

## THE ELECTROCHEMICAL DEPOSITION OF Cu/CuO<sub>x</sub> SOLAR SELECTIVE COATINGS WITH CONTROLLED MORPHOLOGY

Cristina BOGATU,<sup>a</sup> Mihaela VOINEA,<sup>a\*</sup> Anca DUȚĂ,<sup>a</sup>  
Irina Mihaela PELIN<sup>b</sup> and Gabrielle Charlotte CHIȚANU<sup>b</sup>

<sup>a</sup>Transilvania University of Braşov, The Centre Product Design for Sustainable Development, Eroilor 29, 500036 Braşov, Phone: 0268-475594, Roumania

<sup>b</sup>Petru Poni Institute of Macromolecular Chemistry of the Roumanian Academy, Aleea Grigore Ghica Vodă 41A, Iaşi, Roumania

Received September 4, 2008

The electrochemical deposition and characterization of Cu/CuO<sub>x</sub> thin films (on copper substrate) is reported in this study using precursor's solution based on copper and sodium acetate. Maleic anhydride copolymers with controlled solubility were added for tailoring the layers morphology. The optimum electrodeposition parameters were obtained from the voltammetric studies.

The stability of the polymer–copper ion structures and the electrical-induced conformational transitions of the polymers in the precursors' solution are studied by cyclic voltammetry and correlated with the nucleation and growth mechanisms of the thin films.

The thin films were characterized using AFM studies (morphology), XRD analysis (crystalline structure/composition) and UV-VIS-IR spectroscopy (optical characterization). The results proved that efficient solar selective coatings based on Cu/CuO<sub>x</sub> can be obtained by electrodeposition.

### INTRODUCTION

Solar-thermal systems can be efficiently used in applications like: domestic hot water and space heating, swimming pool heating, solar desalination.<sup>1-3</sup> Flat plate collectors are the most common solar collectors, their components being: (a) solar absorber: transforms the incident radiation into heat; (b) absorber's channels: in which the thermal agent is transporting the produced heat; (c) insulation: to minimise the heat losses; (d) glazing - monolayer or double layer; (e) a weather tight container which encloses the above components.<sup>4</sup>

Considering the solar thermal conversion, the most important component of the solar collector is the absorber, which influences the degree of use of the solar radiation and has a cost much higher compared to other components. The absorber is, generally, a metallic surface coated with a spectrally selective surface. To compare the performance of two absorbers, the following parameters are being used: solar absorption ( $\alpha_s$ ), thermal emittance ( $\varepsilon_T$ ). In an ideal absorber all the incoming solar radiation ( $\lambda = 0.29 \mu\text{m} \div 2.5 \mu\text{m}$ ) is

absorbed, thus  $\alpha_s = 1$  and there are no heat losses through infrared radiation ( $\lambda > 2.5 \mu\text{m}$ ),  $\varepsilon_T = 0$ . This property is called selectivity; several methods to achieve solar selectivity are available. The metallic surfaces used as absorbers have a high I.R. reflection coefficient, therefore low heat emissivity. In order to obtain high values for  $\alpha_s$ , the metal absorber must be covered with a coating which strongly absorbs in the solar radiation wavelength range.<sup>5</sup> The solar selective coatings have been studied since 1950, when Tabor has introduced the concept of solar selectivity by creating the first materials with these properties (black nickel deposited via electrolysis on a copper substrate or bright nickel and by anodising aluminium on bright aluminium).<sup>6-7</sup> Six main categories of such coatings are currently accepted: (a) intrinsic, (b) semiconductor–metal tandems, (c) multilayer absorbers, (d) multielectric composite coatings, (e) textured surfaces, and (f) selectively solar-transmitting coatings.<sup>8</sup> Each category has several types of coatings, with specific functioning domains, depending on the application for which they were designed: low, medium or high temperatures applications.

\* Corresponding author: m.voinea@unitbv.ro

The optical performance ( $\alpha_s$ ,  $\epsilon_T$ ) and the long term stability are the critical parameters. Metal oxides are expected to be more immune to thermal and environmental conditions. Several of them have been already assessed as active materials for selective coatings (e.g. copper, chrome, nickel, aluminium, titanium oxides).<sup>9</sup> As a substrate, one can use, given the low emissivity coefficient: copper, aluminium, or alloys: nickel – chrome, nickel – vanadium or nickel – copper.

The most studied surfaces are: black paints (in the beginnings), black chrome and black nickel, both obtained by electrodeposition,<sup>10,11</sup> alumina composites with Mo, Ni,<sup>12</sup> etc. The solar absorbers popular on the market (Sunselect<sup>13</sup> and TINOX<sup>14</sup> – in which the selective surfaces contains titanium oxide or nitrate), although they are performing, their overall cost is high, increasing the collector's price.

The present paper reports the electrodeposition (ED) and characterization of Cu/CuO<sub>x</sub> solar absorber (on copper substrate) using a precursor solution based on copper and sodium acetate. The ED method can be easily used for large scale applications. Maleic anhydride copolymers with controlled solubility were added as morphology tailoring agents.

## EXPERIMENTAL

### Sample preparation

Thin films of black copper were electrodeposited onto copper substrate from electrolytic baths containing (CH<sub>3</sub>COO)<sub>2</sub>Cu 0.01 M (Scharlau, >98 %) and CH<sub>3</sub>COONa 0.1 M (Scharlau, >96 %) at pH=5.5. The pH was adjusted by adding acetic acid or hydrochloric acid. The copper substrate (1.5 x 2.5 cm flat pieces of Cu 99.9% - Beofon), was mechanically polished (sandpaper No. 800) and washed with distilled water before each deposition.

Copolymers of maleic anhydride (synthesised at Petru Poni Institute, Iassy) with concentration: 25, 50, 100, 200 ppm were added in the electrolytic bath as morphology controlling agents. Two types of copolymers<sup>15,16</sup> with controlled hydrophobicity were used: hydrophobic copolymer: sodium maleate – methyl methacrylate (HB) partially hydrolysed and hydrophylic copolymer: sodium maleate – vinyl acetate (HL) partially hydrolysed.

For the electrochemical deposition, a multichannel potentiostat galvanostat (PAR BioLogic VSP with three electrode system: working electrode-sample, counter electrode-platinum plate (1 cm x 1 cm), reference electrode-Ag/AgCl/KCl sat (SAE),  $E_{SAE} = 0.197$  V vs. NHE) was used. The voltammetric curves were swept from potential of 0 V vs SAE, first following the oxidation step and then back to 0 V, through the reduction step. The scan rate was 20 mV/s.

A set of thin films were deposited from the precursor solution at room temperature,  $t = 25^{\circ}\text{C}$  and various deposition potential (0.05 to -1 V). Deposition periods were varied from 5 to 60 minutes. All the potential were measured vs. SAE.

### Sample characterization

The samples topography was studied by Atomic Force Microscopy (AFM/STM, NTEGRA Probe Nanolaboratory), using semi-contact mode with golden silicon cantilever (NSG 10, force constant, tip radius 10 nm).

The films crystalline composition was determined by X-Ray Diffraction (XRD, Bruker-AXS D8 Advance), using CuK <sub>$\alpha$</sub>  radiation ( $\lambda = 0.154059$  nm),  $2\theta = 8-80$  degree.

The solar absorptance( $\alpha_s$ ) and thermal emittance ( $\epsilon_T$ ) were calculated according to Duffie et Beckman<sup>5</sup> from the reflectance spectra measured with UV-VIS Lambda 25 (Perkin Elmer) and FT-IR Spectrum BXII (Perkin Elmer) spectrophotometers, respectively. For the  $\alpha_s$  computation, the reflection spectra were measured in the range of 0.25 to 1.1  $\mu\text{m}$ , whereas the values from 1.1-2.5  $\mu\text{m}$  were calculated by interpolation. For the  $\epsilon_T$  calculation the spectral reflectance from 2.5 to 20  $\mu\text{m}$  was used.

## RESULTS AND DISCUSSION

### Voltammetric study of the polymer influence in the precursor's solution

Thin layer of Cu/CuO<sub>x</sub>, used as solar absorber in flat plate collectors were obtained via electrodeposition following a previously reported recipe,<sup>16</sup> from precursor solution containing (CH<sub>3</sub>COO)<sub>2</sub>Cu and CH<sub>3</sub>COONa. The influence of two types of morphology controlling polymers (hydrophobic copolymer/hydrophilic copolymer) addition in the electrolytic bath is investigated in this work. The voltammetric curves obtained in solutions of (CH<sub>3</sub>COO)<sub>2</sub>Cu 0.01 M and CH<sub>3</sub>COONa 0.1 M (pH=5.5,  $t=25^{\circ}\text{C}$ ) and different concentration of polymers are plotted in Fig. 1 and Fig. 2. The pH was adjusted by adding acetic acid. The role of the acid is to prevents the copper hydroxide precipitation (resulted from copper acetate hydrolysis at natural pH=6.6) and simultaneously to decrease the electrolyte ohmic resistance, increasing the growth rate.<sup>16</sup>

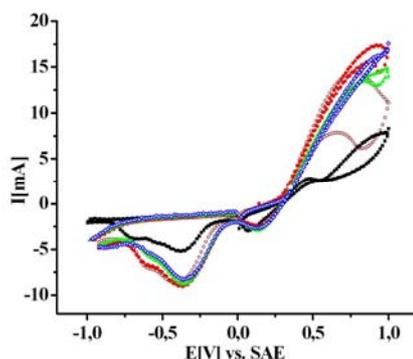


Fig. 1 – Cyclic voltammograms in solutions of (CH<sub>3</sub>COO)<sub>2</sub>Cu 0.01 M + CH<sub>3</sub>COONa 0.1 M +HB polymer: ○ without polymer; (■) 25 ppm; (●) 50 ppm; (▲)100 ppm; (◇) 200 ppm.

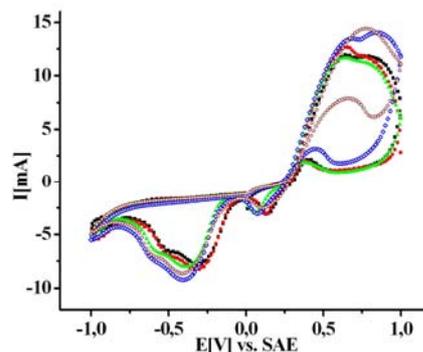
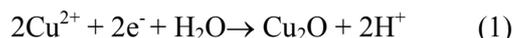


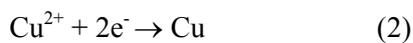
Fig. 2 – Cyclic voltammograms in solutions of (CH<sub>3</sub>COO)<sub>2</sub>Cu 0.01 M + CH<sub>3</sub>COONa 0.1 M +HL polymer: ○ without polymer; (■) 25 ppm; (●) 50 ppm; (▲)100 ppm; (◇) 200 ppm.

In the absence of polymer addition the voltammetric curves show two cathodic peaks:

The first peak is positioned at 0.12 V ( $E_{1/2}=0.203$  V) vs SAE and indicates the deposition of Cu<sub>2</sub>O:



The deposition of Cu over the Cu<sub>2</sub>O film at -0.40 V ( $E_{1/2}= -0.24$  V) vs SAE is described by the reaction:



Similar cathodic peaks are reported in the literature on nanocrystalline TiO<sub>2</sub> substrate<sup>17</sup> or on the Ti substrate,<sup>18</sup> but these are slightly shifted compared with the present results.

Previous studies<sup>16,18</sup> on the influence of the precursor solutions pH on the deposition of Cu/Cu<sub>2</sub>O

layer showed that a slightly acidic medium is favourable to the deposition of copper over the Cu<sub>2</sub>O.

In the presence of polymer, the voltammograms show the same peaks described by the equations (1) and (2), for both hydrophobic/ hydrophilic copolymer and for the whole range of tested concentration. Still, a slight shift in the peaks position is observed, indicating modifications in the electrode processes, depending on the polymer type and concentration.

In order to understand better the interactions copper ions – polymer and the influence of the modification of the macromolecular coil conformation on the deposition process, parallel voltammetric studies in solutions containing only polymer (HB, HL) and water were performed (Fig. 3 and Fig. 4).

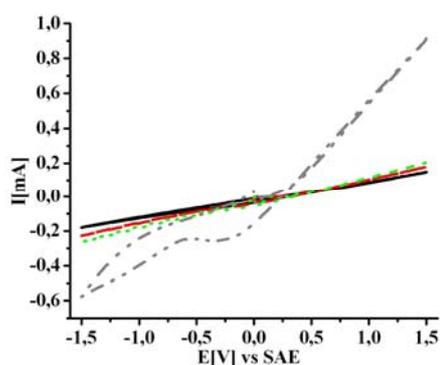


Fig. 3 – Cyclic voltammograms water-hydrophobic polymer solutions: — 25 ppm; - - - 50 ppm; . . . . 100 ppm; - · - · 200 ppm.

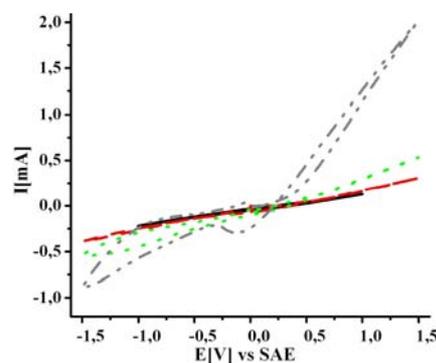


Fig. 4 – Cyclic voltammograms water-hydrophilic polymer solutions: — 25 ppm; - - - 50 ppm; . . . . 100; - · - · 200 ppm.

When hydrophobic copolymer is added in the precursor solutions the peak II is shifted anodically about 50 mV for entire range of concentration, while no modifications are observed for the peak I in the entire range of concentration. In addition, the

voltammograms for HB polymer-water solutions show conformational modifications of the HB, only at high values of polymer concentration. Thus, the Cu<sup>2+</sup> ions produce a stabilization of the macromolecular coil conformation, leading to Cu-

polymer structures which are not dependent of the polymer concentration.

In contrast, for electrolytic bath containing hydrophilic copolymer, the peaks position depends on the polymer concentration. At low HL polymer concentration (25 ppm and 50 ppm) the peaks are anodically shifted with about 10 mV (peak I) and respectively with 100 mV (peak II). Higher concentrations of HL polymer (100 ppm, 200 ppm) leads to a cathodically shift in the peaks I (about 50 mV). This fact is in accordance with the behaviour of the water-HL solutions. By applying electrical field important modifications of the macromolecular coil are recorded, only at high polymer concentration: 100 ppm and respectively 200 ppm. These modifications can be associated with a stretching process of the polymeric chain.

Therefore, the stability of the polymer-Cu<sup>2+</sup> structures, together with the nucleation and growth reaction rate is strongly influenced by the polymer type and concentration and most probably by the presence of other additives in the electrolytic bath (CH<sub>3</sub>COONa, CH<sub>3</sub>COOH, HCl), influencing the ionic strength.<sup>19</sup>

#### Determination of the optimum deposition conditions

A set of thin films were electrodeposited at various deposition potential (0.05 V.....-1V), from solutions containing copper acetate, sodium acetate and polymer (HB/HL) at pH=5.5, t=25°C. The deposition period

was varied from 5 to 60 minutes. The pH was adjusted with acetic acid or hydrochloric acid. The voltammograms in the presence of hydrochloric acid show the same cathodic peaks as the voltammetric curves with acetic acid addition. The peaks are positioned closer each, other indicating a much easier codeposition of Cu and Cu<sub>2</sub>O.

Literature<sup>18</sup> mentions the possibility of codeposition of Cu and Cu<sub>2</sub>O on Ti substrate for potential ranging from -400 V to -600 V (measured versus saturated calomel electrode), but even at lower cathodic potentials.

The experimental tests on copper substrate indicate at deposition potential more positive than -0.6V ( $E_{\text{deposition}} > -0.6\text{V}$  vs SAE), formation of very thin films green spots, probably due to the copper hydroxide or other hydrated copper compounds, while from potential of -1V vs SAE, parallel hydrogen formation give a weak adherence of the deposit. Therefore, the next deposition tests have been done by varying the deposition potential, step to step from -0.6 V to -0.9 V.

#### Optical characterization

Table 1 gives the values of solar absorptance ( $\alpha_s$ ) and thermal emittance ( $\epsilon_T$ ) for the electrodeposited films, calculated from the UV-VIS and FTIR reflectance spectra<sup>5</sup>. This was a determinant criterion for choosing the optimum deposition conditions.

Table 1

Optical properties of the Cu/CuO<sub>x</sub> films in different electrodeposition conditions

Sample	C <sub>Polymer</sub> [ppm]	E <sub>deposition</sub> [V]	t <sub>deposition</sub> [min]	$\alpha_s$	$\epsilon_T$
Precursor solution: (CH <sub>3</sub> COO) <sub>2</sub> Cu 0.01 M + CH <sub>3</sub> COONa 0.1 M + CH <sub>3</sub> COOH (pH=5.5)					
Cu_01		-0.75		0.62	0.08
Cu_02	0	-0.9	20	0.43	0.08
Cu_03		-0.6		0.48	0.09
Precursor solutions: (CH <sub>3</sub> COO) <sub>2</sub> Cu 0.01 M + CH <sub>3</sub> COONa 0.1 M + CH <sub>3</sub> COOH (pH=5.5)+HB					
Cu_HB_1		-0.7		0.80	0.09
Cu_HB_2	25	-0.75	20	0.91	0.08
Cu_HB_3		-0.8		0.84	0.09
Cu_HB_4		-0.6		0.76	0.10
Cu_HB_5	200	-0.75	20	0.85	0.08
Cu_HB_6		-0.8	60	0.79	0.09
Cu_HB_7			5	0.88	0.09
Cu_HB_8	25	-0.75	10	0.89	0.08
Cu_HB_9			15	0.90	0.08
Cu_HB_10	50	-0.75	20	0.98	0.07
Cu_HB_11	100			0.82	0.08
Precursor solution: (CH <sub>3</sub> COO) <sub>2</sub> Cu 0.01 M + CH <sub>3</sub> COONa 0.1 M + CH <sub>3</sub> COOH (pH=5.5)+HL					
Cu_HL_1	25			0.58	0.09
Cu_HL_2	50			0.62	0.08
Cu_HL_3	100	-0.9	20	0.60	0.08
Cu_HL_4	200			0.45	0.09

Table 1 (continued)

Precursor solution: (CH <sub>3</sub> COO) <sub>2</sub> Cu 0.01 M + CH <sub>3</sub> COONa 0.1 M +HCl (pH=5.5)+HB					
Cu_HBC_1	25			0.81	0.08
Cu_HBC_2	50			0.87	0.07
Cu_HBC_3	100	-0.8	20	0.80	0.09
Cu_HBC_4	200			0.75	0.08

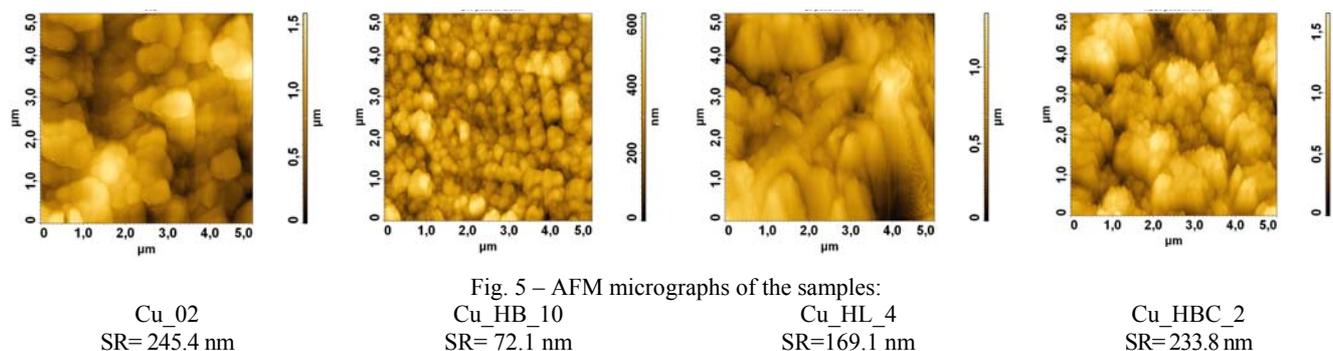
The optimum deposition conditions were obtained as following: first, the influence of different potential (-0.9...-0.6 V) in the absence of any additive (HB, HL) was studied, while the deposition time was kept constant (20 min); the performance is not good (average  $\alpha_s=0.51$ ), the best results were obtained for  $E_{\text{deposition}}=-0.75$  V (step 1). Second, the influence of different potential (-0.8...-0.6 V) in the presence of very high/low HB copolymer (25 and 200 ppm) was studied; the average solar absorptance ( $=0.85$ ) is not optimum ( $>0.9$ ), but in the case of  $E_{\text{deposition}}=-0.75$  V and 25 ppm, good results were obtained:  $\alpha_s=0.91$ ,  $\epsilon_T=0.08$  (step 2). Then the influence of the deposition time ( $= 5, 10, 15$  min) was further investigated; the results proved that lower respectively longer deposition time decrease the performance of the copper oxides based selective coating (step 3). The next deposition conditions which were tested are: fixed deposition potential (-0.75 V) and time (20 min, while intermediate HB concentrations were investigated – 50, 100 ppm); optimum values in terms of solar absorptance and thermal emittance

were obtained in the case 50 ppm HB (step 4). The influence of the HL copolymer form was also studied, this lead to poor quality thin layers (step 5). Also, different electrolyte compositions were tested by varying the similar conditions as in step 4) were tested, but using HCl as pH adjusting agent, instead of CH<sub>3</sub>COOH; the samples are not matching the performance criteria:  $\alpha_s>0.9$ ,  $\epsilon_T<0.1$  (step 6).

Thus we may conclude that the most efficient selective coating was obtained using the following deposition conditions: precursor solutions: (CH<sub>3</sub>COO)<sub>2</sub>Cu 0.01 M + CH<sub>3</sub>COONa 0.1 M + CH<sub>3</sub>COOH (pH=5.5) and 50 ppm HB,  $E_{\text{deposition}}=-0.75$  V and  $t_{\text{deposition}}=20$  min.

### Atomic Force Microscopy

Different surface morphologies (Fig. 5) and roughness were obtained, depending on the additives (HB, HL) and on the pH adjusting agent (CH<sub>3</sub>COOH and HCl).



The AFM image corresponding to the sample obtained without any additive (HB, HL) shows a non-uniform growth, with high surface roughness (SR): 245.4 nm compared to samples deposited in the presence of HB or HL copolymer. The hydrophobic form results in lower surface roughness. The HB is favouring the nucleation rate (the HB macromolecular coil is relaxed) when CH<sub>3</sub>COOH is used for adjusting the pH, resulting in smoother (72.1 nm for sample Cu\_HB\_10) and ordered surfaces, while in the case of using HCl

the growth rate is favoured and/or surface modification occurs due to possible chemical reactions between the thin film compounds and the electrolyte; this leads to large aggregates, thus higher surface roughness (233.8 nm for sample Cu\_HBC\_2). In the HL presence non-regulated, needle like topography results. These are in accordance with stretching process of the macromolecular coil proved by the HL-water voltammograms.

The best morphology, correlated with the coating performance ( $\alpha_s$ ,  $\epsilon_T$ ) were recorded in the presence of 50 ppm HB copolymer (sample Cu\_HB\_10).

### Structural characterization

Structural analyses (Fig. 6) have shown that the films consist mainly of crystalline copper I oxide (cubic, PDF 03-065-3288) and copper oxide II

(based-centred monoclinic, PDF 01-089-5895), in different ratio, depending on the deposition conditions and electrolyte composition. The substrate peaks (cubic, PDF 01-071-3761) have very high intensity; these diffraction line are also determined by the electrodeposited copper (equation 1). For the samples obtained in the presence of HL copolymer and for those with HB and HCl, crystalline  $\text{CuCl}_2$  and NaCl can be formed (Fig. 6).

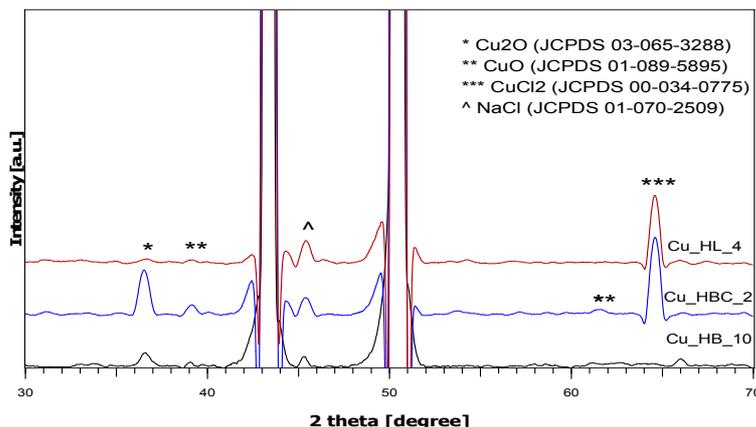


Fig. 6 – XRD patterns of samples: Cu\_HL\_4, Cu\_HBC\_2, Cu\_HB\_10.

The optical and the AFM characterization proved that the copolymers addition improves the selective surfaces performance. The influence of the hydrophilic and hydrophobic form of the copolymer on the crystallite size was investigated (Fig. 7) with the purpose of obtaining further information on the growth mechanism.

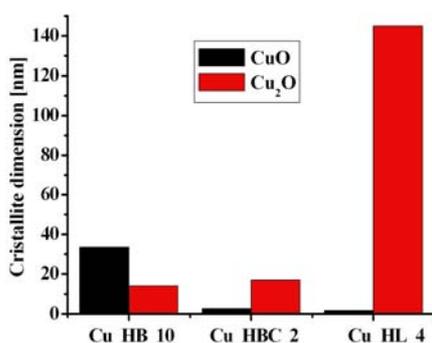


Fig. 7 – The influence of the additive type (HB, HL) on the copper oxides crystallites size.

The hydrochloric acid can have a double role: one the one hand, due to its reduction character, the HCl could reduce the neighbouring species like the copper II oxides to copper I oxides, thus the crystallite size is lowered in the case of  $\text{CuO}$  (sample Cu\_HBC\_2). Also, being a strong acid,

the hydrochloric acid can partially dissolve the  $\text{CuO}$ , also lowering the crystallite dimension, but in the same time creating areas with various shapes morphologies. These assumptions are in accordance with the AFM characterization, when higher surface roughness was obtained for this sample.

The  $\text{Cu}_2\text{O}$  growth rate is favoured in the case of sample Cu\_HL\_1. Moreover, the high copolymer concentration could lead to macromolecular coil conformation which determines the formation of large aggregates.

### CONCLUSIONS

Thin films of black copper were obtained via electrodeposition from copper and sodium acetate solutions. Additive based on maleic anhydride copolymers with controlled water solubility were tested as tailoring morphology agents. Different morphologies were obtained depending on the polymer type and concentration.

Structural analyses have shown that the films consist of Cu,  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  with different crystallite size depends on the additives presence.

The polymer addition in the precursor solution, especially the HB form improves significantly the

optical properties of the Cu/CuO<sub>x</sub> layers, while the HL does not lead to any improvement.

The interaction and stability of Cu-polymer structures, but also the modifications of the macromolecular coil conformation function on the concentration are discussed based on the voltammetric studies and correlated with the optical properties of the black copper thin films.

## REFERENCES

1. P.M.E. Koffi, H.Y. Andoh, P. Gbaha, S. Touré and G. Ado, *Energy Convers. Manage.*, **2008**, *49*, 2279-2290.
2. L. Cindrella, *Sol. Energy Mater. Sol. Cells*, **2007**, *91*, 1898-1901.
3. F. Banat and N. Jwaied, *Desalination*, **2008**, *230*, 27-40.
4. A. F. Peuser, K.-H. Remmers and M. Schnauss, "Solar Thermal Systems", Solarpraxis AG, Berlin, 2002, p.111-114.
5. J. A. Duffie and W. A. Beckman, "Solar Engineering of Thermal Processes", Wiley Interscience, New York, 1991, second edition, p. 196-197.
6. O. P. Agnihotri and B. K. Gupta, "Solar Selective Surfaces", Wiley-Interscience Publication, New York, 1981, p.10-67.
7. M. A. M. Ibrahim, *J. Appl. Electrochem.*, **2006**, *36*, 295-301.
8. C. E. Kennedy, "Review of Mid to High-Temperature Solar Selective Absorber Materials", NREL Technical Report NREL/TP-520-31267, 2002, p.9-14.
9. K. Gelin, "Preparation and characterisation of sputter deposited spectrally selective solar absorbers", PhD thesis, Uppsala, Sweden, 2004, p.17-22.
10. C. Anandan, V.K. William Grips, K.S. Rajam, V. Jayaram and P. Bera, *Appl. Surf. Sci.*, **2002**, *191*, 254-260.
11. M. Lira-Cantú, A. M. Sabio, A. Brustenga and P. Gómez-Romero, *Sol. Energy Mater. Sol. Cells*, **2005**, *87*, 685-694.
12. T. Stephen Sathiaraj, R. Thangaraj, H. Al Sharbaty and O. P. Agnihotri, *Thin Solid Films*, **1991**, *195*, 33-42.
13. www.sunselect.de, 2008.
14. www.tinox.de, 2008
15. E. Bacu, G. C. Chițanu, A. Couture, P. Grandclaoudon, Gh. Singurel and A. Carpov, *Eur. Polym. J.*, **2002**, *38*, 1509-1513.
16. M. Voinea, C. Bogatu, G.C. Chițanu and A. Duță, *Rev. Chim.*, **2008**, *59*, 659-663.
17. Y. Tang, Z. Chen, Z. Jia, L. Zhang and J. Li, *Matter Letter*, **2005**, *59*, 434-438.
18. R. P. Wijesundera, M. Hidaka, K. Koga, M. Sakai and W. Siripala, *Thin Solid Films*, **2006**, *500*, 241-246.
19. A. Duță, C. Bogatu, G. C. Chițanu and M. I. Pelin, *PSSC*, **2008**, *5*, 3530-3534.

