

# Ellipsometric study of oxide formation on Cu electrode in 0.1 M NaOH

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**Abstract** A single wavelength ellipsometry and cyclic voltammetry measurements were simultaneously used for the investigation of oxide growth on copper in 0.1 M NaOH solution. These investigations were part of joint research of electric and physical properties of cuprous and cupric oxide during layer formation and growth. This type of joint impedance and ellipsometric study has not been performed before. In this paper, authors discuss composition of multilayer film structure using various models and fitting methods enabling interpretation of multilayer oxides structure formation during passivation process. It is shown that implementation of effective medium approximation allows to obtain an accurate model fitting, using Levenberg–Marquardt optimization algorithm and mean square error.

## Introduction

Copper is one of the most often studied metals—for its mechanical properties and good conductivity. It owes its popularity to corrosion stability which is the result of formation of oxide and hydroxide layers on the metal surface in oxidizing

electrolytes. Semiconducting products of oxidation processes are used in the electronic and energy industry, for photocatalytic applications and for solar energy converters. The knowledge about the passivation behavior of copper and of the structure of its anodic oxide layer is of great importance in this context.

Jovic and Jovic [1] observed  $\text{OH}^-$  adsorption/desorption process taking place in the underpotential region of  $\text{Cu}_2\text{O}$  formation. The copper surface in adsorbed phase eventually reconstructs to form  $\text{Cu}_2\text{O}$  layer. Through this film, there is a diffusional process of  $\text{Cu(II)}$  soluble species which, together with the electrooxidation of  $\text{Cu(I)}$  to  $\text{Cu(II)}$ , leads to the formation of a thicker and complex passive film. In ellipsometric and photocurrent investigations performed by Zerbino [2], cuprous oxide formation was explained as a sequence of  $\text{Cu}_2\text{O}$  growth of inner layer and dissolution precipitation of  $\text{Cu(II)}$  outer hydrated layer. The resulting photocurrent was proportional to the thickness of inner layer. According to Seo et al. [3], the average composition of the outer oxide layer could conventionally be represented as  $\text{CuO}_x(\text{OH})_{2-2x}$ . The value of  $x$  is variable in the range of 0–1. The value of  $x$  increases with the increase of anodic potential as well as oxidation time. The oxidation of copper in alkaline solutions was studied by cyclic voltammetry, photocurrent spectroscopy, and capacitance measurements by Abrantes et al. [4]. This study showed that the layer of  $\text{Cu}_2\text{O}$  was formed initially by the oxidation of Cu on the forward sweep as an overlayer of  $\text{Cu(OH)}_2$  or as a reduction of  $\text{CuO}$ . The total thickness of the anodic layer depends much on such properties as concentration of hydroxide ions in the solution or electrode potential. However, it cannot be greater than 6 nm for duplex oxide film. Maurice et al. [5] have investigated nonordered layers obtained in borate buffer solutions on  $\text{Cu(111)}$ . They indicated a strong anion and/or pH effect on the crystallinity of the anodic oxide films.

Babic et al. [6] used electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to study the

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characteristics of passive film formed potentiodynamically on copper in slightly alkaline solutions. They found the strong correlation between the impedance and the changes in the composition and structure of passive film.

In frame of presented studies model of copper oxide layer and structure was evaluated. The model including optical properties of each system element is required for the application of ellipsometry, which allows investigation of dynamics of oxide formation. The ellipsometric measurements were used to evaluate the thickness and structure of oxides layers under electrochemical oxidation in sodium hydroxide. The layer appearance and structure were studied as a function of the applied potential.

Ellipsometric investigations carried out by authors are introduction to joint optical and impedance data analysis. EIS measurements have to be carried out in stationary conditions because instantaneous impedance spectra cannot be obtained during oxide layer formation. Authors propose to use dynamic electrochemical impedance spectroscopy (DEIS). Its theoretical background was described elsewhere [7–11]. Simultaneous use of the DEIS and the single wavelength ellipsometry techniques enable detailed characterization of the optical and impedance parameters in the field of nonstationary systems. The aim of this research was to describe adequate optical model that will characterize formation and reduction of oxide and hydroxide layers on copper electrode during the polarization sweep.

## Experimental and theoretical

### Background

The ellipsometry is an optical method for thin layer analysis. It is based on polarization state measurement of the light beam reflected from the sample. Such a procedure is used for thickness monitoring of dielectric and semiconductor layers synthesized during physical vapor deposition or chemical vapor deposition processes. However, the described procedure had been adapted with respect to that of Tomkins [12], particularly in examination of the measurement data, theoretical modeling, and fitting.

Following assumptions describing the analyzed optical model should be made. A model of a single layer as adequate for copper oxidation process is considered [13]. Linearly polarized light beam is incident on the sample at  $\phi_0=70^\circ$  angle, where layer thickness is  $d_1$ .  $N_0$  is a refractive index of passivation medium, where substrate is located. Thin oxide films cover the strongly absorbing metal substrate characterized by refractive index  $N_2$ . The complex refractive indices of investigated layers are denoted as  $N_1$ . For ellipsometric purposes, the complex-

amplitude parameter  $\rho$  is defined as a ratio of total reflection coefficients:

$$\rho = \frac{r^p}{r^s} = \tan \Psi e^{j\Delta}. \quad (1)$$

The ellipsometric angles  $\Delta$  and  $\Psi$  represent the amplitude and phase ratio difference between  $p$ - and  $s$ -polarization of light beam [12]. The amplitude reflectance coefficients in both polarization modes are expressed as follow:

$$\frac{r^p}{r^s} = \frac{\left[ \frac{r_{01}^p + r_{12}^p \exp(-j2\beta_1)}{1 + r_{01}^p r_{12}^p \exp(-j2\beta_1)} \right]}{\left[ \frac{r_{01}^s + r_{12}^s \exp(-j2\beta_1)}{1 + r_{01}^s r_{12}^s \exp(-j2\beta_1)} \right]} \quad (2)$$

where  $r_{01}$ ,  $r_{12}$  are the Fresnel reflection coefficient defined at boundaries of various  $i$ -medium, which depends on  $N_i = n_i - ik_i$  complex refractive index [14]. The phase shift due to light beam refraction of angle  $\phi_1$  is expressed by:

$$\beta_i = 4\pi \left( \frac{d_i}{\lambda} \right) N_i \cos \phi_i. \quad (3)$$

All refractive indices  $N_0$ ,  $N_1$ , and  $N_2$  are complex functions of the  $\lambda$  wavelength of incident light beam. The substitution of Fresnel reflection coefficients and Eqs. 2 and 3 in Eq. 1 gives complex ratio  $\rho$  as a function of medium refractive indices, light wavelength, and layer thicknesses.

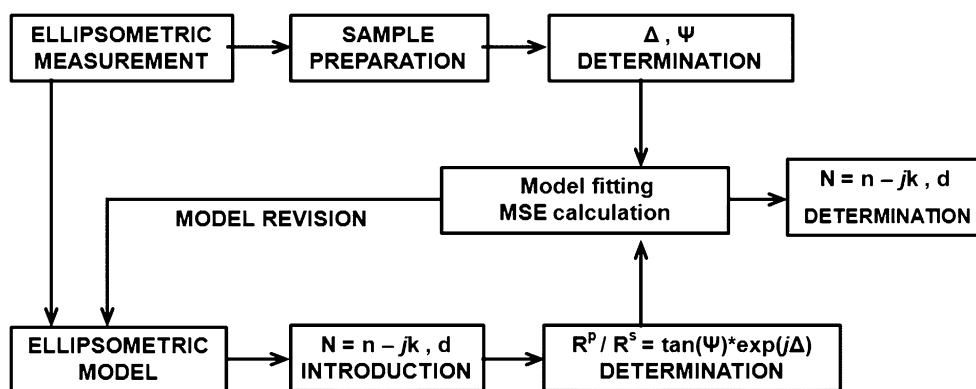
The first step of ellipsometric analysis is assumption of model using number of layers and layer type. Introductory parameterization of optical indices of each layers is necessary to calculate angles  $\Delta$  and  $\Psi$  using the formulas of Eqs. 1–3 (see Fig. 1). The last step of data investigation is fitting of the model to the experimental results. The selection of suitable optical model is the most important part of the research.

Efficient an error-based figure of merit is crucial to know whether the assumed model fits the experiments. As the fitting measure mean square error (MSE) was utilized [12], which is given by:

$$\text{MSE} = \frac{1}{2N - M} \sum_{i=1}^N \left[ \left( \frac{\Psi_i^{\text{mod}} - \Psi_i^{\text{exp}}}{\sigma_{\Psi_i}^{\text{exp}}} \right)^2 + \left( \frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta_i}^{\text{exp}}} \right)^2 \right]. \quad (4)$$

In Eq. 4,  $\Delta_i^{\text{exp}}$ ,  $\Delta_i^{\text{mod}}$ ,  $\Psi_i^{\text{exp}}$ ,  $\Psi_i^{\text{mod}}$ , and  $\sigma_i$  represent the investigated, calculated, and standard deviations at data set  $i$ , while  $N$  is the number of measurement points and  $M$  is the number of fitted parameters.

The variation of ellipsometric angles turns out to be nonlinear during passivation process with respect to the layer composition deviation. Thus, the adequate multidimensional nonlinear algorithm with rapid convergence capability should be applied. For this purposes, the Levenberg–Marquardt nonlinear least-squares algorithm was used to develop the modeling program.

**Fig. 1** The schema of ellipsometry measurement algorithm

### Ellipsometric setup and sample preparation

The working polycrystalline copper electrodes having area of  $0.2 \text{ cm}^2$  were prepared from high purity copper 99.999% and immobilized in epoxy resin. Prior to each experiment, the electrodes were mechanically polished with abrasive paper of 400–1,500 gradation and subsequently polished with 1 and  $0.05 \mu\text{m}$  alumina paste to get a mirror quality surface.

Chronovoltammetry measurements were carried out with the use of potentiostat from GAMRY Instruments. Prior to experiment, sample was conditioned for the period of 20 min at potential equal to  $-0.9 \text{ V}$ . Polarization sweep rate was  $5 \text{ mV/s}$ . Measurements were carried out in a three-electrode electrochemical cell.  $\text{Ag}/\text{Ag}_2\text{O}$  electrode was used as the reference electrode and platinum mesh was the counter electrode. All potentials in this paper refer to  $\text{Ag}/\text{Ag}_2\text{O}$  reference electrode. Solution used for the investigations was  $0.1 \text{ M}$  sodium hydroxide.

The in situ ellipsometric measurements were carried out with single wavelength ellipsometer (DRE GmbH, ELX-02C), which uses a  $1\text{-mW}$  He–Ne laser operating at wavelength of  $632.8 \text{ nm}$ . The ellipsometer configuration is based on fixed Glan-Thomson polarizer, a sample and rotating analyzer (see Fig. 2a). The stepper motor with 360,000 steps per turn and unique Minsearch algorithm (DRE GmbH) enable kinetic investigation of even monatomic films created during oxidation. The ellipsometer is connected to a PC, which controls  $\Delta$  and  $\Psi$  acquisition. The electrochemical cell with two quartz windows is fixed to the ellipsometer goniometer for simultaneous recording of

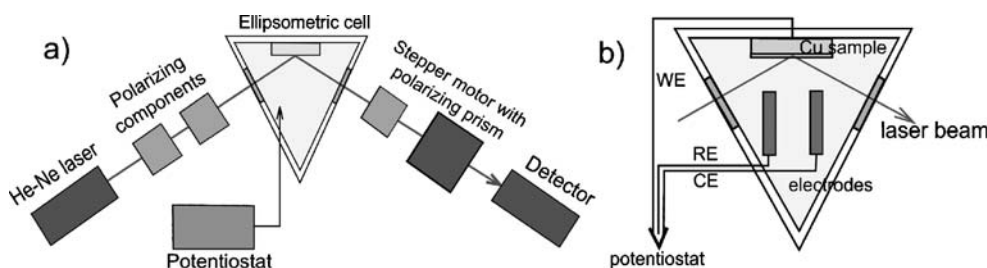
ellipsometric and potentiodynamic data. The configuration of electrochemical cell (volume of  $2 \text{ ml}$ ) was shown in Fig. 2b. The angle of light incidence is set at  $70^\circ$  due to copper Brewster angle [14]. The ellipsometric measurements were performed simultaneously with cyclic polarization scans in time interval of  $0.5 \text{ s}$ .

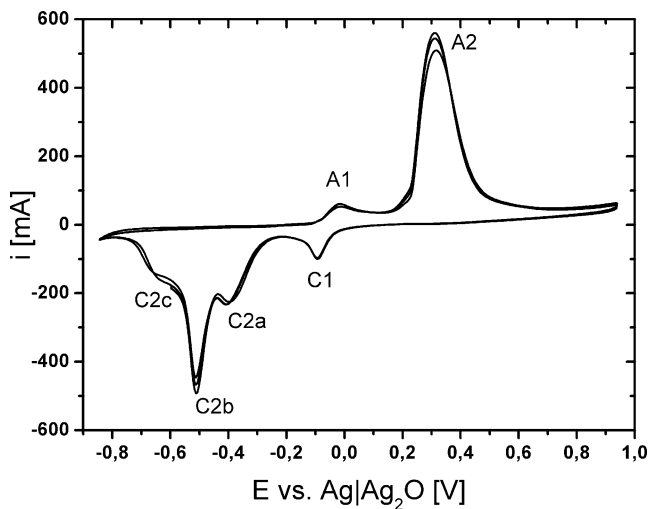
## Results and discussion

### Chronovoltammetric characterization

Chronovoltammetric examination of copper electrode in  $0.1 \text{ M NaOH}$  solution was presented on Fig. 3. It is in good agreement with similar measurements made in alkaline solutions [6, 15–18].

During the anodic polarization of the sample, two peaks occur. They correspond to oxidation reactions of  $\text{Cu}$  to  $\text{Cu}_2\text{O}$  (A1) and subsequent oxidation of  $\text{Cu}/\text{Cu}_2\text{O}$  to  $\text{CuO}$  and  $\text{Cu}(\text{OH})_2$  (A2). For small applied potential sweep rates, formation of both cuprous oxide and cuprous hydroxide is represented by common anodic peak. During the cathodic polarization sweep, a few more peaks are evident. These peaks were observed and interpreted by M. Kang and A.A. Gewirth [18] on voltammetric and force microscopic examination of oxide formation on copper in basic solution. They stated that cathodic peak C1 might be connected with reduction of soluble and adsorbed materials to  $\text{Cu}_2\text{O}$ . As the voltammetry in Fig. 3 clearly shows, peak C2 for low polarization rates is composed of three different peaks. The highest peak C2b is considered to be connected with

**Fig. 2** Schematic configuration of ellipsometer (a) and electrochemical cell (b) with Cu sample as working electrode (WE),  $\text{Ag}/\text{Ag}_2\text{O}$  as reference electrode (RE), and platinum mesh as counter electrode (CE)



**Fig. 3** Cyclic voltammograms for polycrystalline copper sample in 0.1 M NaOH solution obtained at the scan rate 5 mV/s

reduction of CuO and Cu<sub>2</sub>O surface oxides to Cu metal. Full interpretation is given elsewhere [18, 19].

#### Ellipsometric measurements and fittings

In Fig. 4, experimental and calculated variations of ellipsometric angles for 632.8 nm of copper sample in the NaOH solution are illustrated. The  $\Delta$  and  $\Psi$  dependences on the potential during polarization sweep were particularly studied. The  $\Delta$  cycle indicates the oxide layer growth and its reduction in function of potential, while variations of  $\Psi$  are the result of optical constant changes related to variable oxide structure. After full cycle, the  $\Delta$  and  $\Psi$  values result similar to those measured for the bare electrode.

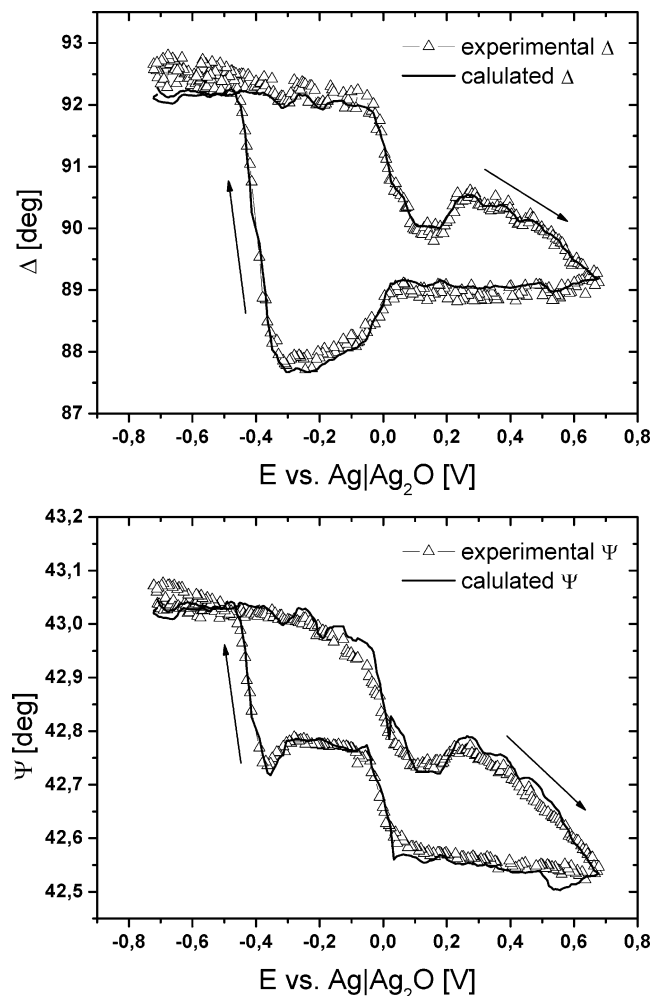
Ellipsometric angles are strongly sensitive to surface and interface layers. Thus, it is necessary to incorporate even small roughness and inhomogeneities of layer into an optical model in data analysis. The thin layer growing during potential cycle is a dynamic mixture of oxides. It also maps roughness of the substrate. These facts suggest assuming a single layer model to evaluate the ellipsometric parameters.

The optical constants of layer were simulated by the effective medium approximation (EMA) [20]. From the analysis using EMA, volume fractions in composite layer were obtained. The layer thickness due to very thin structure was calculated as  $\Delta$  difference [12]. Such the starting parameters were applied to self-designed Matlab software illustrated in Fig. 5. Program utilizes the fitting algorithm of calculated data assuming the formation of measured layer [21]. The algorithm is based on Levenberg–Marquardt nonlinear optimization and MSE to minimize the difference between the experimental and calculated data (see Fig. 5). This approach enables good fit calculated and measured ellipsometric parameters (MSE better than 0.1).

Assuming a single BEMA film, the nonlinear fitting of ellipsometric angles allowed the estimation of layer thickness  $d$  and optical indices  $n$  and  $k$ . Figure 6 shows the thickness dependence of the oxide layer versus potential. As it can be seen, the potential strongly influences the oxide thickness.

The  $d$  values strongly increase for the potential higher than  $E = -0.1$  V indicating the Cu<sub>2</sub>O layer growth. This fact is also confirmed by value of the refractive index and extinction coefficient, which are illustrated in Fig. 7. Above the potential values corresponding to the formation of first anodic peak A1,  $n$  is decreasing and  $k$  is increasing up to values of  $n = 2.51$  and  $k = 0.6$  in agreement with oxidation reactions and higher Cu<sub>2</sub>O admixture. The final EMA mixture of 13% Cu and 87% of Cu<sub>2</sub>O at potential of 0.05 V is obtained.

The variation of optical constants of layer for the potential lower than  $-0.1$  V could be explained by the dynamic Cu<sub>2</sub>O layer nucleation processes and valence change from Cu to Cu(I). The layer thickness was below 0.25 nm and copper admixture gets relatively high amount of 20%.



**Fig. 4** Ellipsometric angles  $\Delta$  and  $\Psi$  variation obtained during a potential cycle

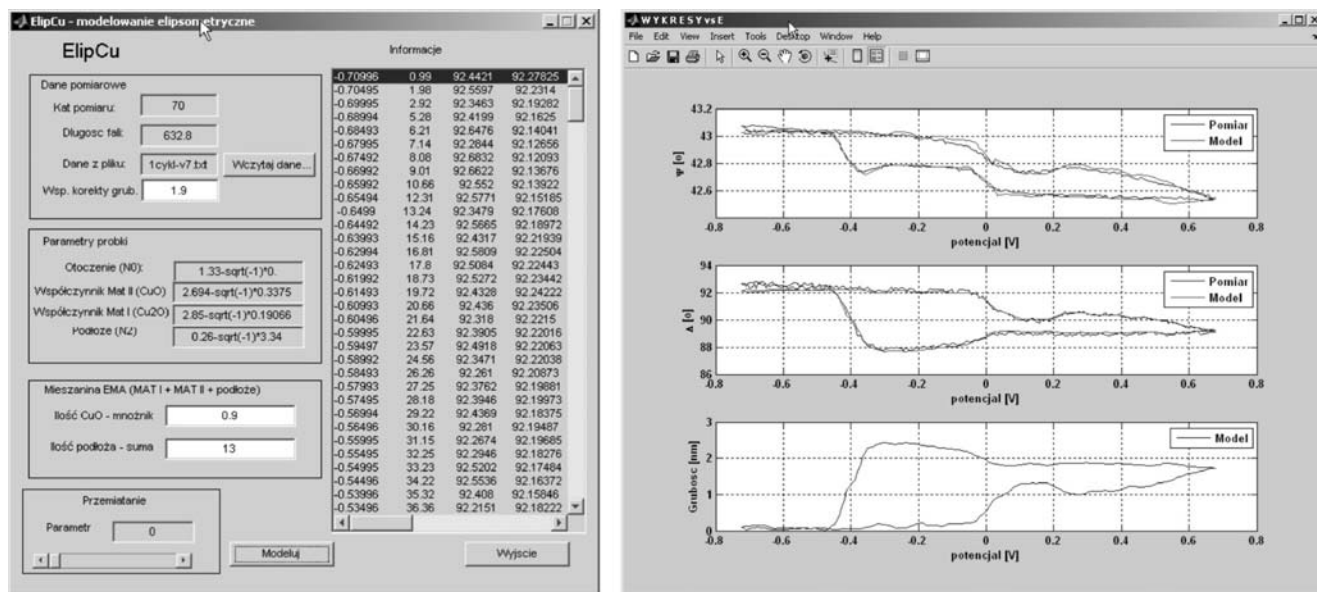


Fig. 5 Ellipsometric modeling interface designed in Matlab for dynamic data analysis

At the  $E=0.2$  V, thickness reaches 1.25 nm and starts to slightly decrease down to 1 nm at the  $E=0.25$  V. Lower thickness is related to partial reconstruction of layer from the  $Cu_2O$  to the  $CuO$  and  $Cu(I)$  to  $Cu(II)$  valence transition. Thermodynamic calculations indicate that at least one monovalent or two divalent soluble copper species are expected to be formed in alkaline electrolytes. Possibility of formation of such soluble species  $CuO_2^{2-}$  and/or  $HCuO_2^-$  at range of peak A2 from  $Cu(OH)_2$  should also be taken into consideration [18, 21]. At potential range above 0.25 V, continuous increase of thickness is observed. It reaches 1.8 nm at the highest anodic potential. Increase of thickness results from continuation of  $CuO/Cu(OH)_2$  growth. These effects are also observed as the shift of optical parameters. The admixture of  $CuO$  increases from the 0.2 V potential up

to 67% at the end of anodic polarization sweep. The rest of layer fractions get following composition at this potential point:  $Cu$ —13%,  $Cu_2O$ —12%,  $Cu(OH)_2$ —8%. In this point, the refractive index and extinction coefficient reach the values of  $n=2.61$  and  $k=0.77$ .

In the range of cathodic scan down to 0 V, the thickness is saturated at 1.8 nm. Whereas, the optical indices are slightly shifted to the typical values of  $Cu_2O$  to  $Cu$  mixture.

From the point of zero potential down to  $E=-0.3$  V, the layer thickness increase up to 2.4 nm. Increase of surface thickness in this region might be connected with consecutive reduction of soluble species formed in the region of anodic peak A2 to  $Cu_2O$  oxide layer. The copper changed valence from  $Cu(II)$  to  $Cu(I)$ . The smaller incorporation of pure copper has been detected (only 4%) in this potential

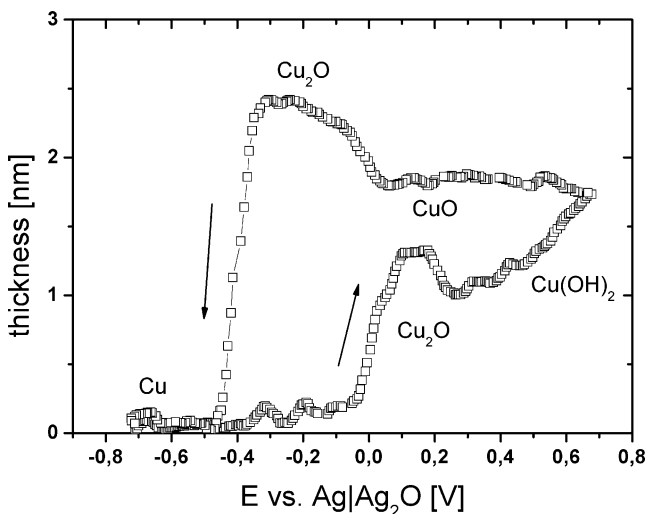


Fig. 6 Thickness dependence of the oxide layer versus potential

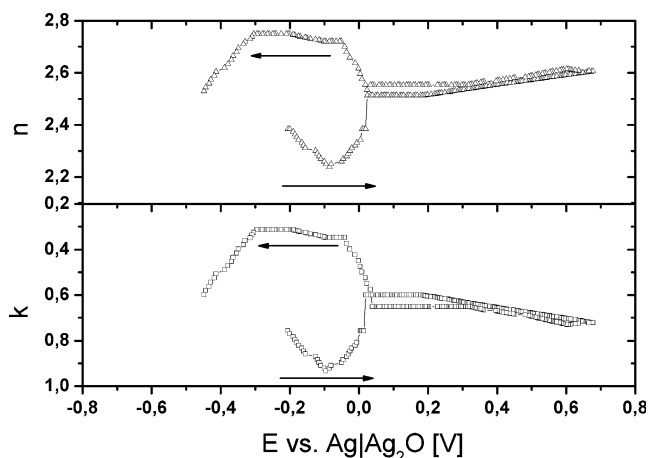


Fig. 7 The potential variation of the refractive index and extinction coefficient of the cuprous oxide layer

range. The layer is almost pure  $\text{Cu}_2\text{O}$  and optical constants are equal to  $n=2.74$  and  $k=0.32$  [22].

The last step of polarization cycle is copper oxides reduction starting at  $E=-0.3$  V. The layer thickness falls down almost to zero nanometers and the admixture of  $\text{Cu}_2\text{O}$  in layer decreases. The optical parameters obtain the values similar to those at the first steps of anodic cycle, when the very thin layer was nucleated.

Over the potential of  $-0.5$  V, the  $\Delta$  and  $\Psi$  values exhibit typical amount of the bare copper electrode. It should be added that analyzed layer parameters obtained by ellipsometry vary properly at the scale of oxidation and reduction time. The ellipsometric angles and current response characteristics were collected simultaneously.

## Conclusions

In situ ellipsometry and cyclic voltammetry measurements were simultaneously used for the investigation of oxide growth on copper in 0.1 M NaOH solution. The layer parameters such as thicknesses and optical constants need to be calculated from measured data. The calculations require an optical model. The model of a single composite layer was assumed as adequate for copper oxidation and reduction processes. The special Matlab program for nonlinear fitting of dynamic ellipsometric ( $\Delta$  and  $\Psi$ ) data was developed. The algorithm is based on Levenberg–Marquardt nonlinear optimization and mean square error. The comparison of experimental and calculated  $\Delta$  and  $\Psi$  angles were presented. Program utilizes the fitting algorithm of calculated data assuming the formation of measured layer. The layer was simulated by BEMA with dynamic volume fractions of Cu,  $\text{Cu}_2\text{O}$ , CuO, and  $\text{Cu}(\text{OH})_2$ . The thickness, optical constants, and volume fractions of layer were calculated as a function of anodic and cathodic potential range. The studies showed that ellipsometry is an efficient ultrathin layer monitoring technique and can be used to improve electrochemical results.

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