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Morphology, hardness, wettability and free surface energy of various copper surfaces

ABSTRACT

This paper aims to analyze wettability and the free surface energy of various copper surfaces. The Cu deposits produced galvanostatically from the basic sulphate electrolytes without and with an addition of levelling and brightening additives, and cold-rolled (c-r) Cu simultaneously used as the cathode in Cu electrodeposition processes have been investigated. Hardness of electrolytically produced Cu deposits was also determined. The wettability and the free surface energy of Cu surfaces were examined applying the OWRK (Owens–Wendt–Rabel–Kaelble) method, while morphology and hardness characterization of the surfaces was done by atomic force microscope (AFM) and Vickers microindentation, respectively. The surface roughness obtained by AFM software was used as a parameter for comparison of a state of various Cu surfaces. The Jönsson–Hogmark composite hardness model was used to determine the absolute hardness of Cu electrodeposits, and the obtained values of 1.509 GPa for microcrystalline (mc) deposit obtained from the basic sulphate electrolyte and 1.130 GPa for the nanocrystalline (nc) deposit obtained from the electrolyte containing levelling/brightening additives were in excellent agreement with those found in literature for copper. The surface roughness of Cu increased in the row: nc (30.84 nm) < c-r (83.22 nm) < mc (129.3 nm), causing the change of a state of Cu surfaces from hydrophilic to hydrophobic. Analysis of tensile and yield strengths of Cu surfaces computed from microhardness data, and the free surface energy values determined by the OWRK method also indicated on the strong correlation between a roughness and these properties of Cu surfaces.

Keywords: *copper; electrodeposition; film; morphology; hardness; wettability; the free surface energy.*

1. INTRODUCTION

Thanks to extraordinary characteristics, such as high electrical and good thermal conductivity, copper in the form of thin film/deposit found wide applications in electronics, optoelectronics, and materials science [1]. In the last time, Cu thin deposits are used for energy storage as current collectors and electrodes in batteries and supercapacitors. Also, Cu shows antimicrobial properties. A wide application of Cu is closely related with the facts that it is abundantly available and relatively cheap metal, making it a favourable choice for large-scale production.

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The different methods are proposed to produce Cu in the form of thin deposits such as physical vapour deposition, chemical vapour deposition, and electroplating [1]. Electroplating or electrodeposition has certain advantages over the other techniques that are related with easy control of surface morphology by a simple selection of parameters and regime of electrodeposition [2]. Morphology of the electrodeposits depends on chemical (composition of electroplating bath, pH), electrical (constant – potentiostatic/galvanostatic and pulse reverse current (PRC) regimes of electrodeposition) and physical (electrodeposition time, i.e. thickness, temperature, agitation of electroplating bath, kind and preparation of the cathode) parameters.

Hardness of the electrodeposits represents one of the most pertinent mechanical properties of deposits, because many of their applications are closely related with this property [3]. When microindentation technique is used to determine deposit hardness, researchers meet with a challenge how to determine an absolute (true) hardness of deposit without a contribution of a substrate to a measured hardness value. Generally, two ways are proposed to do it: (a) use of low indentation loads, and (b) use of composite hardness models (CHMs), such as Chicot–Lesage (C–L) model [4-6], Korsunsky (K) model [7,8], Chen–Gao (C–G) model [9,10], Jönson–Hogmark (J–H) model [11], Puchi–Cabrera (P–C) model [12], etc.

The concept of a contact angle has been proposed to quantitatively describe hydrophilicity and hydrophobicity of solid materials [13]. A solid surface is described as hydrophilic if its contact angle is less than 90°, and hydrophobic if contact angle is greater than 90° [13].

The free surface energy can be calculated using different methods [13]. The calculation methods using a contact angle include the Fowkes method [14], the Wu average method [13] and the OWRK (Owens–Wendt–Rabel–Kaelble) method [13]. In this paper, the OWRK method is applied to calculate the free surface energy of copper substrate and deposits. The OWRK method divides the free surface energy into two components: dispersive (non-polar) and polar interactions. Fluids suitable for this method are distilled water and glycerine, although diiodomethane is the most often used as dispersive component in a practice. However, diiodomethane is toxic, light-sensitive, and non-stable fluid, making it less desirable in lab environments. On the other hand, glycerine is a non-toxic, safe, and easier to handle in a lab conditions. In some cases, diiodomethane also gives contact angles too close to zero, what reduces an accuracy of the OWRK model, while the use of two polar components such as water and glycerine gives relevant results for the free surface energy.

The value of the free surface energy of a film means how well liquids spread on a film surface. A high free surface energy value indicates good wetting of the film and the presence of strong adhesion. Also, the high free surface energy value of a film can indicate a type of nucleation, the so-called layer-by-layer growth [15]. Modification of copper surfaces by electrodeposition is a common way to increase the polar surface energy parts, thereby achieving improved adhesion and reduced delamination of the surface.

In this study, morphologies of the electrodeposits obtained from electrolytes of various compositions (without/with an addition of levelling/brightening additives) are correlated with their hardness, wettability and the free surface energy values. Cu electrodeposits were produced galvanostatically using magnetic stirring of the electrolyte, while an absolute (true) hardness of the electrodeposits was estimated by an application of Jönsson–Hogmark (J–H) CHM. Subsequently, the wettability and the free surface energy of the copper films were calculated using the OWRK method. Comparison with cold-rolled Cu surface which was used as a substrate for Cu electrodeposition was made. The surface roughness was used as a parameter for a comparison of various Cu surfaces.

2. EXPERIMENTAL

Copper was electrodeposited galvanostatically at a current density of 50 mA cm^{-2} from:

(a) Basic sulphate electrolyte: 240 g L^{-1} $CuSO_4 \cdot 5H_2O$ + 60 g L^{-1} H_2SO_4 (Cu-Basic), and

(b) Electrolyte with addition of levelling/brightening additives: 240 g L^{-1} $CuSO_4 \cdot 5H_2O$ + 60 g L^{-1} H_2SO_4 + 0.124 g L^{-1} NaCl + 1 g L^{-1} PEG 6000 (polyethylene glycol) + 0.0015 g L^{-1} MPSA (3–Mercapto–1–propanesulfonic acid), (Cu-Additives).

Cu electrodeposition was performed at room temperature applying magnetic stirring of the electrolyte in an open cell of the prismatic shape. The thicknesses of deposits were 10 μm. Both cathode and anode were of pure copper. The cold-rolled Cu cathode (1.0 × 1.0) cm^2 surface area was situated between two parallel Cu anodes. The doubly distilled water and p.a. reagents were used for the electrolyte preparation.

The surface characterization of Cu deposits was done by atomic force microscopy (AFM; model Auto Probe CP Research; TM Microscopes – Veeco Instruments) technique, using Gwyddion – Free SPM data analysis software.

Hardness of Cu films was done by Vickers microindentation, using loads between 0.049 and 2.94 N, and a dwell time of 25 s.

Tensile (T_s) and yield strengths (Y_s) of Cu surfaces were computed from the microhardness data, i.e. from the absolute hardness of the surfaces.

To investigate the effect of a microstructure on the wettability of copper, two kinds of Cu deposits were fabricated, and compared with cold-rolled Cu (cathode) surface area. Using a high-resolution camera and an optical microscope, images of liquids drop on Cu cathode without and with the synthesized Cu deposits after few days were taken. The 5 μL of double distilled water and glycerine were dripped onto them at six different locations. Using an image processing programme (GYMP), the water contact angles were calculated as the average value from independent measurements by drawing a tangent between the solid (Cu surface) and the drop (water and glycerine). The method is known as the drop sessile method with multiple liquids. It is important to note that the droplet was photographed 3 seconds after it touched the solid surface. The measured values of contact angles for water and glycerine were used to calculate the free surface energy of Cu using OWRK model.

3. RESULTS AND DISCUSSION

The 2D (two dimensional) AFM pictures of various Cu surfaces are shown in Figure 1 (Figure 1a–the Cu deposit obtained from the additive-free electrolyte, Figure 1b–the Cu deposit obtained from the electrolyte containing additives, and Figure 1c–the cold-rolled copper foil (cathode)).

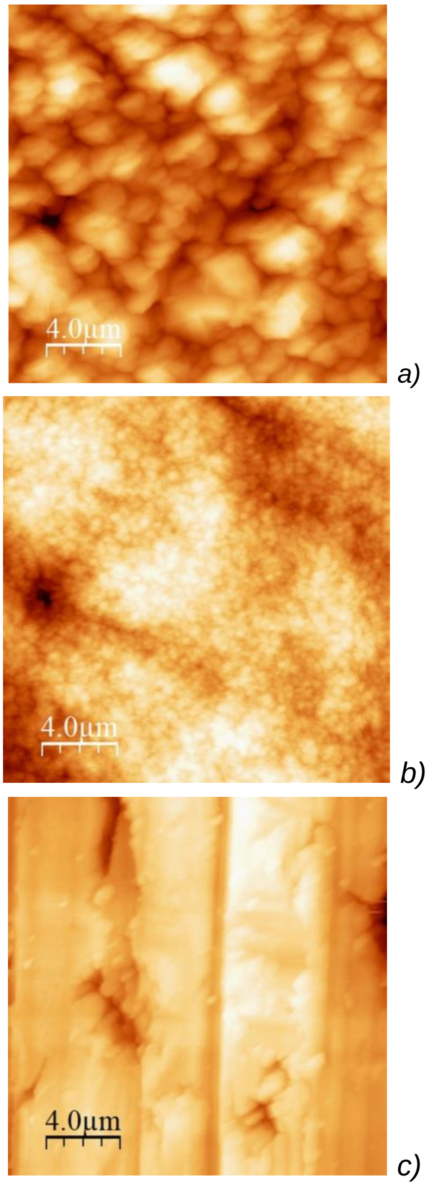

Figure 1. The 2D AFM images of various copper surfaces: a) the Cu deposit electrodeposited from the basic sulphate electrolyte, b) the Cu deposit electrodeposited from the electrolyte with additives, and c) the Cu substrate. The scan size was 20×20 μm^2

The microcrystalline (mc) deposit with clearly visible grains was obtained by the electrodeposition from the basic sulphate solution (Figure 1a). The Cu film obtained from the electrolyte containing additives is very smooth, and individual grains were not detected in it, indicating on nanocrystalline (nc) character of this deposit (Figure 1b). The cold-rolled Cu surface (cathode) had numerous channels and other imperfections formed during the process production (Figure 1c). The values of an arithmetic average of the absolute surface roughness (S_a) for these Cu deposits were: 129.3 nm for the Cu deposit obtained from the basic sulphate electrolyte, 30.84 nm for that obtained from the electrolyte with added levelling/brightening additives. The roughness parameter (S_a) of the copper foil was 83.22 nm. The area from which the surface roughness parameters are calculated were 20 × 20 μm^2.

The Vickers microhardness is defined by Eq. (1) [16]:

$$H_c = \frac{1.8544 \cdot P}{d^2} \tag{1}$$

where H_c is the measured hardness of the deposit, P is the applied load, and d is a size of an imprint diagonal in a deposit. The diagonal size is related with a depth of indentation, h as $h = d/7$.

This measured hardness usually contains contributions of hardness both film (deposit) and substrate (cathode), and for that reason, it is referred as the composite hardness. There is no unique opinion when commences an effect of substrate on the measured hardness of a film. The oldest rule is so-called Buckle`s rule predicting that an effect of a substrate commences above 10 % from the overall film thickness, i.e. for $h_c > 0.10\delta$ (h_c – the critical indentation depth; δ – the film thickness) [17]. Also, there are other opinions taking into consideration the film/substrate hardness ratios. So, the conditions $h_c > 0.20\delta$ for “soft polycrystalline film on hard substrate”, and $h_c > 0.070\delta$ for “hard polycrystalline film on soft substrate” systems were proposed [18]. The condition $h_c \geq 0.14\delta$ was proposed for “soft polycrystalline film on hard substrate” systems, such as copper films electrodeposited on the brass and Si(111) substrates by constant galvanostatic (DC) and by the pulsating current (PC) regimes [16,19].

As already mentioned, one of ways to separate a contribution of substrate (cathode) in a measured (composite) hardness, and hence, to determine a pure (absolute) deposit hardness is an application of composite hardness models (CHMs). The 10 μm thick Cu deposits on Cu cathode belong to "hard polycrystalline film on soft substrate" type, and almost all recorded H_c values were situated in so-called composite zone, i.e. in the zone where Cu cathode strongly contributed to measured value of the hardness [20]. Hence, it is necessary to apply an appropriate CHM to obtain the absolute hardness of the Cu deposits, and Jönsson–Hogmark (J–H) CHM [11] was selected to do it.

According to Jönsson–Hogmark (J–H) model, correlation among composite hardness, H_c, the absolute hardness of a deposit, H_f, substrate hardness, H_s, deposit thickness, δ and diagonal size, d can be represented by Eq. (2), [11]:

$$H_c = H_s + \left[2C\left(\frac{\delta}{d}\right) - \left(C\left(\frac{\delta}{d}\right)\right)^2\right]\cdot\left(H_f - H_s\right) \qquad (2)$$

In Eq. (2), C = 0.50 is taken for "hard film on soft substrate" composite system [11]. The hardness of used Cu substrate (cathode) was 0.56 GPa [20]. Figure 2 shows the dependencies of H_c on δ/d, together with the dependencies obtained by the fitting of Eq. (2).

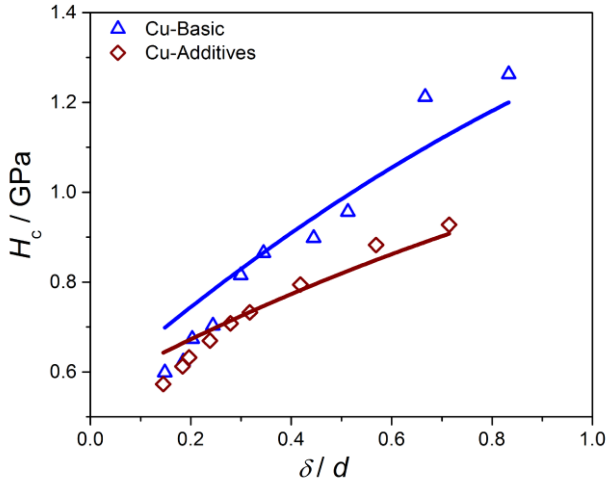

Figure 2. The dependencies of H_c on δ/d with included fitting dependencies according to Jönsson–Hogmark (J–H) model

The calculated values of the absolute hardness of deposits were: 1.509 GPa for the microcrystalline Cu deposit obtained from the pure sulphate electrolyte, and 1.130 GPa for the nanocrystalline Cu deposit obtained from the electrolyte with the additives. The obtained values were in excellent agreement with those found in different researches, since the values in a range between 0.70 and 1.74 GPa were usually reported [21, 22, 23]. Also, the obtained values were in accordance with those obtained by application of Korsunsky (K) model for the same Cu deposits (1.351 GPa for the deposit obtained from the pure sulphate electrolyte, and 1.135 GPa for the deposit obtained from the electrolyte with the additives) [20]. This clearly points out that J–H CHM is successfully applied in an evaluation of the absolute hardness of the Cu deposits, and as such, it represents a valuable way for hardness analysis of thin metal deposits which belong to "hard polycrystalline film on soft substrate" type. The calculated values of hardness of the deposits and the substrate are summarized in Table I.

Table I. Results of calculated hardness, and strengths (tensile and yield) of Cu substrate and Cu deposits using microhardness data

No.	Hardness (H_s or H_f) / [MPa]	T_s [N/mm^{-2}]	Y_s [N/mm^{-2}]
Cu substrate	560	1989	1519.9
Cu deposit without additives	1509	5528.8	4249.2
Cu deposit with additives	1130	4115.1	3159.2

According to linear model, a tensile strength T_s, and an yield strength Y_s of a deposit or a substrate can be represented by Eq. (3) for tensile, and by Eq. (4) for yield strengths [24, 25, 26]:

$$T_s = -99.8 + 3.73 H_f \qquad (3)$$

$$Y_s = -90.7 + 2.876 H_f \qquad (4)$$

The calculated values of tensile strength, T_s and yield strength Y_s for Cu substrate and Cu deposits are given in Table I.

It can be seen from Table I that Cu deposits made by the electrodeposition processes without/with additives tend to have higher strengths than the Cu substrate made by rolling. The micro-grained deposit electrodeposited from the electrolyte without additives showed higher strengths than the nano-grained deposit obtained from the electrolyte with additives. The relationship between the tensile strength and the grain size in the copper deposits is a classic example of how microstructure influences on mechanical properties of a deposit, especially in thin films: smaller grain size generally increases a tensile strength due to the Hall-Petch relationship, but there is a limit due to an inverse Hall-Petch effect [27]. In the case of Cu deposit obtained with additives, grain sizes drop below ~100 nm, and the Hall-Petch relationship makes an inverse effect, causing the decrease of strengths. For this scale, grain boundary sliding and diffusion-based deformation dominate, causing softening instead of strengthening effect. By comparing the tensile strengths, microcrystalline copper deposit shows an increase in the strength of 34 % compared to the nanocrystalline copper deposit, and 178 % compared to cold-rolled bulk Cu foil.

For an application of Cu deposits in various industrial conditions, especially in harsh weather conditions, there is a high demand for a surface hydrophobicity of a film [28]. In this study, a sessile drop test is performed to determine the water contact angle (WCA) and the glycerine contact angle (GCA) of all surfaces (Cu substrate (foil), additive-free Cu deposit, and Cu deposit obtained with additives), and thus determine whether Cu surfaces are hydrophobic or hydrophilic.

A WCA for Cu foil was estimated to be ~90.6 ° as shown in Figure 3a, which indicates that the cold-rolled foil used as the cathode is at a limit of hydrophobicity (i.e. it has a moderate wettability). The microcrystalline Cu deposit electrodeposited from the basic sulphate electrolyte exhibits a full hydrophobic character with WCA of ~118.4 °, as shown in Figure 3b. Certainly, it can be ascribed to the increase in the surface roughness relative to the Cu substrate. The addition of levelling/ brightening additives in the electrolyte contributes to a reduction in the contact angle values and a complete transition from a hydrophobic to a hydrophilic deposit was observed. It can be seen from Figure 3c that the additives switches the Cu surface from hydrophobic to hydrophilic, especially when amphiphilic molecules like MPSA are used [29]. PEG has long $–CH_2CH_2O$-parts that increase a polar component, while MPSA has thiol group (-SH) and sulfonic acid ($-SO_3H$) groups. A hydrophilic part of MPSA molecule (sulfonic acid group) is a highly polar part that has hydrophilic nature. The synergistic effect of polar and non-polar parts of additives will be explained through the value of the free surface energy (polar/dispersive parts and total).

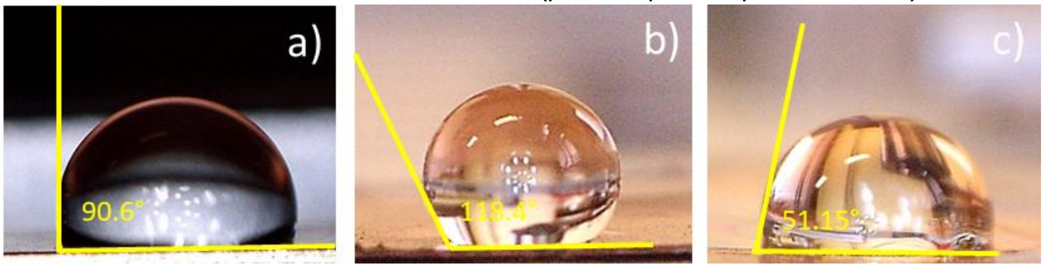

Figure 3. Images of water droplet on the surface of the Cu: a) substrate, b) Cu deposit without additives, and c) Cu deposit with additives

A GCA for Cu substrate (foil) was estimated to be ~83.58°, as shown in Figure 4a, and 98.80° for the additive-free Cu deposit, as shown in Figure 4b. The addition of all three additives contributes to a reduction in the GCA to ~78.80°, see Figure 4c.

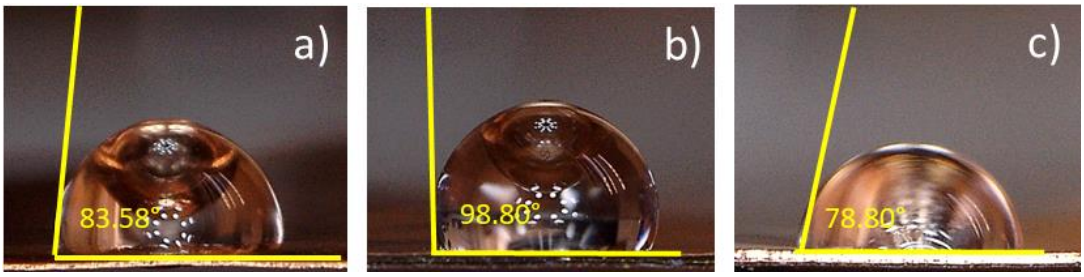

Figure 4. Images of glycerine droplet on the surface of the Cu: a) substrate, b) Cu deposit without additives, and c) Cu deposit with additives

For a calculation of the free surface energy with two polar liquids, the surface force parameters for water and glycerine were taken from literature and include a surface tension, a dispersion force and a polarity force for both liquids [13]. These parameters are given in Table II.

Using the surface tension and the dispersion/polar force values for water and glycerine, the free surface energy of solid and its dispersion/polar parts of surfaces can be calculated using Eq. (5) [30]:

Table II. Surface force parameters for a calculation of the total free surface energy of various Cu surfaces according to OWRK method

liquid	Surface tension, γ_l [mJ/m^2]	Dispersion force, γ^D [mJ/m^2]	Polarity force, γ^P [mJ/m^2]
water	72.8	21.8	51.0

glycerine	64	34.0	30.0

$$\cos(\theta) = -1 + 2\sqrt{\gamma_s^D}\left(\frac{\sqrt{\gamma_L^D}}{\gamma_L}\right) + 2\sqrt{\gamma_s^P}\left(\frac{\sqrt{\gamma_L^P}}{\gamma_L}\right) \quad (5)$$

The calculated values of the total free surface energy and their components for copper substrate and deposits without/with additives are presented in Table III.

Table III. Contact angles (WCA and GCA) and surface free energy (polar, dispersive and total) of the copper substrate and the copper deposits

No	WCA / °	GCA / °	Dispersion energy of Cu, γ^D [mJ/m^2]	Polar energy of Cu, γ^P [mJ/m^2]	Total free energy of Cu, γ [mJ/m^2]
Cu substrate	90.6	83.58	12.6	7.4	20.0
Cu deposit without additives	118.4	98.80	31.7	1.0	32.7
Cu deposit with additives	51.15	78.80	10.1	106.9	117.0

It is clear from Table III that the total free surface energy of Cu increased from Cu substrate to Cu deposits from 20.0 to 32.7 and 117.0 mJ/m^2 when a combination of levelling/brightening additives was added. However, moderate wettability properties of copper substrate and low value of the free surface energy indicates that there is an effect of the substrate texture and roughness, considering that the substrate was obtained by cold rolling. However, hydrophobicity and the higher dispersion energy part of the additive-free copper deposit relative to cold-rolled substrate and the Cu deposit obtained with additives indicate that this copper deposit surface is a less polar. The possible reason for it is a rapid oxidation of this Cu deposit, a rougher surface susceptible to a penetration of gases from the environment (hydrocarbons or oxygen-containing molecules), which can increase a hydrophobicity and a dispersion energy [30]. The dramatic increase of the polar component of the free surface energy was observed in the copper deposit with a combination of all three additives. It is due to the thiol group from MPSA having a strong Cu-S bond and self-assembled monolayers (SAMs) on the Cu surface as very strong hydrophilic and polar part [29]. The sulfonic acid as a terminal group makes the surface highly polar and hydrophilic. PEG has the same effect due to the presence ether groups (hydrophilic effect).

In the overall view, the additives change the free surface energy of the deposit through their combined effect that is also reflected in the topography. It is therefore not possible to say with a certainty whether the more dominant effect is the roughness of the deposit surface or the effect of individual functional groups from the additives. It can only be said with a certainty is that glossy and smooth deposits have much higher surface free energy values than rough films.

4. CONCLUSION

The two kinds of deposits produced by the galvanostatic regime of the electrodeposition were analyzed: (a) the microcrystalline deposit formed by the electrodeposition from the basic sulphate electrolyte, and (b) the nanocrystalline deposit formed by the electrodeposition from the electrolyte with added additives for levelling and brightness. The absolute hardness of produced electrodeposits was determined by application of Jönsson–Hogmark (J–H) composite hardness model.

The estimated absolute hardness of the microcrystalline deposit (H_f = 1.509 GPa) was larger than the nanocrystalline deposit (H_f = 1.130 GPa). The calculated values were in a good agreement with known values for Cu films/deposits, confirming a successful implementation of this CHM in a determination of the absolute hardness of Cu deposits.

The microcrystalline copper deposit exhibits an increase in the tensile strength of 34 % compared to nanocrystalline copper deposit and 178 % compared to cold-rolled bulk copper substrate.

The wettability properties of the Cu cathode and Cu deposits were analysed by WCA measurements. In a comparison with Cu substrate (WCA is 90.6°), it is found that the increase of the hydrophobicity was observed for the microcrystalline Cu deposit obtained from the basic sulphate electrolyte (WCA is 118.4°), and the decrease for the Cu deposit obtained from electrolyte with all three additives (WCA is 51.15°). Hence, the surface of Cu deposits became more hydrophilic or hydrophobic compared to pure copper surface.

Based on the analysis of the free surface energy values, there is a correlation between the wettability and the free surface energy of copper. For the electrodeposited copper films, the free surface energy had an opposite trend to the surface roughness parameters. As the surface roughness increased, the free surface energy of the film decreased. The Cu deposit obtained with additives showed a significantly increase in the polar component of the surface energy, which makes such deposits extremely hydrophilic towards polar solvents, i.e. wetting is significantly improved.

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IZVOD

MORFOLOGIJA, TVRDOĆA, KVAŠLJIVOST I SLOBODNA POVRŠINSKA ENERGIJA RAZLIČITIH POVRŠINA BAKRA

Ovaj rad ima za cilj da analizira kvašljivost i slobodnu površinsku energiju različitih površina bakra. Talozi bakra proizvedeni galvanostatski iz osnovnih sulfatnih elektrolita bez i sa dodatkom aditiva za poravnavanje i sjaj, i hladno valjani (h-v) Cu istovremeno korišćen kao katoda u procesima elektrohemijskog taloženja bakra su bili istraženi. Tvrdoća elektrolitički proizvedenih bakarnih taloga je bila takođe određena. Kvašljivost i slobodna površinska energija bakarnih površina su bile ispitane primenom OWRK (Owens–Wendt–Rabel–Kaelble) metode, dok morfolologija i tvrdoća su bile urađene mikroskopom na bazi atomskih sila (AFM) i Vikersovom mikroindentacijom, respektivno. Površinska hrapavost dobijena primenom AFM računarskog paketa je korišćena kao parametar za poređenje stanja različitih površina bakra. Jönsson–Hogmark kompozitni model tvrdoće je bio korišćen da se utvrdi absolutna tvrdoća elektrohemijski istaloženih taloga bakra, i dobijene vrednosti od 1,509 GPa za mikrokristalni (mk) talog dobijen iz osnovnog sulfatnog elektrolita i 1,130 GPa za nanokristalni (nk) talog dobijen iz elektrolita koji sadrži aditive za poravnavanje i sjaj su bile u odličnom slaganju sa onima nađenim u literaturi za bakar. Površinska hrapavost bakra se povećavala u nizu: nk (30.84 nm) < h-v (83.22 nm) < mk (129.3 nm), prouzrokujući promenu stanja bakarnih površina iz hidrofilne u hidrofobnu. Analiza zatezne čvrstoće i granice tečenja bakra sračunatih iz podataka mikrotvrdoće, i vrednosti slobodne površinske energije određene OWRK metodom su takođe ukazale na strogu korelaciju između hrapavosti i ovih osobina bakarnih površina.

Ključne reči: *Bakar; elektrodepozicija; film; morfologija; tvrdoća; kvašivost; slobodna površinska energija.*

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