Wettability of electrodeposited copper films and correlation with morphology and surface chemistry

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***Abstract*— In this study, different forms of copper films were electrodeposited (ED) on silicon wafer, copper and brass foils. The effect of monocrystalline Si(111) surface cleaning method and electrodeposition conditions and regimes (frequency in the pulsating current (PC) regime, an addition of additives in electrolyte for the constant galvanostatic (DC) regime, and thickness) on surface morphology and wettability of copper films was investigated. Optical microscopy equipped with high-resolution camera, scanning electron microscopy (SEM) and an atomic force microscopy (AFM) were used for thin film characterization and to evaluate wettability of copper films. The sessile drop method was used for the measurement of water contact angle. According to the obtained results, choice of electrolyte used in ED greatly affects wettability of copper films. It was also shown that copper films electrodeposited from basic sulfate electrolyte with varying current regimes frequencies, thicknesses, and cathode types have opposite trends between roughness parameter values and the water contact angle value. Structural-morphological changes of a film or bulk solid surface are key parameters in determining wettability properties and the analysis of the wetting angle oscillations, but not the only one.**

***Index Terms*— wettability, water contact angle, sessile drop method, copper films, hydrophilic, image analysis.**

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I. INTRODUCTION

WETTABILITY of the solid surface such as thin metallic films is typically measured by the water contact angle (θ_C) and sliding angle (θ_{SA}), using goniometry [1, 2]. Water contact angle is defined as the angle between the solid surface, in this case surface of electrodeposited copper films, on different cathode materials, and the tangent to the liquid drop surface (polar type liquid in this study). If the value of the water contact angle is less than 90°, the film surface has hydrophilic nature and solid surface prefers to be covered by water [1-3]. If the value of the water contact angle is greater than 90°, the solid surface has hydrophobic nature and surface of the film prefers to stay dry [1-3].

Wetting of a smooth or low roughness and chemically uniform films surface depends only on the intrinsic chemistry of the films, while wetting of a rough film surface depends on both, the intrinsic chemistry and the roughness topography [4]. It is known that the mechanism of wetting of a solid rough substrate or films is described by the Wenzel's model [4, 5]. This model was developed to estimate the wettability of rough surface, because the wetting on rough surface has two mechanisms: 1) homogeneous wetting (water completely penetrates into grooves), and 2) heterogeneous wetting (the air first penetrates into rough groove and then water) [4, 5]. The Wenzel's equation is given as [4, 5]:

$$cos(\theta_C) = r \cdot cos(\theta_Y) \quad (1)$$

where, θ_C is water contact angle, r is roughness ratio (the ratio of the actual area of the surface to its projection (r equal 1 for a smooth surface) and θ_Y is the Young contact angle (contact angle of the smooth surface). Young contact angle can be calculated as [4, 5]:

$$cos(\theta_Y) = \frac{\sigma_S - \sigma_{SL}}{\sigma_L} \quad (2)$$

where σ_S, σ_{SL}, and σ_L are the surface tensions of the solid (σ_S), liquid (σ_L) and the solid-liquid interfacial tension (σ_{SL}) or free surface energy (γ) [4, 5]

The interaction between water drops and solid films is given in Fig. 1. The water resistivity of films can be divided in

two basic categories: clear hydrophilic films (10° < θ_C < 90°), and clear hydrophobic films (θ_C > 90°), and three secondary categories: super-hydrophilic (θ_C < 10°), super-hydrophobic (θ_C > 150°) and neutral water resistivity films (θ_C = 90°) [6], see Fig. 1.

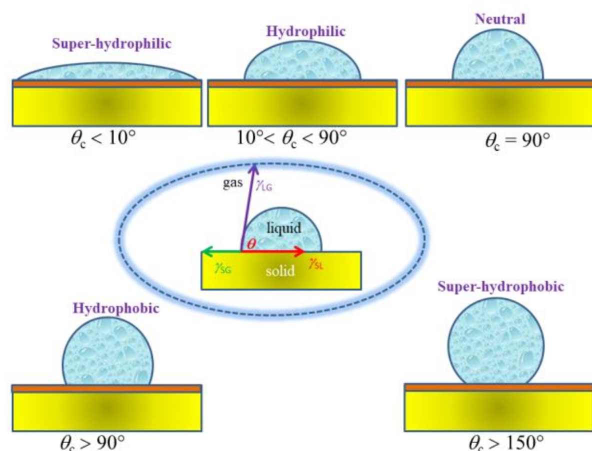

Fig. 1. Graphical representation of wetting of solid surface (substrate + film) with limit cases for water contact angle size, and solid-liquid, solid-gas, and liquid-gas interfacial tensions.

Electrodeposition is a relatively fast eco-friendly scalable technique for the fabrication of variable textured surfaces with micro- or nanostructured characteristics of all technologically important metal films such as Cu, Ni, Au, Ag, etc. [7-10]. This technique can be used to control surface topography with the ability to monitor and adjust surface roughness and crystallite size [11]. Easy control of the layer thickness on the conductive substrate is another advantage of this technique and is determined by the electrochemical parameters such as: current density for galvanostatic regime, voltage for potentiostatic regime, deposition time, types of electrolyte mixing and composition of electrolyte, bath temperature and cathode types [12].

In our previous studies, it was shown that the increasing deposition time (i.e. coating thickness) during electrodeposition of copper coatings on brass and silicon substrates from basic sulfate electrolyte results in an increase of surface roughness [13-15] and leads to drastically change in mechanical features of the films (hardness, adhesion, and creep resistance).

The goal of this investigation is the fabrication of less hydrophilic copper films and investigation of microstructural modification and correlation with wettability. This trend is very important because the wetting resistant copper film has better adhesion strength to the substrate [16] and better corrosion properties [17]. The decrease of wettability makes the minimum surface contact between copper and pathogens, and as a result of this, antimicrobial action will be slower [18] causing an increase of the range of application of copper films (e.g., sensors for microbiological purposes and medicine).

Within this work, few key wetting parameters were observed: 1) the influence of the substrate wafer cleaning method on the wetting of the adhesion/nucleation layer of Cr/Au on silicon, 2) the influence of the frequency (i.e. duty cycle or an average current density) in the pulse mode of deposition copper films on brass, 3) the influence of the film thickness in the pulse mode on Si/Cr/Au substrate and 4) the influence of the composition of the electrolyte on copper film wettability after deposition on copper substrate.

II. Experimental

A. *Cleaned process of silicon wafer and metallic foils*

The wettability of the silicon substrates depends on many factors such as cleaned process, aging of the silicon wafer after cleaning and type of silicon wafer (orientation, doping elements) [19]. Two different types of standard cleaning process of Si(111) substrates (p-type, resistivity: 5 000 Ω·cm, depth: 300 ± 15 µm, Wacker-Chemitronic GMBH, Germany) were applied: 1) using piranha solution (3:1 mixing of 96% H_2SO_4 and 30% H_2O_2 at 100 C°) and 2) HF acid (49%) at the room conditions. After that we have chosen better cleaning method according to criteria “hydrophilic nature” (cleaning in piranha) for sputtering thin adhesion/nucleation seed layers of Cr/Au = 30/100 nm for electrochemical deposition of copper films.

Before the deposition of copper films on the metallic foils (copper and brass) they are first washed, degreased and polished.

B. *Preparation of electrolyte for copper film deposition*

Electrodeposition of copper coatings was performed using four electrolyte types. The recipes of the used electrolytes are given, and notated as **E**$_1$-**E**$_4$:

1) Basic acidic sulphate electrolyte (240 g/L $CuSO_4 \cdot 5\ H_2O$ in 60 g/L H_2SO_4)-**E₁**,

2) Basic sulphate electrolyte with additions of Cl^- ions (240 g/L $CuSO_4 \cdot 5H_2O$, 60 g/L H_2SO_4, 0.124 g/L NaCl)-**E₂**,

3) Basic sulphate electrolyte with additions of Cl^- ions and polyethylene glycol (240 g/L $CuSO_4 \cdot 5H_2O$, 60 g/L H_2SO_4, 0.124 g/L NaCl, 1 g/L PEG 6000)-**E₃**, and

4) Basic sulphate electrolyte with additions of Cl^- ions, polyethylene glycol and 3−Mercapto−1−propanesulfonic acid (240 g/L $CuSO_4 \cdot 5H_2O$, 60 g/L H_2SO_4, 0.124 g/L NaCl, 1 g/L PEG 6000, 0.0015 g/L MPSA)-**E₄** [20].

C. *Electrodeposition parameters*

The parameters of the PC regime used in the electrodeposition processes are: the current density amplitude (j_A), deposition time (t_{on}), pause time (t_{off}), the average current density (j_{av}), and frequency (f). The duration of the deposition process (τ) was calculated based on Faraday's law for a limited deposition surface area.

Electrodeposition of copper films (20 µm thick) on prepared brass substrate was obtained from basic sulphate electrolyte ($\boldsymbol{E}_1$) in the PC regime. Series **A** with four samples was made at constant deposition pulse (t_{on} = 5 ms) and the current density amplitude (j_A = 100 mA·cm^{-2}) with variations of t_{off}, and consequently j_{av} and f. Samples are as follows: **A₁** (τ = 60’ 11’’, j_{av} = 15 mA·cm^{-2}, t_{off} = 5 ms, f = 30 Hz), **A₂** (τ

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=36’ 7’’, j_{av} = 25 mA·cm^{-2}, t_{off} = 15 ms, f = 50 Hz), **A$_3$** (τ = 22’ 35’’, j_{av} = 40 mA·cm^{-2}, t_{off} = 7.5 ms, f = 80 Hz), and **A$_4$** (τ = 18’ 3’’, j_{av} = 50 mA·cm^{-2}, t_{off} = 5 ms, f = 100 Hz).

Series **B** of copper films on silicon substrate was obtained from basic acidic sulphate electrolyte in pulsating current (PC) regime with variation thickness, δ, (**B**$_1$ (δ = 10 μm, τ = 9’ 2’’), **B**$_2$ (δ = 20 μm, τ = 18’ 4’’), **B**$_3$ (δ = 40 μm, τ = 36’ 8’’), and **B**$_4$ (δ = 60 μm, τ = 54’ 12’’)) at: j_{av} = 50 mA·cm^{-2}, t_{off} = 5 ms, and f = 100 Hz.

Series **C** of copper films on copper substrate was obtained from four electrolytes given in the *section B* (samples are: **C$_1$** (from electrolyte **E**$_1$), **C$_2$** (from **E**$_2$), **C$_3$** (from **E**$_3$), and **C$_4$** (from **E**$_4$)) at the room temperature by the regime of direct current (DC) with magnetic stirring of electrolytes. The current density in DC regime (j) was 50 mA·cm^{-2} and film thickness was 10 μm.

D. Characterization

The morphology of the 10 μm Cu films on Cu foils in DC regimes with variation electrolyte types was examined by scanning electron microscope (SEM)—model JEOL JSM-6610LV (JEOL Ltd., Tokyo, Japan). Morphology of Cu coatings in PC regimes on Si and brass substrate can be seen in our earlier publications [13-15]

The surface topography of all Cu coatings with (50 × 50) μm^2 scan area was examined using an atomic force microscope (“Auto Probe CP Research; TM Microscopes, Veeco Instruments, Santa Barbara, CA, USA”) in the contact mode. The values of an arithmetic average of the absolute (R_a) and Root Mean Square (R_q) roughness parameters were measured from the mean image size 256 × 256 pixels, using software Gwyddion [21].

The wetting properties of the copper coatings and substrates were measured using an optical microscope and high-resolution camera (“Smart 5MP Pro, Delta Optical Instruments, Inc, North Little Rock, Arkansas, USA”) with 5 μL water drops (double distilled), using sessile drop method [1]. The water drops and static contact angles (θ_w) were analyzed after take of photography of drops on solid surface (5 seconds after placing the drop) and determined using the image analysis software Image-Pro Plus 4.0 (“Media Cybernetics Inc, Rockville, Maryland, USA”) [22]. The water contact angle measurement was repeated five times at different location of the sample and an average value was taken as the relevant measurement results. The sessile drop method was performed at room conditions (temperature: 25°C and relative humidity: 50 %).

III. Results and Discussion

A. Microstructural analysis

The series “**C**” was chosen for microstructural analysis of copper films electrodeposited on copper foil by applying DC current regime, using different electrolyte types (noted as **E**$_1$-**E**$_4$). Depending on a combination of additives added in the basic sulphate electrolyte, there is a change in the microstructure and appearance of the morphologies of the copper films, as shown in Fig. 2.

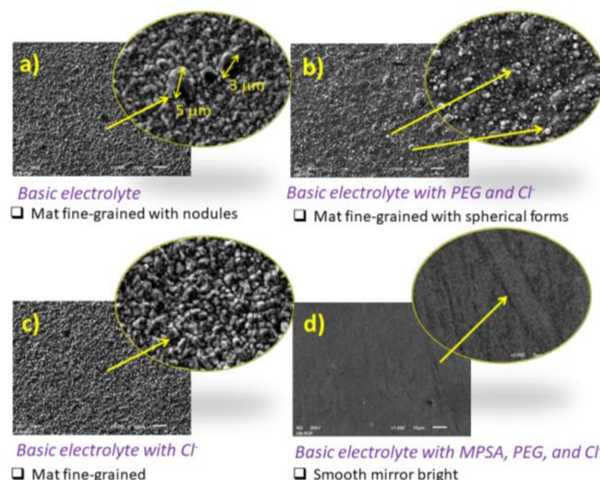

Fig. 2. SEM micrographs for 10 μm thick Cu films electrodeposited on Cu foils in DC regime with magnetic stirring of the electrolyte from: a) electrolyte **E**$_1$, b) electrolyte **E**$_3$, c) electrolyte **E**$_2$, and d) electrolyte **E**$_4$. Magnification for square images were ×1000 and for details ×3000 (oval images).

The copper film with mat appearance and fine-grained microstructure was obtained from the electrolyte **E**$_1$ without any additives (Fig. 2a). The random arrangement of nodules was observed and their size was between 3 and 5 μm. The additives used in the Cu plating electrolyte are generally organic compounds, and act as accelerators or suppressors of the electrodeposition process with dual effect such as brighteners, levelers, grain refiners, and ductilizers co-deposited with copper [23]. The additives in the plating electrolyte have functionality effects on surface structure. For the combination of the suppressor agent such as Polyethylene glycol (PEG), organic polymer with high molecular weights, long-chain, and low solubility, with Cl^- ions (electrolyte **E**$_3$) the degree of adsorption and inhibition of suppressors is further enhanced [23] and bright spherical forms can be seen in Fig. 2b (yellow line). Figure 2c shows the morphology of the copper film deposited only in the presence of Cl^- ions in the basic electrolyte. By comparing Fig. 2a and Fig. 2c it can be concluded that there is no significant change in the structure of the film, only the film with Cl^- ions is more homogeneous and without nodular forms. Brightener/leveler additive is typically sulphonic compound (in this case 3−Mercapto−1−propanesulfonic acid- MPSA) that enhances nucleation of new grains during deposition, reducing grain size and surface roughness parameters (see Fig. 2d). The copper film obtained from electrolyte **E**$_4$ has mirror bright appearance, very smooth surface, without clear boundary among grains. A layered structure with a stepwise transition between layers can be observed. Generally, the nanocrystalline form of the copper film (*nc-Cu*) was obtained from the electrolyte **E**$_4$, while the microcrystalline form of the deposit (*mc-Cu*) was obtained from the other electrolytes (**E**$_1$, **E**$_2$, and **E**$_3$).

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B. *Roughness of electrodeposited copper films*

All series of prepared copper samples electrodeposited on brass (series **A**), silicon (series **B**) and copper (series **C**) substrates were analyzed using AFM images and roughness parameters (R_a and R_q) were measured. The two-dimensional (2D AFM) images are given in Fig. 3 for series **A**, Fig. 4 for series **B** and Fig. 5 for series **C**.

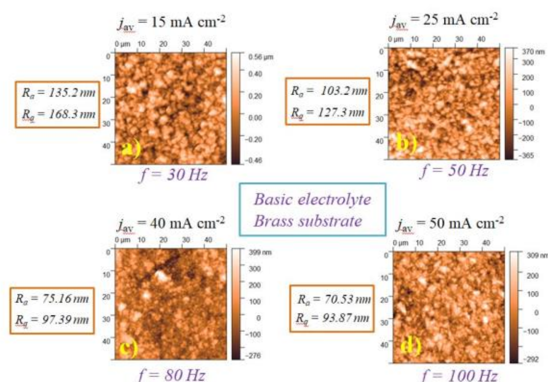

Fig. 3. AFM topographies for series **A** (20 μm thick Cu films electrodeposited on brass foils in PC regime from electrolyte $\mathbf{E}_1$) for samples: a) sample $\mathbf{A}_1$ b) sample $\mathbf{A}_2$, c) sample $\mathbf{A}_3$, and d) sample $\mathbf{A}_4$ Scan size: (50 ×50 μm^2).

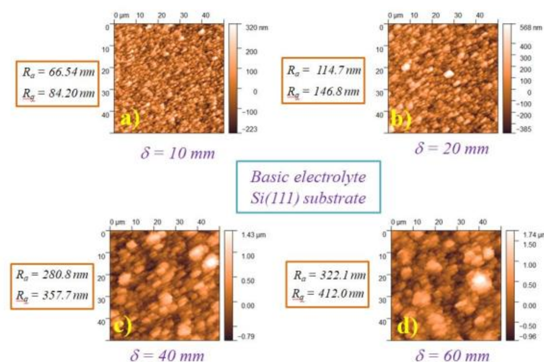

Fig. 4. AFM topographies for series **B** for Cu films electrodeposited on silicon substrate in PC regime from electrolyte $\mathbf{E}_1$. The samples are: a) $\mathbf{B}_1$, b) $\mathbf{B}_2$, c) $\mathbf{B}_3$, and d) $\mathbf{B}_4$. Scan size: (50 ×50) μm^2.

According to results from Fig. 3 the values of both roughness parameters obtained for Cu films electrodeposited in PC regime on brass foils decreased with increasing the average current densities and frequencies. The reduction of crystal size was evidenced for higher value of the average current densities [24, 25].

In summary, by comparing the roughness parameters obtained according to 2D-AFM images given in Fig. 4, it is evident that by increasing the layer thickness of electrodeposited Cu on silicon wafer (from electrolyte $\mathbf{E}_1$), the coating surface roughness is increased gradually [13].

Figure 5 represents 2D-AFM images of the surface for copper films series **C** and the influence of the presence of additives in the electrolyte on roughness modifications.

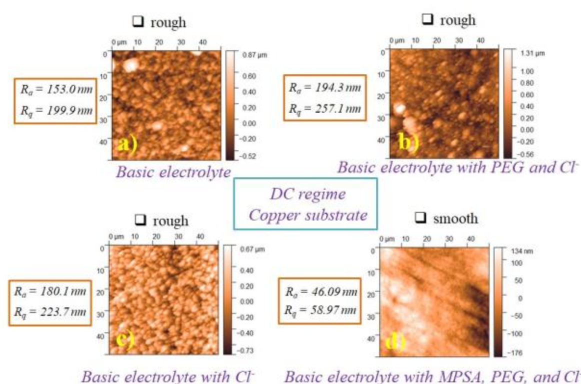

Fig. 5. AFM topographies for series **C** - 10 μm thick Cu films electrodeposited on Cu foils in DC regime from electrolytes: a) $\mathbf{E}_1$ (sample $\mathbf{C}_1$), b) $\mathbf{E}_3$ (sample $\mathbf{C}_3$), c) $\mathbf{E}_2$ (sample $\mathbf{C}_2$), and d) $\mathbf{E}_4$ (sample $\mathbf{C}_4$). Scan size: 50 ×50 μm^2.

The presence of only the Cl^- ions in basic sulfate electrolyte has little effect on structure, but roughness increases (see Fig. 5a and 5c). The copper sample deposited with combination of PEG and Cl^- ions in the bath, has maximal value of roughness parameters (see Fig. 5c). This behavior can be explained according to presence of bigger spherical balls of polymer (see SEM picture on Fig. 2b) and its co-deposition with copper on top surface. The obtained film shows a high degree of anisotropy and inhomogeneity, so there are large oscillations between peaks and valleys (height and depth) during scanning (Fig. 5b). The presence of three additives (brightener/leveling) in the electrolyte, the obtained copper film was smooth and the decrease of the values of roughness parameters (see Fig. 5d) [14].

C. *Wettability analysis of substrates and films*

The wettability of the silicon substrates depends on many factors such as cleaning process, aging behavior of the Si wafer after cleaning, the thickness of native oxides, etc. [19]. The Si substrates cleaned in the piranha solution has water contact angle less than 90° (hydrophilic nature), and when cleaned in HF (the native films of SiO_2 comes off) the surface has hydrophobic nature. The measured value of water contact angle (θ_C) on Si substrate with sputtered gold layers was 64.10°, and for deposited copper films 67.69° (see Fig. 6a). The sputtered gold film on silicon substrate as adhesive/conductive seed layer for plating copper film is more hydrophilic than copper films. This property can be explained according to increasing roughness of deposited films compared to the roughness of the Si substrate [19]. The value of θ_C obtained on brass substrate was in the range of 51.4° to 61.20°. Large deviations of the contact angle values can be associated with deep tracks and trenches that are the result of mechanical preparation of the brass substrate and bending on the edges, see Fig. 6b.

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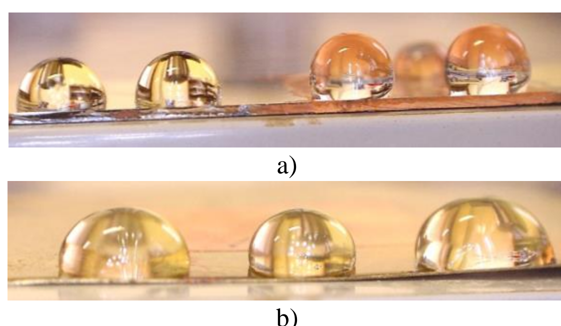

Fig. 6. Images of the water drops on different substrate and films photographed in the order to measurement the values of water contact angle according to sessile drop method. The images present: a) wettability on the Si/Cr/Au substrate (left) and electrodeposited copper films (right) and b) wettability on mechanical treated brass substrate.

In order to assess the effect of electrodeposition conditions on wetting properties of copper films, sessile drop method applied, and water contact angle measurements using image analyzes on all series (**A**, **B**, and **C**). The values of θ_C were displayed on a histogram (Figs. 7 - 9).

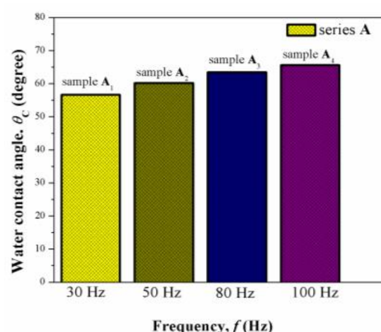

Fig. 7. Wettability properties of 20 μm copper films electrodeposited on brass substrate in PC regime from electrolyte $\mathbf{E}_1$ with variation frequencies (i.e., an average current densities).

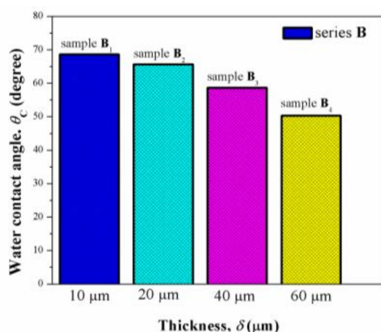

Fig. 8. Wettability properties of copper samples - series **B** (electrodeposited on silicon substrate in PC regime from electrolyte $\mathbf{E}_1$) with variation of film thickness (i.e., duration of electrodeposition).

From the values of water contact angle given on histograms (Figs. 7 and 8), samples prepared from basic sulfate electrolyte ($\mathbf{E}_1$) in PC regime has opposite trend between values of roughness parameters (Figs. 3 and 4).

Increasing the frequency and an average current density can reduce the roughness parameters of the copper films, makes the Cu films surface more smoother and number of peaks and size of bulge decreases significantly and results in a larger water contact angle [24].

The copper films with higher values of roughness parameters show a lower water contact angle, but the samples of series **C** deviate from this rule. Because the wettability in the case of series **C** is strongly affected by chemical composition of the films and presence of additives in the electrolyte (see, Fig. 9). The other reason for this behavior lies in the fact that porous films could be contaminated with hydrocarbons in air or be affected by oxidation, and wettability properties could be changed [26].

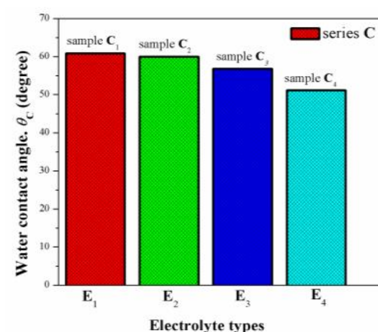

Fig. 9. Wettability properties of 10 μm copper samples from series **C** (electrodeposited on copper substrate in the DC regime) from different electrolytes.

The images of water drops on Cu films electrodeposited from different electrolytes on Cu foils were shown in Fig. 10.

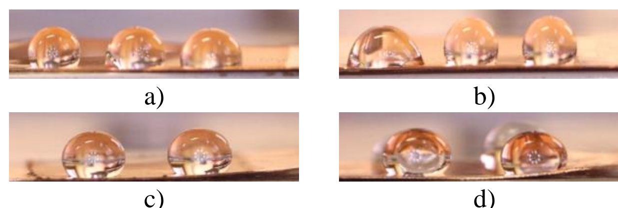

Fig. 10. Wettability properties of 10 μm copper samples from series **C** (electrodeposited on copper substrate in DC regime) from different electrolytes: a) $\mathbf{E}_1$ (sample $\mathbf{C}_1$), b) $\mathbf{E}_2$ (sample $\mathbf{C}_2$), c) $\mathbf{E}_3$ (sample $\mathbf{C}_3$), and d) $\mathbf{E}_4$ (sample $\mathbf{C}_4$). The volume of water drop was 5 μL.

The addition of only the chloride ions (electrolyte $\mathbf{E}_2$) to the basic sulfate electrolyte ($\mathbf{E}_1$) has little influence on the water contact angle. However by adding PEG (electrolyte $\mathbf{E}_3$) we drastically change the wettability of the produced copper films. The surface of PEG is extremely hydrophilic (the water contact angle was about 20° [25]), and its co-deposition with copper on the surface contributes to an increase in hydrophilicity, i.e., in a decrease in the water contact angle. In the presence of chlorides, this process is accelerated, as well as adsorption on the ligand on surface and contamination of clear metals. In the presence of MPSA, PEG and Cl^- ions together in electrolyte ($\mathbf{E}_4$), the obtained films were smooth, with minimal values of water contact angle.

The nanocrystalline copper film on copper foil electrodeposited from electrolyte $\mathbf{E}_4$ has smooth surface,

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which is main factor for reducing the water contact angles of the surface of the Cu films. Less gas can be absorbed on a smooth surface compared to a rough surface and smooth surface has the lower sliding resistance to the water, so that could be the explanation of the reduction of the water contact angle.

IV. Conclusion

An extensive analysis of differently synthesized composite systems was presented. Changes in the water contact angle on surface of electrodeposited copper films were described. The reduction in the water contact angle value reveals a modification in the Cu films structures. Copper films electrodeposited from electrolyte without additives have inverse correlation between roughness parameters and the water contact angle value. As the frequency in the PC regime increases from 30 Hz to 100 Hz, grain size and roughness reduces. The wettability of thicker copper films is higher compared to thinner films. Successive inclusion of additives to the basic electrolyte results in the decrease of the water contact angles and more hydrophilic copper films.

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