SURFACES, INTERFACES, AND THIN FILMS

Morphology, Optical, and Adsorption Properties of Copper-Oxide Layers Deposited from Complex Compound Solutions

L. B. Matyushkin[a]*, A. A. Reshetnikova[a], A. O. Andronov[a], P. K. Afonicheva[a], S. V. Myakin[b], N. V. Permiakov[a], and V. A. Moshnikov[a]

[a] *Saint Petersburg Electrotechnical University "LETI", St. Petersburg, 197376 Russia*
[b] *Saint Petersburg State Technological Institute, St. Petersburg, 190013 Russia*
* e-mail: leva.matyushkin@gmail.com
Submitted November 17, 2016; accepted for publication November 28, 2016

Abstract—A technique for synthesizing gas-sensing copper-oxide layers by layer-by-layer deposition onto glass and plastic substrates is considered. Deposition is based on the oxidation of a copper–ammonia complex by hydrogen peroxide. Layers synthesized at various numbers of deposition cycles are studied by atomic-force microscopy and transmission spectroscopy methods (300–1000 nm). The spectral shape indicates the mixed nature of the oxide with predominant copper oxide (I) Cu_2O with a corresponding band gap of 2.1 eV. The layers have a continuous granular structure. The surface concentration of Brönsted acid adsorption sites with $pK_a \approx 2.5$ (OH acid groups), determined by the indicator method, is 560 µmol/m^2 for the initial films, and threefold increases after heat treatment at 80°C for 30 min. The results obtained are interesting for the use of the described technology for fabricating copper-oxide active layers in gas-sensing sensors operating at room temperature.

1. INTRODUCTION

In the development of sensors for monitoring the composition of atmospheric air, of great interest are such materials as metal oxides, in particular, copper oxides (CuO and Cu_2O with band gaps of 1.2 eV and 2.1 eV, respectively) [1]. The advantages of copper oxides are their low cost and chemical resistance. Copper-oxide films have proven themselves as sensitive layers of gas sensors, i.e., ammonia NH_3 [2], nitrogen oxide NO_2 [3], and hydrogen sulfide H_2S [4] sensors. For the latter gas, this material is also used in combination with tin oxide [5].

The operation of metal-oxide gas-sensing sensors is based on a change in the sample resistivity upon exposure to a detected gas adsorbed on the semiconductor surface. To significantly change the resistivity, development of the surface of the sensitive layer is required, i.e., a high specific sample surface area. For the adsorption of detected molecules, the surface state, i.e., the number and nature of surface adsorption sites plays an important role. In the case of gas-sensing metal-oxide layers, Brönsted acid sites with $pK_a \approx 2.5$ are of particular importance [6, 7].

Among the various methods for growing thin films, the ion deposition (ID) method has an important place, which is known in foreign publications as SILAR (Successive Ionic Layer Adsorption and Reaction) [8]. The method consists in the successive adsorption of ions on the substrate surface, e.g., metal ions A and chalcogen ions B to obtain II–VI and IV–VI semiconductor compound films. In the case of the standard ID technique, e.g., for growing metal-chalcogenide thin films (PbSe, CdTe, ZnS, and others), two solutions are used as sources: a salt solution containing the necessary metal cations (A^{2+}, e.g., for Cd^{2+}, $CdCl_2$ can be a source), and a salt solution containing chalcogen anions (B^{2-}, e.g., for S_2, Na_2S is commonly used as a source). The substrate functionalized by OH groups is sequentially immersed into source solutions placed in separate vessels. When the substrate is immersed into a metal source solution, the preferential adsorption of metal cations A^{2+} occurs due to preliminary functionalization of the substrate surface (e.g., by OH groups); the cation excess is removed in the following vessel with solvent (usually, distilled water). Then the substrate with adsorbed A^{2+} ions is immersed into a solution with a chalcogen source whose ions (B^{2-}) chemically interact with the adsorbed layer, which results in the formation of an insoluble AB compound layer on the substrate. Excess B^{2-} anions physically adsorbed on the sample, but not involved in the chemical interaction, are removed by subsequent immersion into a vessel with solvent. This is a procedure corresponding to one cycle, commonly

performed using an automated electromechanical setup. To obtain films of specified thickness, the procedure is repeated the necessary number of times.

The advantages of such a technique are the possibility of growing films under normal conditions (room temperature and atmospheric pressure) on substrates of different nature (material, morphology, sizes) with a high accuracy of synthesized-layer thickness control and the comparative ease of setting the chemical composition of the final film by varying the composition of the ion source solutions. A distinctive advantage of the technique for the developing direction of flexible electronics is the possibility of growing thin films at comparatively low temperatures, which makes it possible to use a flexible polymer base, including that of a bent shape.

However, in comparison with the conventional ID method considered as applied to MeX metal chalcogenides [8], in the case of oxide compounds of the general form MeO_x, application of this technique is complicated. This is due to the presence of oxygen in the used solvents and in the ambient atmosphere, and the complicated controlled use of any salt source of oxygen. Therefore, of interest is the use of complex compounds decomposing to oxides as a result of a change in acidity, thermal or chemical exposures, and others. To obtain metal-oxide powders, true solutions of metal salts are also used, which form a metal hydroxide during interaction with alkalis, which then decomposes upon heating,

$$Me(OH)_2 \rightarrow MeO + H_2O.$$
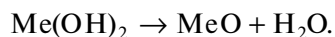
However, the necessity of high-temperature annealing neutralizes in this case such an advantage of the method as low synthesis temperatures. Furthermore, as shown in [9], complex compounds, especially the zinc−ammonia complex, makes it possible to grow ZnO films with a higher quality, than when using true solutions (e.g., $ZnCl_2$). The film growth process can be controlled by such factors as the pH of the medium [10−12], the reaction temperature [13], the additional use of other ion sources [14, 15], and thermal annealing [11].

In this paper, we propose a technique for producing copper oxides for gas-sensing structures, based on the fact that, in contrast to the conventional ion deposition method, instead of a metal source dissociating in a solution, its complex compound is used, and instead of a chalcogen source, hydrogen peroxide is used. In view of the significantly different nature of layer deposition, copper-oxide film growth with a developed granular surface can be expected in this method. It is important that a large number of hydroxyl centers of OH group adsorption are formed on the sample surface, since aqueous solutions of salts are used as ion

sources in the described method. Thus, the proposed technique is interesting for producing gas-sensing structures.

2. EXPERIMENTAL

An automated setup previously described for the case of ion deposition by the example of cadmium sulfide [16, 17] was used to obtain metal-oxide films.

Slide glass and polyester were chosen as substrates. The substrates were 1×2 cm in size and 1 mm and 0.1 mm thick for glass and polyester, respectively. The substrates were preliminarily cleaned in an ultrasonic bath sequentially in acetone, isopropyl alcohol, and distilled water. To produce OH groups, both glass and plastic substrates were treated in a concentrated alkali (NaOH) solution, after which they were again rinsed in distilled water.

The transmission spectra of the prepared samples were measured using a PE-5400 UV spectrophotometer (190−1000 nm). The sample morphology was studied with an NT-MDT NTEGRA Therma atomic-force microscope.

Thin copper-oxide films were synthesized via the interaction of the copper−ammonia complex and hydrogen peroxide. Four solutions were used to synthesize films: (i) copper−ammonia complex $[Cu(NH_3)_4]^{2+}$ solution obtained by mixing aqueous solutions of copper chloride, distilled water, and ammonia:

(1) $CuCl_2 \rightleftarrows Cu^{2+} + 2Cl^-$,

(2) $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$.
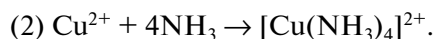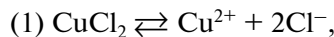
(ii) and (iv) distilled water, (iii) aqueous solution of hydrogen peroxide H_2O_2. Distilled water in intermediate vessels is necessary to both remove complex molecules not adsorbed on the substrate and to lower the complex solution and hydrogen-peroxide contamination with each other.

During sequential substrate transfer, i.e., immersion into solutions, (i) complex molecules are adsorbed on the substrate surface, (ii) excess complex is removed from the surface by distilled water, (iii) the adsorbed complex decomposes on the substrate surface by hydrogen peroxide, and (iv) hydrogen-peroxide excess is removed.

The film was a uniform yellow color in the first cycle, this color was further retained, and became brighter. The procedure was repeated a set number of times. To reveal the dependence of the number of deposition cycles on the film thickness, the synthesis procedure was repeated to perform 2, 5, 10, 15 deposition cycles. The described experiment was performed for both substrate types.

To measure the concentration of Brönsted acid adsorption sites with $pK_a \approx 2.5$ (OH acid groups) on
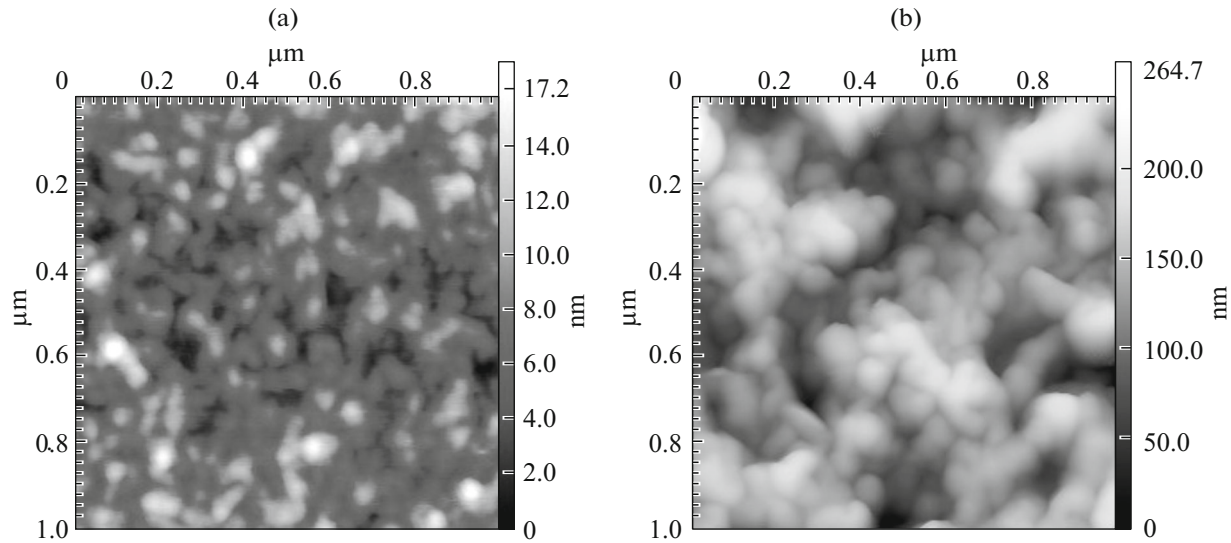
(a)

(b)

Fig. 1. AFM image of the CuO$_x$ film topology; the scan size is 1×1 µm: (a) on a glass substrate and (b) on a polyester substrate.

the film surface, the chemical indicator method previously described in [7, 18] was used. For adsorption sites with $pK_a \approx 2.5$, m-nitroaniline [6] is an indicator. The concentration of surface active sites with this pK_a is determined from photometric data by the expression

$$q(pK_a) = \left\| \frac{|D_0 - D_1|}{m_1} \pm \frac{|D_0 - D_2|}{m_2} \right\| \cdot C_{ind} \cdot V_{ind} / D_0,$$

where D_0 is the optical density of the blank control sample obtained by adding distilled water to the indicator taken with the volume V_{ind} and concentration C_{ind}, D_1 is the optical density of the indicator solution with a sample after reaching adsorption–desorption equilibrium, D_2 is the optical density of decanted water in which the sample was kept for an hour with added indicator, m_1 and m_2 are the masses of the sample under study (the surface concentration was determined with respect to the substrate area in the case at hand), for measurements of optical densities D_1 and D_2, respectively,.

3. EXPERIMENTAL RESULTS

The thin copper-oxide films grown by the reaction of decomposition of the ammonia complex by hydrogen peroxide had a dense homogeneous structure and adhered to both the glass and polyester substrates. The films did not delaminate upon long-term exposure to ultrasound.

The atomic-force microscopy of the morphology of the synthesized CuO$_x$ film after 15 deposition cycles is shown in Fig. 1. The films on both substrate types have the expected granular structure. In the 1×1 µm

micrograph (Fig. 1a), we can see that the height difference does not exceed 20 nm and 260 nm for the glass and polyester substrates (Fig. 1b). Since the initial substrate roughness had close values, we can assume that there are different film growth mechanisms resulting in a significant difference in the sample surface roughness. First of all, such deposition depends on the number of adsorption sites on the substrate surface.

In the case of glass, a higher concentration of OH groups can be expected after preliminary treatment in alkali, hence, a less loose structure of the obtained layer.

The optical spectroscopy results for films on glass substrates are shown in Fig. 2. The optical film density increases with the amount of deposited material. In this case, the curve shape does not change at different numbers of deposition cycles, hence, the deposition process in the first stages and further has the same nature. A similar shape is characteristic of the layers grown on the plastic substrate.

The optical band gap determined in Tauc coordinates was 2.1 eV which corresponds to the reference band gaps of copper oxide (I) Cu$_2$O [1]. In all optical density spectra, we can see an inflection point separating the spectrum into short-wavelength and long-wavelength regions. The value obtained by interpolation of the short-wavelength spectral region to the intersection with the energy axis corresponds to the indicated energy gap. We can assume that the obtained oxide is of mixed nature, which is indicated by the long-wavelength spectral region corresponding to copper oxide (I) CuO being a narrower-gap material.
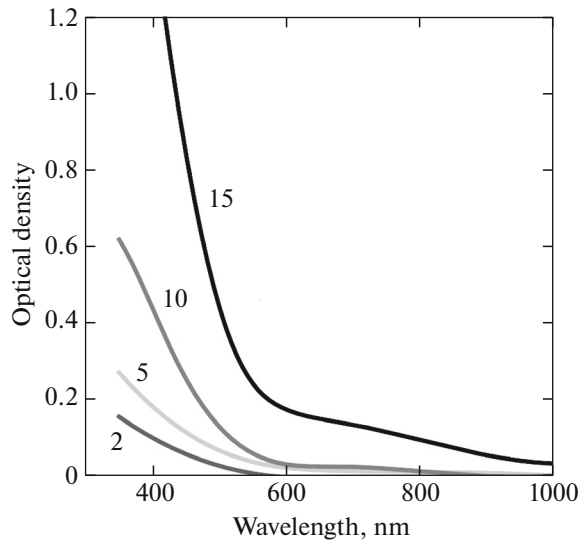
Fig. 2. Dependences of the optical density of CuO_x films grown by ion deposition after 2, 5, 10, and 15 cycles.
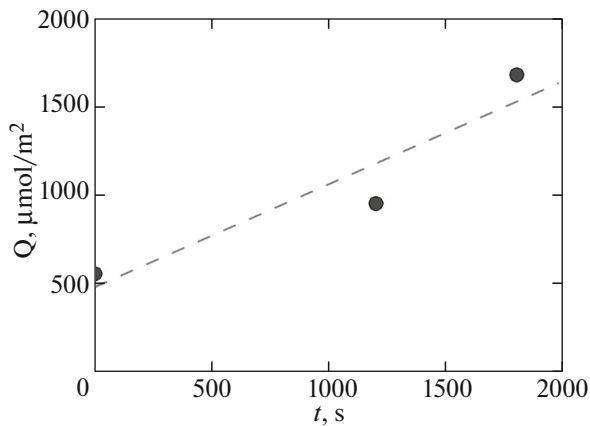

Fig. 3. Dependence of the surface concentration of adsorption centers with $pK_a \approx 2.5$ on the heat-treatment time.

The spectral shape was identical for both substrate types.

When comparing the optical density spectra, it can be concluded that film deposition is enhanced with increasing the number of deposition cycles (Fig. 2). This can be associated with the necessity of the formation of a certain "seed" layer for copper-oxide layer growth, and the fact that copper released during the reaction is a catalyst of hydrogen-peroxide decomposition.

The nature of the developed surface and the mixed-oxide type point to the possible existence of a large number of surface adsorption sites that are of interest for gas-sensing structures. Therefore, the content of

Brönsted acid sites with $pK_a \approx 2.5$, i.e., OH acid groups, was measured, whose number, according to the results of previous studies [18], can correlate with the gas sensitivity of oxide sensors on the copper-oxide sample surface on a glass substrate, depending on the heat-treatment time at a temperature of 80°C. The data obtained (Fig. 3) show that the content of surface sites under consideration increases with the heat-treatment time; for 30-min heat treatment, this value approximately threefold increases in comparison with the initial concentration of 560 μmol/m². The observed dependence can be explained by surface peroxide compound decomposition and activation of the chemisorption of physically sorbed water molecules with the formation of additional hydroxyl groups on the film surface.

4. CONCLUSIONS

The proposed technique of the layer-by-layer oxidation of copper–ammonia complex molecules by hydrogen peroxide showed the possibility of growing continuous homogeneous copper-oxide layers with adhesion to both glass and flexible plastic substrates. The technique allows the use of automated setups for ion deposition from solutions (SILAR method).

The study of grown layers by atomic-force microscopy methods showed their homogeneous granular structure. The optical density spectra of the samples point to the mixed copper-oxide type with predominant copper oxide (I) Cu_2O with a band gap of 2.1 eV. The surface concentration of Brönsted acid sites with $pK_a \approx 2.5$ (OH acid groups), determined by the chemical indicator method, is 560 μmol/m² for the initial films and threefold increases after heat treatment at 80°C for 30 min.

The results obtained are interesting for the use of the described technology for fabricating active copper-oxide layers in gas-sensing sensors operating at room temperature.

ACKNOWLEDGMENTS

REFERENCES

1. V. Dhanasekaran, Thin Solid Films **520**, 6608 (2012).
2. T. A. Moiseeva, Inzhen. Vestn. Dona 23 (4) (2012).
3. S. T. Shishiyanu, T. S. Shishiyanu, and O. I. Lupan, Sens. Actuators B: Chem. **113**, 468 (2006).

4. J. Chen, J. Phys. Chem. C **112**, 16017 (2008).

5. Chowdhuri, J. Appl. Phys. **92**, 2172 (2004).

6. K. Tanabe, *Solid Acids and Bases* (Academic, New York, London, 1970).

7. S. S. Karpova, V. A. Moshnikov, S. V. Mjakin, and E. S. Kolovangina, Semiconductors **47**, 392 (2013).

8. H. M. Pathan and C. D. Lokhande, Bull. Mater. Sci. **27**, 85 (2004).

9. M. Ristov, Thin Solid Films **149**, 65 (1987).

10. M. Nair. Appl. Surf. Sci. **150**, 143 (1999).

11. I. Truijen, M. K. Van Bael, H. van den Rul, J. D'Haen, and J. Mullens, J. Sol-Gel Sci. Technol. **41**, 43 (2007).

12. R. Chand, A. Gaur, and A. Kumar, Superlatt. Microstruct. **60**, 129 (2013).

13. Z. Yang, J. Solid State Chem. **180**, 1390 (2007).

14. Y. Gulen, Ceram. Int. **39**, 6475 (2013).

15. Yu. V. Vaganova, V. R. Mirolyubov, S. V. Katyshev, A. V. Ishchenko, and E. O. Klyukina, Sovrem. Probl. Nauki Obrazov., No. 3, 817 (2014).

16. L. B. Matyushkin, D. V. Khondryukov, and A. O. Aleksandrova, RF Patent No. 156478 (2015).

17. A. O. Andronov, L. B. Matyushkin, and D. V. Hondryukov, in *Proceedings of the IEEE NW Russia Young Researchers in Electrical and Electronic Engineering Conference* (St. Petersburg, Russia, 2016), p. 19.

18. S. S. Karpova, V. A. Moshnikov, A. I. Maksimov, S. V. Mjakin, and N. E. Kazantseva, Semiconductors **47**, 1026 (2013).

Translated by A. Kazantsev