Oxide nanofilms on copper and silver: anodic synthesis and semiconducting properties

D S Eliseev, S N Grushevskaya, A V Vvedenskii, D A Kudrayshov

1 Voronezh State University, 1 Universitetskaya pl, 394006, Voronezh, Russia
2 St Petersburg Academic University, 8/3 Khlopina Str., St Petersburg, 194021, Russia
3 E-mail: sg@chem.vsu.ru

Abstract. Structure-sensitive properties of oxide nanofilms anodically formed on single crystals and polycrystalline silver and copper were determined by photoelectrochemical methods and scanning electron microscopy. At transition from polycrystalline substrate to single crystals the structural disordering decreases for Ag(I) oxide and increases for Cu(I) oxide in accordance with morphological modification.

1. Introduction
Semiconducting metal oxides are perspective materials for photolytic hydrogen evolution, electrocatalysis, current-generating devices, UV- and IR-sensors. The field of application of semiconducting oxides is determined by their structure-sensitive parameters. These parameters depend on the conditions of oxide formation that involve chemical composition of solution and substrate, the structural and crystallographic orientation of metal surface. The list of structure-sensitive in situ methods of investigation of oxide films is short; among them the photocurrent measurements occupy an important place [1-3].

The aim of the paper was to reveal the influence of the crystallographic orientation of metal surface on the structural parameters of anodically formed oxide nanofilms. We carried out photoelectrochemical in situ and physical ex situ measurements.

2. Experimental
The potentiostatic formation of Ag(I) and Cu(I) oxides was carried out in deoxygenated aqueous solution of 0.1 M KOH (analytical grade) on polycrystalline silver or copper and their single crystals 100, 110 and 111. Copper single crystals with a working surface of 0.2 cm² were produced by “Materials Technology & Crystals for Research, Development and Production” (Juelsch, Germany) with an accuracy of 2°. Silver (100), (110) and (111) single crystals with a working surface of 0.38; 0.52 and 0.60 cm² were grown in a horizontally moving furnace at temperatures from 1273 to 673 K with the subsequent cooling and orientation with an accuracy of 3°.

Before the electrochemical measurements the electrode surface was mechanically ground on grain paper, polished with aqua-MgO suspension, chemically polished, rinsed with double-distilled water and polarized in cathodic potential range during 10 minutes.

The morphology of the surface was monitored before and after electrochemical measurements was carried out by the scanning electron microscope JEOL 6380LV.
The concentration of prevailing structure defects, the coefficient of optical transition and the length of the space charge region (SC) for oxides were determined from photocurrent \( i_{ph} \) measurements in accordance with the equation obtained in [4] for thin oxide films:

\[
i_{ph} = e\eta f \Phi_0 \left(1 - R_{out}\right) \left(1 - e^{-2aL}\right) \approx i_{ph}^{\max} \left(1 - e^{-2aL}\right).
\]  

(1)

Here \( \eta \) is the quantum yield; \( f \) is the coefficient, that takes into account the difference in the rate constants of electron-hole recombination and hole consumption in an electrochemical reaction on the oxide/solution interface, \( R_{out} \) is the reflection coefficient of light flux from the oxide/solution interface; \( \alpha \) is the light absorption coefficient and \( L \) is the film thickness. If the film thickness reaches the length of SC then the photocurrent reaches maximal values of \( i_{ph}^{\max} \).

Photocurrent was measured using original equipment with a low-noise amplifier under potentiostatic polarization conditions with accuracy of 10 nA. Emitting diodes with wave length of 400 or 470 nm were used as a quasi-monochromatic light source. The density of light flux \( \Phi_0 \) was equal to \( 3.6 \cdot 10^{15} \) photon s\(^{-1}\) cm\(^{-2}\). The details of the environment were described in [4].

3. Results and discussion

3.1. Morphology of oxide films

The Ag\(_2\)O film formed on polycrystalline silver and its single crystals consists of well-resolved individual clusters of the oxide phase (figures 1). At transition from polycrystalline silver to single crystals the morphology of the Ag(I) oxide film slightly changes. The size of separate agglomerates reaches 400 nm although an average thickness of the oxide film does exceed 120 nm. The size of agglomerates and the distance between them increase in a series: Ag\(_{pol}\) < Ag\(_{110}\) < Ag\(_{100}\) < Ag\(_{111}\).

![Figure 1. SEM-images of Ag(I) oxide formed in 0.1 M KOH at \( E = 0.56 \) V on Ag\(_{pol}\) (a), Ag\(_{110}\) (b), Ag\(_{100}\) (c) and Ag\(_{111}\) (d).](image-url)
On polycrystalline copper (figure 2a) the size of agglomerates is lower as compared with polycrystalline silver. The film thickness reaches 20 nm. The crystallinity of Cu(I) oxide phase decreases in the following series: Cu_{poly} > Cu_{100} > Cu_{110} > Cu_{111}. It is hard to observe separate agglomerates of the oxide phase on single crystals of copper. The most patterned film is formed on Cu_{100} (figure 2b). Most probably, on Cu_{poly} and Cu_{100} 3D-nucleation is realized while on Cu_{110} and Cu_{111} 2D-nucleation is possible [5]. The change of nucleation mechanism can be the reason for the difference in the Cu_{2}O properties formed on different substrates.

![Figure 2. SEM-images of Cu(I) oxide formed in 0.1 M KOH at $E = -0.20$ V on Cu_{poly} (a), Cu_{100} (b), Cu_{110} (c) and Cu_{111} (d).](image)

3.2. Photocurrent measurements in oxide films

The photocurrent in silver oxide was measured at the potentials from 0.51 to 0.56 V/SHE. The first 5-7 seconds of potentiostatic polarization the photocurrent is not registered or does not exceed the noise level. When the oxide film with a significant thickness is formed the anodic photocurrent will arise. At the constant values of $L$ and $E$ the photocurrent in Ag_{2}O on single Ag crystals is always less as compared with Ag_{poly} substrate. Positive photocurrent proves n-type conductivity and prevailing of donor defects in Ag_{2}O on all substrates.

The growth of the amplitude with the film thickness proves that the film is thin. It does not exceed the length of SC and the equation (1) is valuable. The numerical processing of experimental data in accordance with this equation makes it possible to obtain the coefficient of optical transition, the length of SC for oxides and the concentration of prevailing structure defects. On single crystals the length of SC region of Ag_{2}O is higher by an order and $\alpha$ is noticeably lower as compared with Ag_{poly} substrate (table). The concentration of donor defects in Ag(I) oxide formed on single silver crystals is almost 10 times lower than in Ag(I) oxide formed on polycrystalline silver. Hence, the degree of deviation from the stoichiometric composition Ag_{2}O decreases. For Ag_{2}O formed on single crystals the length of SC increases in the following series: Ag_{poly} < Ag_{100} < Ag_{111} < Ag_{110}. The values of $\alpha$ and $N_0$ decrease in the same manner. This series does not coincide accurately with the series of morphology changing.
On polycrystalline copper and its single crystals the cathodic photocurrent arises in Cu$_2$O after 20-30 seconds of the polarization at the potentials between -0.22 and -0.05 V/SHE. The cathodic photocurrent reflects the p-type of conductivity and the prevailing of acceptor defects in Cu$_2$O formed on all substrates. The amplitude of photocurrent on single crystals is significantly lower than on Cu$_{\text{poly}}$ which is caused most probably by the structural and electronic state of Cu$_2$O film. The numerical processing was carried out for Cu$_{\text{poly}}$, Cu$_{100}$ and Cu$_{111}$ substrates where the amplitude of photocurrent in Cu$_2$O reached sufficient values. In Cu$_2$O on Cu$_{100}$ we did not observe photocurrent hence we could not calculate the structural parameters.

The amplitude of photocurrent as well as the length of SC decrease at transition from Cu$_{\text{poly}}$ to Cu$_{100}$ and then to Cu$_{111}$ (table). The optical density and the concentration of acceptor defects increase in the same manner. Note that this series in general coincide with the series of decreasing crystallinity in Cu$_2$O formed on different substrates.

| Potential | 0.56 V | -0.20 V |
|-----------|--------|---------|
| Substrate |        |         |
| Ag$_{\text{poly}}$ | Ag$_{100}$ | Ag$_{111}$ | Ag$_{110}$ | Cu$_{\text{poly}}$ | Cu$_{100}$ | Cu$_{111}$ |
| $\alpha \cdot 10^{-5}$/ cm$^{-1}$ | 2.3    | 1.4     | 1.0     | 0.7     | 7.6    | 11.1    | 19.2    |
| $W$/ nm | 100    | 164     | 230     | 329     | 40.7   | 28.9    | 21.5    |
| $N_D \cdot 10^{-15}$/ cm$^{-3}$ | 22.4   | 8.3     | 4.2     | 2.1     | 48.0   | 113.0   | 204.0   |
| $N_A \cdot 10^{-15}$/ cm$^{-3}$ |        |         |         |         |        |         |         |

4. Conclusion
The polarity of photocurrent points to n-type conductivity in Ag(I) oxides and p-type conductivity in Cu(I) oxides anodically formed in alkali on polycrystalline silver or copper and their single crystals. A decrease of photosensitivity of oxide nanofilms grown on single crystals is determined by their morphology, structure and electronic state. The transition from polycrystalline silver to its single crystals results in a decrease of optical density and donor defects. The transition from polycrystalline copper to its single crystals results in a growth of optical density and acceptor defects. Hence, the degree of deviation from the stoichiometric composition or the structural disordering decreases for Ag(I) oxide and increases for Cu(I) oxide.

Acknowledgements
The investigations were carried out under financial supporting of the Ministry of Education and Science of the Russian Federation (project 675).

References
[1] Gurevich YV and Pleskov YY 1986 *Semiconductor photoelectrochemistry* (New York: Consultants Bureau)
[2] Bard AJ and Faulkner LR 2001 *Electrochemical methods: Fundamentals and Applications* (Hamilton: John Willey)
[3] Bockris JO’H and Khan SUM 1993 *Surface Electrochemistry: A Molecular Level Approach* (New-York, London: Plenum Press)
[4] Kudryashov DA, Grushievskaya SN, Ganzha SV and Vvedenskii AV 2009 *Prot Met* 45 501
[5] Gamburgh YD and Zangari G 2011 *Theory and Practice of Metal Electrodeposition* (Boston, New York, Heidelberg: Springer)