

Thin Oxide Films on Copper Single Crystals: Anodic Formation and Photoelectrochemical Properties

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(Received 01 February 2012; published online 18 July 2012)

Thin oxide films were grown anodically on polycrystalline copper and single crystals Cu(100), Cu(110) and Cu(111). Semiconductor properties of copper oxides were obtained by photocurrent measurements. The morphology of the anodic oxides was monitored by SEM. A p-type conductivity was established for Cu₂O and CuO formed on Cu during the anodic polarization. The main semiconductor properties do not depend on the crystal face; the band gap in thin Cu₂O is equal to 2.2 eV.

Keywords: Copper, Single crystals, Anodic oxide formation, Photocurrent, Spectroscopy.

PACS number: 82.45. – h

1. INTRODUCTION

Metal oxides are widely used in photolytic hydrogen evolution, electrocatalysis as well as in the production of current-generating devices, UV- and IR-sensors. Cu(I) oxide is considered as a perspective material due to the optimal combination of the number of parameters such as non-toxicity, low cost, simple production and the bandgap, providing the adsorption of most spectrum. Cu(II) oxide films can be grown much thicker than Cu(I) oxide, being using in barrier devices.

The properties of thin oxide films and the kinetics of their formation depend on the electrode potential and solution composition as well as the crystal structure and chemical composition of the electrode surface. The latter is revealed for nanosized films of Ag(I) oxide on Ag and Ag-Au alloys [1, 2].

The aim was to establish the role of crystal structure of copper surface in the kinetics of anodic growth and properties of nanosized films of semiconductor Cu(I) and Cu(II) oxides.

2. EXPERIMENTAL

The investigation were carried out on polycrystalline copper (0.9999) and single crystals Cu(100), Cu(110) and Cu(111) (0.99999) in deaerated 0.1 M KOH prepared from double-distilled water and reagent-grade chemicals. Single crystals were prepared by "Materials Technology & Crystals for Research, Development and Production" with accuracy $\leq 2^\circ$.

The kinetics of anodic formation and the properties of Cu(I) and Cu(II) oxides were examined by cyclic voltammetry and chronoammetry with synchronous registration of photocurrent. The polarization of static electrodes during the preparation and the film growth was carried out using the computerized potentiostatic complex IPC-Compact (Institute of Physical Chemistry and Electrochemistry of Russian Academy of Science). The potentials are given in s.h.e. scale.

The super-bright light emitting diodes "LIGITEK" were used as a source of quasi-monochromatic UV-irradiation ($\lambda = 385\text{-}875$ nm) in the photoelectrochemical measurements. The density of photon flux was con-

stant and equal to $3.04 \cdot 10^{15}$ photon \cdot cm $^{-2}$ \cdot s $^{-1}$. The duration and frequency of light pulses were 50 ms and 5 Hz.

The morphology and the chemical composition of the electrode surface were monitored by scanning electron microscopy (JEOL JSM 6380LV) and energy dispersion X-ray analysis (INCAx – sight 250).

3. ANODIC FORMATION OF THIN OXIDE FILMS

The voltammograms of copper in a wide potential range show the two main peaks A1 and A2, corresponding to Cu(I) and Cu(II) formation (Fig. 1a). The peak potential A2 ennobles and the peak current decreases: Cu(poly) > Cu(110) > Cu(111) > Cu(100).

The potential and current of A1 peak on Cu(111) and polycrystalline copper are identical. On Cu(110) and Cu(100) the peak potential A1 is more negative and the peak current is lower as compared with polycrystalline copper (Fig. 1b); the difference in the cathodic peaks C1 and C2 is less significant.

The processing of the voltammograms in the criterial coordinates shows that the anodic formation and cathodic reduction of Cu(I) oxide on polycrystalline copper and single crystals proceeds with a noticeable diffusion limitation in solid phase. The charge transfer is not equilibrium.

In the potential range more negative than the equilibrium potential of Cu(I) oxide formation we managed to reveal the weak anodic and cathodic peaks (Fig. 2a), corresponding to the adsorption of hydroxyl-ion with charge transfer [3, 4] and subsequent desorption of hydroxyl-radical:



The integer of anodic currents gives the values of q_a , corresponding to the charging of pseudo-capacity of the adsorption and the extent of surface filling by oxygen (Fig. 2b). In general the values of surface filling are low; Cu(111) shows the maximal surface filling. At $E < -0.7$ V the chemisorption of OH $^-$ on copper does not occur.

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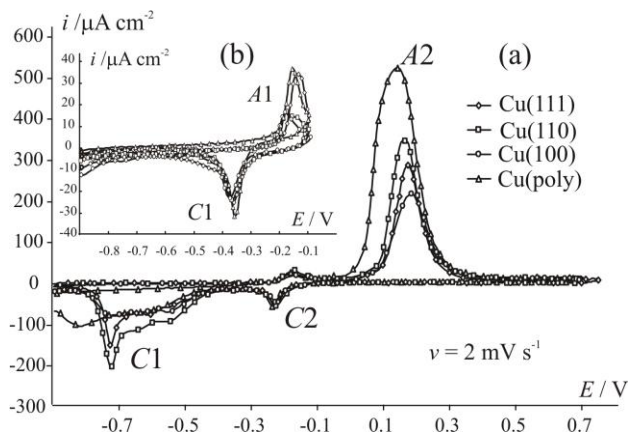


Fig. 1 – Cyclic voltammograms of polycrystalline copper and single crystals in 0.1 M KOH

The values of current efficiency of oxide formation on different single crystals are similar and hardly differ from the current efficiency obtained for polycrystalline copper (Table 1). The film thickness sharply increases and the current efficiency noticeably decreases at transition to positive potentials where the formation of Cu(II) oxide is possible.

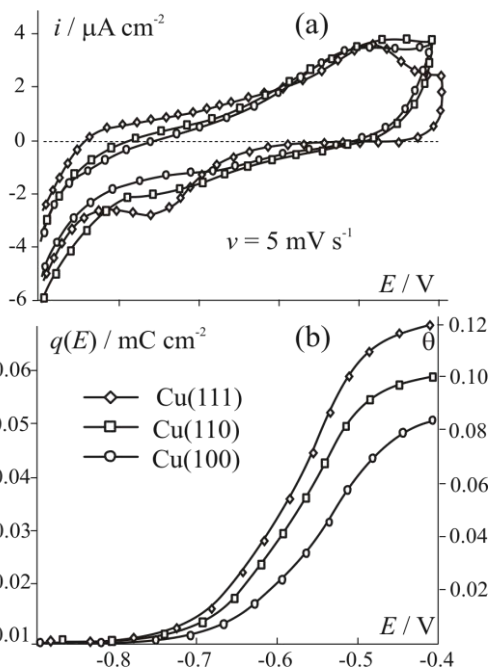


Fig. 2 – Cyclic voltammograms (a) and the dynamics of oxygen adsorption (b) on single crystals of copper in 0.1 M KOH

Table 1 – Anodic charge of Cu(I) and Cu(II) oxide formation Q_a , cathodic charge of reduction Q_c , current efficiency Ψ and the average thickness of oxide film L

Substrate	Oxide	E / V	Q_a / mC	Q_c / mC	$\Psi / \%$	L / nm
Cu(111)	Cu ₂ O	-0.16	0.29	0.26	90	1.6
	CuO	0.10	15.2	7.9	52	52
Cu(110)	Cu ₂ O	-0.16	0.78	0.77	99	4.7
	CuO	0.10	21.0	12.8	61	84
Cu(100)	Cu ₂ O	-0.16	0.43	0.37	85	2.3
	CuO	0.10	15.3	10.4	68	68
Cu(poly)	Cu ₂ O	-0.17	1.00	0.99	99	1.9
	CuO	0.10	10.0	6.3	63	6.5

4. PHOTOELECTROCHEMICAL PARAMETERS OF CU(I) AND CU(II) OXIDE FILMS

The negative photocurrent appears 10-30 minutes after the start of the anodic potentiostatic polarization of Cu(111) and Cu(100), proving the formation of p-type oxide film. The amplitude of the photocurrent increases with film thickness and then stabilizes (Fig. 3). The theory of thin semiconducting films [1, 2] makes it possible to obtain the parameters of oxide phase (Table 2). The values of optical density α , space charge region W and concentration of acceptor defects N_A do not vary with the crystal face of the substrate. Besides, they are close to similar parameters of the oxide formed on polycrystalline copper. However, the values of maximal photocurrent i_{ph}^{max} and of complex parameter $\eta f(1 - R_{ref}^{out})$ on Cu(100) exceed the values obtained on Cu(111) and polycrystalline copper. One can assume that the oxide formed on Cu(100) has a high effectiveness η of light adsorption and of subsequent assimilation f of electrons in the electrochemical reaction. On the other hand, the different values of i_{ph}^{max} and $\eta f(1 - R_{ref}^{out})$ can be caused

by the different coefficients R_{ref}^{out} of light reflection from the oxide/solution interface, since the morphology of oxide film on Cu(poly) and Cu(111) sharply differ from the oxide film on Cu(100).

Spectral dependence of photocurrent in Cu₂O films on Cu(110) and Cu(100) has two peaks in short-wave range (Fig. 4). Cu₂O oxide formed on Cu(111) generates

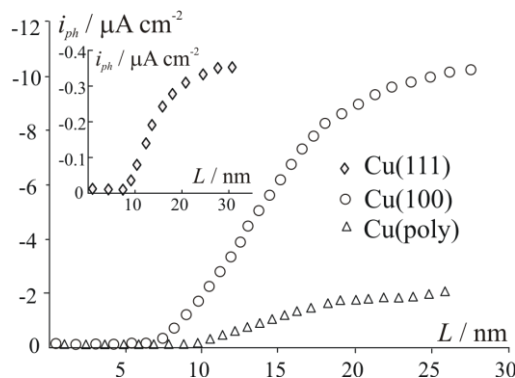


Fig. 3 – Photocurrent dependence on the thickness of Cu(I) oxide film at $E = -0.20 V$

Table 2 – The structural and optical characteristics of Cu₂O at $E = -0.20$ V, $\lambda = 400$ nm and $\Phi_0 = 3.04 \cdot 10^{15}$ photon cm⁻² s⁻¹

Substrate	$i_{ph}^{max} / \mu A cm^{-2}$	$\eta/(1 - R_{ref}^{out}) \cdot 10^4$	$\alpha \cdot 10^{-5} / cm^{-1}$	W / nm	$N_A \cdot 10^{-17} / cm^{-3}$
Cu(111)	0.35	7.2	19.2	21.5	2.04
Cu(100)	11.9	240.3	11.1	28.9	1.13
Cu(poly)	2.20	45.2	7.6	40.7	0.48

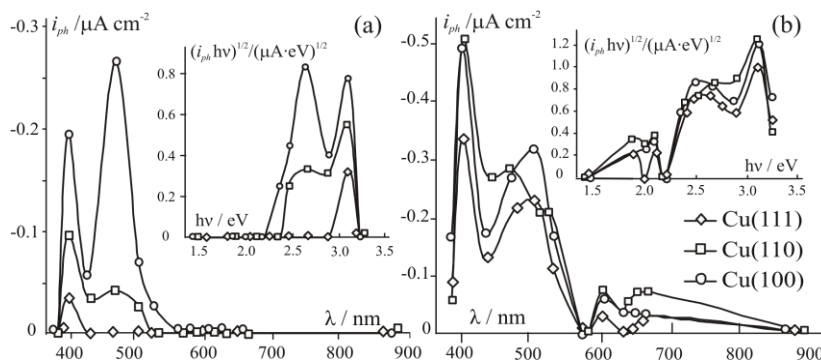


Fig. 4 – Spectral dependence of photocurrent in Cu(I) (a) and Cu(II) (b) oxides on single crystals of copper at $E = -0.17$ V

the negative photocurrent only at $\lambda = 400$ nm. The reliable linearization in coordinates criterial for non-direct transitions occurs for Cu(100). The band gap is equal to 2.2 eV as it was obtained for Cu₂O on polycrystalline copper.

At the potentials of CuO formation an additional peak appears in the spectral dependence at low energy ($\lambda = 600$ nm). The linearization is not possible, however a red boundary of the additional peak is close to CuO band gap (1.5 eV). The position of two main peaks remains the same as it was during Cu₂O formation. Hence, the film consists of both Cu(I) and Cu(II) oxides. Cu₂O makes the main contribution in the photocurrent amplitude. In general, band structure of anodic oxides Cu(I) and Cu(II) is invariant to the crystal state of the electrode.

5. THE MORPHOLOGY OF OXIDE FILMS

The more relief Cu₂O film formed on Cu(100) (Fig. 5b) is similar to the film formed on polycrystalline copper (Fig. 5a). High and comparative photocurrents are typical for these two cases. Since oxide films formed on Cu(110) and Cu(111) look like “smooth” and do not show clear structural elements (Figs. 5c and 5d), they

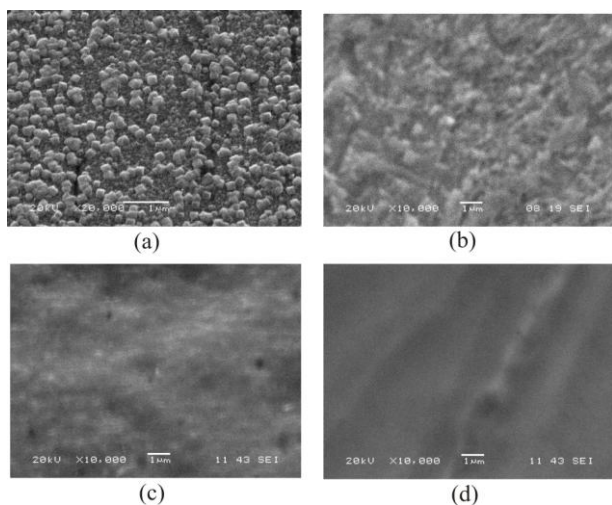


Fig. 5 – SEM-images of Cu(I) oxide film (20 nm) formed on polycrystalline copper (a), Cu(100) (b), Cu(110) (c) and Cu(111) (d) at $E = -0.19$ V (60 min)

generate low photocurrent. Most probably, the anodic growth of Cu₂O is realized in two different ways, i) the formation and overlapping of 3D-nuclea on Cu(100) and Cu(poly), ii) the formation of 2D-layers on Cu(110) and Cu(111). A noticeable difference in the electrochemical behavior, morphology and photocurrent amplitude for the oxides on different substrates proves the direct electrochemical way of oxide formation, not the mechanism of dissolution/precipitation.

In the potential range of Cu(II) oxide growth the amplitude of photocurrent is nearly constant for different single crystals and three times higher than it was for polycrystalline copper.

The results of SEM confirm the lack of noticeable difference in the structure and shape of crystals of oxide phase (Fig. 6). One can see large needle-shaped objects apparently corresponding to CuO with monoclinic crystal system. Besides large CuO crystals, the particles with smaller size present, probably Cu₂O undelayer. In general, the influence of crystal structure of the substrate to the photoelectrochemical, structural and morphological properties of oxide is negligible.

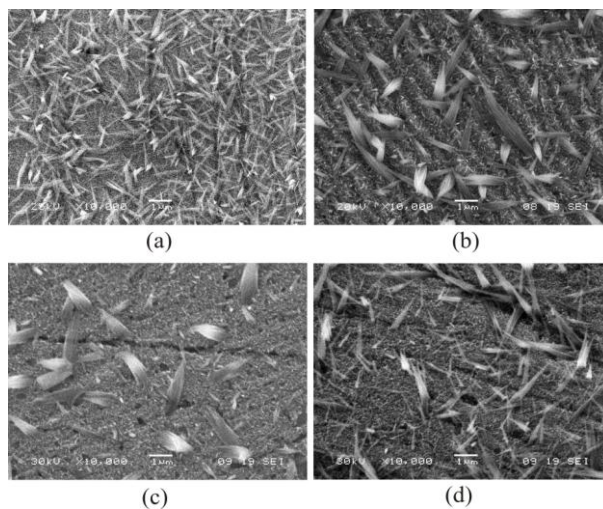


Fig. 6 – SEM-images of Cu(II) oxide film (60 nm) formed on polycrystalline copper (a), Cu(111) (b), Cu(110) (c) and Cu(100) (d) at $E = 0.10$ V (20 min)

6. CONCLUSION

The anodic oxidation of single crystals of copper in 0.1 M KOH proceeds with a noticeable diffusion limitation in solid phase. The oxide formation is preceded by chemisorption of OH-ions above -0.7 V. The extent of surface filling by oxygen does not exceeds 0.12 in the potential range up to -0.4 V and it is maximal for Cu(111). The current efficiency of the Cu(I) oxide formation is about 90 ÷ 100 %, the current efficiency of Cu(II) oxide formation is about 50 ÷ 60 %. At the poten-

tials of Cu(II) formation both Cu₂O and CuO are incorporated into the oxide film. The negative photocurrent proves the p-type of Cu(I) and Cu(II) oxides. The oxide parameters slightly change with the crystal structure of the substrate. The morphology of the oxide phase plays an important role.

ACKNOWLEDGEMENTS

Authors are grateful for financial supporting to RFBR (project 09-03-00554-a).

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