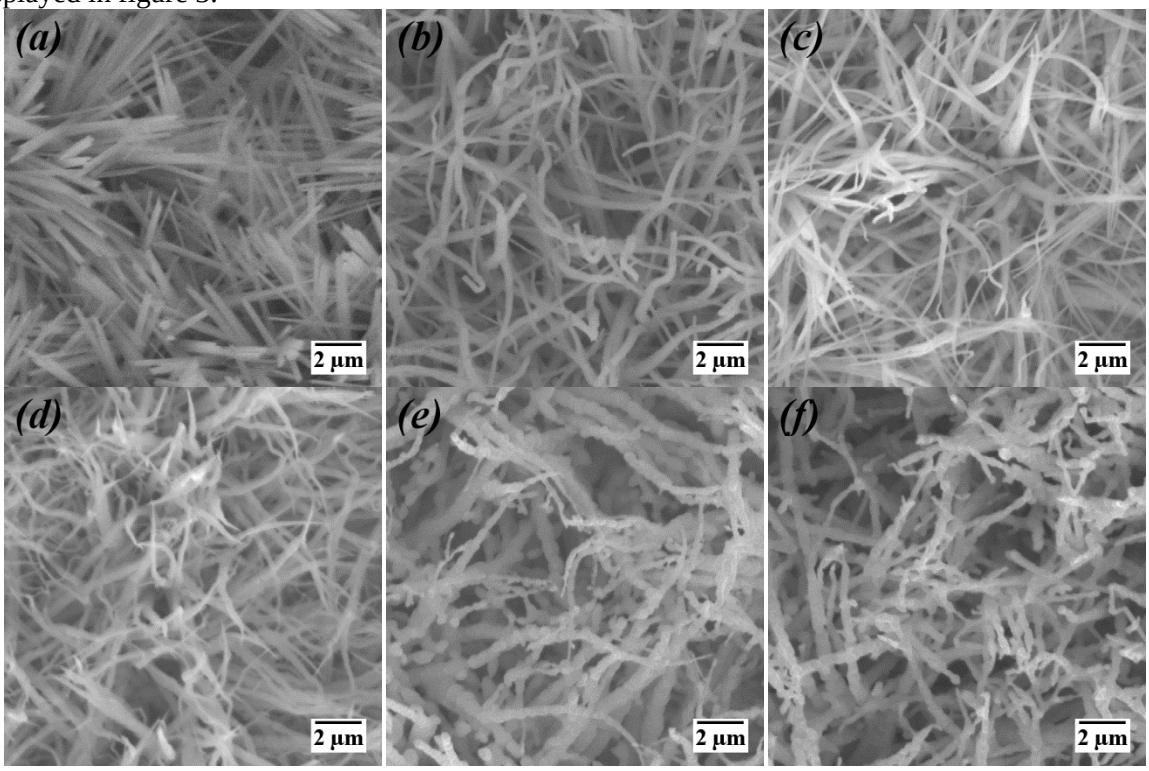

Figure 3. SEM images of samples (*a*) after anodization 5 mA/cm^2 during 10 minutes (source sample); after annealing of source sample during 1 hour at (*b*) 200°C, (*c*) 300°C, (*d*) 400°C, (*e*) 500°C, (*f*) 600°C.

All wires have been curved after thermal treatment at temperatures 200 – 600°C in nitrogen atmosphere during 1 hour. Annealing at temperatures from 200 to 400°C leads to bending of source wires, but the dimensions of wires still remain the same (figure 3 *b* – *d*). At the temperatures 500 and 600°C apparent change in the shape of wires to coral-like structures can be observed (figure 3 *e*, *f*), moreover length and thick are changed (L = 5 – 7 μm, D = 300 – 500 nm).

3.2. XRD characterization

The phase composition of the samples were determined by using of XRD method, as shown in Figure 4. The XRD pattern of copper plate is also displayed for comparison.

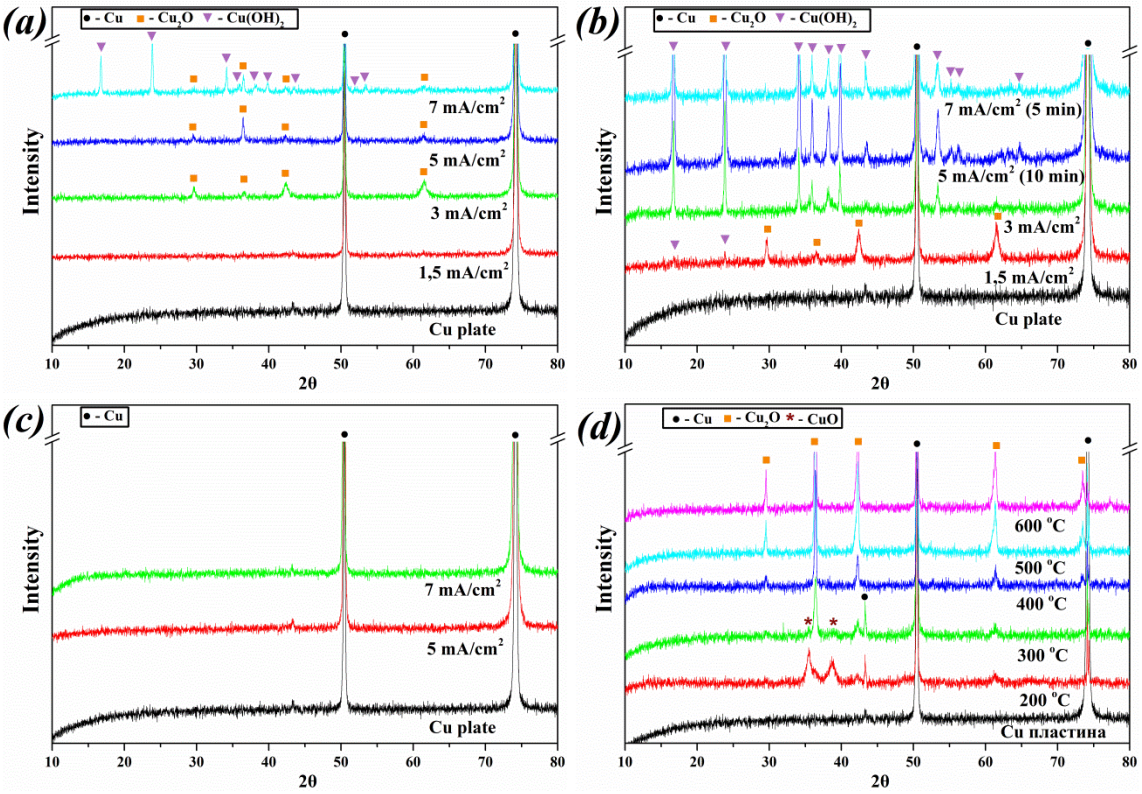

Figure 4. X-ray diffraction patterns of oxidized samples (*a* – *c*) and after thermal reduction (*d*).

The XRD pattern of the samples, obtained after anodic oxidation at 3 and 5 mA/cm^2 under solution stirring (figure 4 *a*), shows that all of the peaks (except peaks, which belong to copper substrate) can be readily indexed to cubic-phase Cu_2O (JCPDS card No. 78-2076). If current density during anodic oxidation process achieves value 7 mA/cm^2, then the diffraction peaks indexed to orthorhombic-phase $Cu(OH)_2$ (JCPDS card No. 72-140) appear along with the same peaks, which belong to Cu_2O and Cu substrate.

Anodization without stirring (figure 4 *b*) leads to formation of $Cu(OH)_2$ phase from 1,5 mA/cm^2, this reveals that convection currents, during solution stirring, prevent from appearing $Cu(OH)_2$ phase on substrate's surface. XRD pattern of the sample, which have been fabricated at 1,5 mA/cm^2 contains peaks, which can be attributed to Cu_2O, Cu and $Cu(OH)_2$ phases, and the larger a value of current density is, the higher intensity of peaks is which belong to $Cu(OH)_2$, in addition with growth of current density diffraction peaks of Cu_2O are disappear. But process of anodic oxidation are limited by tear off of film from substrate surface: anodization at 5 and 7 mA/cm^2 during 30 minute lead to tear off of $Cu(OH)_2$ film from surface and layer of roentgenamorphous product are fabricated on this place (figure 4 *c*). To prevent $Cu(OH)_2$-foil from destructing during oxidation at 5 and 7 mA/cm^2, the time of process was reduce to 10 and 5 minutes respectively and in this case XRD patterns include diffraction peaks of $Cu(OH)_2$ phase only, moreover peaks of $Cu(OH)_2$ phase for sample, which have been obtained at 5 mA/cm^2 during 10 minutes, have higher intensity compared to others samples, which have been obtained in another conditions. Decrease of intensity of peaks for sample which have been obtained by anodic oxidation at 7 mA/cm^2 during 5 minutes may be due to processes of tearing off foil from substrate's surface.

Transformation from Cu_2O to $Cu(OH)_2$ during anodization of copper foil, according to [20], is caused by formation of Cu_2O phase at the initial time. Increase of current density leads to formation $Cu(OH)_2$ phase on the surface preferably.

Thermal reduction of oxidized samples leads to disappearing of diffraction peaks of $Cu(OH)_2$ phase and appearing of peaks, which belong to Cu_2O and CuO phases that indicate the transformation of $Cu(OH)_2$ through thermal reduction in nitrogen atmosphere was completed (figure 4 *d*). This transformation according to [9] is caused by processes of dehydrate and deoxidization of source sample. XRD patterns for samples, after annealing at 200 and 300°C, have diffraction peaks from CuO phase at 35,56° ($\bar{1}11$) and 38,74° (111) (JCPDS card No. 89-5895) and with the increasing of the temperature of thermal treatment, this diffraction peaks reduce and disappear when temperature of annealing reach a value 400°C. At the same time the intensities of peaks, which can be attributed to Cu_2O phase, start to grow with increasing of temperature from 300°C and reach the high value at 600°C.

All this variations in structures correlate with the finding of SEM, and also confirm the formation of curl-like and coral-like Cu_2O wires.

3.3. Raman characterization

The transformation of the films and the effect of thermal treatment were also studied by Raman spectroscopy (figure 5).

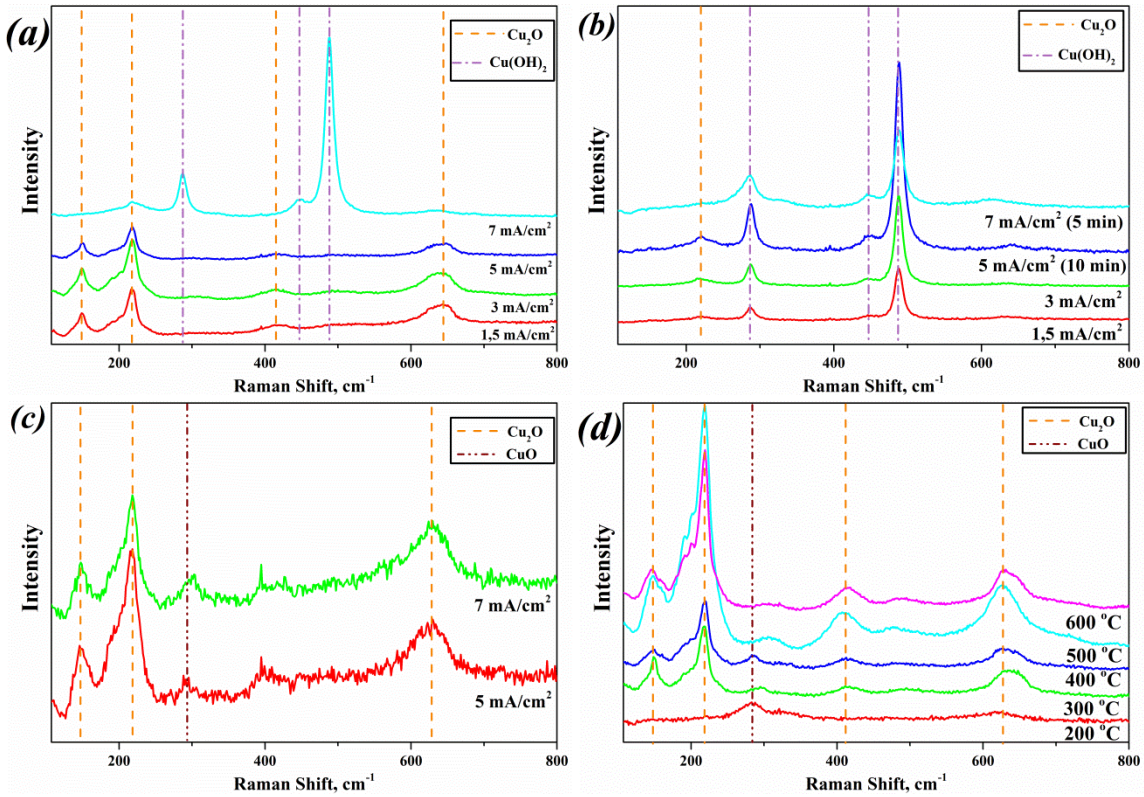

Figure 5. Raman spectra of oxidized samples (*a* – *c*) and after thermal reduction (*d*).

Spectra of samples, which have been obtained via anodic oxidation with solution stirring, include phonon modes of $Cu(OH)_2$ and Cu_2O (figure 5 *a*). Two peaks at 150 cm^{-1} can be attributed to IR active modes $\Gamma_{15}^{-(1)}$ and $\Gamma_{15}^{-(2)}$ accordingly. The peaks at 218 cm^{-1} originated from the second-order Raman-allowed mode of the Cu_2O crystals Γ_{25}^{+}. The peak at 416 cm^{-1} is assigned to four-phonon mode $3\Gamma^{-12} + \Gamma^{-25}$ [9, 21-23]. With increasing of current density, the strongest peak of 218 cm^{-1} from Cu_2O became smaller. For sample, which have been fabricated after anodic oxidation at 7 mA/cm^2, peaks 286, 445 and 488 cm^{-1}, which can be attributed to $Cu(OH)_2$, appear [23, 24].

In spectra from sample, which have been fabricated by anodic oxidation without solution stirring (figure 5 *b*), peaks of $Cu(OH)_2$ phonon modes appear at current density from 1,5 mA/cm^2 and achieves

the maximum value of the intensity of peak at 488 cm^{-1} for sample at 5 mA/cm^2. The results correlate with data obtained from XRD, and confirmed that the best crystallization of $Cu(OH)_2$ can be achieved by oxidation at 5 mA/cm^2 without solution stirring. Moreover in Raman spectra for samples, from surfaces of which the films torn off (figure 5 *c*), peaks at 150, 218, 630 cm^{-1}, which can be attributed to phonon modes of Cu_2O, and 298 cm^{-1}, which can be attributed to phonon modes of CuO (phonon mode A_g) [25], are present. This indicate that after the tearing off of $Cu(OH)_2$ films on the surfaces of the samples the layer of roentgenamorphous product which consist from mixture of cuprous and cupric oxides stays.

Raman spectra of annealed sample contain one wide peak at 298 cm^{-1} which attribute to phonon mode of CuO and with the growing of annealing temperature intensity the peak reduce and disappear at 500^{o}C. In the same time with the increase of temperature of treatment peaks at 150, 218, 413 and 630 cm^{-1}, which belong to phonon modes of Cu_2O, they appear (from 300^{o}C) and increase, the high value is reached at 500^{o}C. According to [9], the presence of CuO phase is associated with the structural transformation through dehydrate of $Cu(OH)_2$ and subsequent deoxidization of CuO to Cu_2O.

4. Conclusions

Copper oxides films were successfully synthesized via anodic oxidation of copper foil at various conditions followed by thermal reduction of oxidized samples in inert nitrogen atmosphere. The morphology and phase composition of final and intermediate products were determined by scanning electron microscopy, X-ray diffraction and Raman spectroscopy techniques. Optimal conditions, for obtaining of $Cu(OH)_2$ foil on copper foil surface, is 5 mA/cm^2 during 10 minutes without solution stirring. Thermal reduction of the $Cu(OH)_2$ foil lead to transfer to Cu_2O foil through dehydrate and deoxidization processes under nitrogen atmosphere and from XRD data the optimal temperature of annealing is 500^{o}C.

Acknowledgments

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