

Electrical and optical properties of cobalt oxide thin films, prepared by ion-beam sputtering

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Optical and electrical properties of cobalt oxide thin films obtained by ion-beam sputtering in argon atmosphere and argon with the addition of oxygen ($P_{Ar} = 1.1 \cdot 10^{-5}$ Torr) has been investigated in the work. Optical properties investigations showed that, for films of cobalt oxide obtained in argon atmosphere, the optical band gap is independent of the film thickness and is 3.24 eV, which is in the range of given in the literature for the CoO phase values. For cobalt oxide films obtained in mixed atmosphere of argon with the addition of oxygen, two direct optical transitions with energies of 1.45 and 2.1 eV were detected. The presence of two direct allowed optical transitions is associated with the variable valence of cobalt in the Co_3O_4 compound and the presence of two valence states Co^{2+} and Co^{3+} . The dependences of specific electrical conductivity of the synthesized films on the magnitude of the electric field were studied. It was found that for all investigated samples, the electrical conductivity does not depend on the electric field strength up to the value of $E = 10^6$ V/m. The nonlinearity of the dependence of specific electrical conductivity of the synthesized films on electric field strength at $E > 10^6$ V/m is discussed in terms of the hopping conductivity model and the trap ionization model described by the Poole-Frenkel effect.

Keywords: oxide semiconductors, optical absorption coefficient, electrical conductivity, strong electric fields.

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Introduction

The metal oxide thin films continue to attract the attention of the researchers due to a combination of many useful properties and their low cost [1–4]. The oxygen-containing cobalt compounds can be applied as magnetic [5] and electrode materials of the batteries [6], in solar panels [7], as thermosensitive elements of the sensorics materials [8], as well as in the chemistry industry as catalysts for the heterogeneous catalysis [9,10]. In many industries, the cobalt oxide is used as a thin nanostructured film, whose properties depend on the method and the synthesis conditions [11].

However, the large scope of publications dedicated to the cobalt oxide and the thin-filmed structures based thereon does not allow formulating the regularities of formation of the oxide structures, which should be known in order to create technological approaches when synthesizing these films. That is why the regularities in the row „the synthesis conditions–the structure–the physical and chemical properties“ for this kind of the nanostructured films are still poorly studied, thereby requiring a search for new approaches to film synthesis so as to produce them with high reproducibility in terms of the structural and physical-chemical parameters.

In particular, the thin films of the oxide materials based on the cobalt oxide are promising for the thermoelectrical use, as they are light, small in size and can be easily synthesized. However, the oxide thin films have not been

investigated at the same level, which has been achieved for the respective compounds of bulk ceramic and single-crystalline samples [4]. Taking the above-said into account, the work has synthesized the cobalt oxide thin films by ion-beam sputtering and investigated electrical and optical properties thereof.

1. Procedures of synthesis and investigation

The experimental samples have been produced by using the ion-beam sputtering method, which is realized based on the UVN-2M vacuum station, whose design is described in detail in [12]. The ion-beam sputtering method has a number advantages over the other ones used to synthesize metal oxides and other thin-film systems [13]:

1. The low value of the working pressure of $2-7 \cdot 10^{-4}$ Torr is realized due to that the operating gas (argon) is supplied directly to the anode area.

2. It is possible to sputter magnetic and non-magnetic metal materials, as the magnetic system of the ion source is not correlated to the target material.

3. As the spluttered surface is under the „earth“ potential, available electron sources (compensator) allow neutralizing the excessive positive charge of ions thereon, thereby enabling sputtering the dielectric materials at the anode constant voltage.

4. The substrate surface is slightly heated during sputtering as an area of maximum plasma concentration is within the magnetic gaps of the ion source. That is why there is no interaction of high-energy electrons with the substrate surface and the only energy flux to the substrate comes from atoms of a deposited material.

5. Due to the fact that the operating gas (argon) is supplied directly to the ion source, and the active gases are to the operating chamber, a plasma composition within the magnetic gap of the source changes in lesser proportions than a relationship of the pressures of the chamber gas medium towards excessive argon. It contributes to a lesser impact of the active gases on characteristics of operation of the ion source in reactive sputtering of the materials.

The cobalt oxide thin films have been produced by using a water-cooled target consisting in CoO ceramics plates. The electric properties of the cobalt oxide thin films along the electrotransport direction perpendicular to the film plane have been investigated by applying three-layer metal electrodes Cr/Cu/Cr of the thickness of 1–2 μm and the area of $S = 0.5 \times 0.2 \text{ mm}$. Thus, when investigating the electrotransport perpendicular to the film plane, the Cr/Cu/Cr–the cobalt oxide–Cr/Cu/Cr structures were investigated, i.e. the chromium layers were in direct contact with the film. Two batches of the samples have been produced in the chamber during sputtering to investigate the impact of oxygen adding:

- in the medium of pure argon;
- when adding the oxygen of the partial pressure of $1.1 \cdot 10^{-5}$ Torr into the argon medium.

In order to investigate the structure and optical properties, the cobalt oxide was deposited onto substrates made of single-crystalline silicon and glass, respectively. The thickness of the produced films was measured at an MII-4 interferometer to be 0.13 to 0.3 μm .

The structure and the phase composition of the produced samples were investigated on a Bruker D2 Phaser diffractometer ($\lambda_{\text{CuK}\alpha 1} = 1.54 \text{ \AA}$) using the DIFFRAC.EVA 3.0 software and the ICDD PDF Release 2012 database. The optical properties and the characteristics of the band structure of the oxide semiconductors were investigated by measuring the transmittance factor using the spectrophotometer ECOVIEW UF-6100S.

The influence of the heat treatment on the structure, electric and optic properties was investigated by annealing in the vacuum of 10^{-4} Torr at the temperature of 600°C. The heating and cooling rate was 5 grad/min, so was the time of holding at the annealing temperature — 30 min.

2. Structure of the cobalt oxide thin films

As it is known from literature data, the structure and the physical properties of semiconductors based on the metal oxides are strongly affected by the oxygen stoichiometry. That is why two batches of the samples have been produced in the chamber during sputtering to investigate the impact

of oxygen adding: in the medium of pure argon and with adding oxygen of the partial pressure of $1.1 \cdot 10^{-5}$ Torr into the argon medium. The X-ray diffraction images (Fig. 1) for the films in the initial state, both for the samples sputtered in the atmosphere of pure Ar, and Ar + O₂ evidently show a single wide maximum at the angle of $\theta \approx 36^\circ$. By comparing with the reference data of the PDF2012 base, it has shown that the obtained maximum can correspond either to the planes (111) of the cubic CoO (the space group Fm-2m, the card PDF 01-071-1178), or the planes (311) of the cubic Co₃O₄ (the space group Fd-2m, the card PDF 00-042-1467). At the same time, it should be noted that the film must be strongly textured along the axes with respective directions. The shifting of the maximum position relative to the reference data towards the lesser angles (bigger interplanar distances) is indicative of the availability of compressive macrostresses (the stresses of the first kind). The strong widening of the maximum can be the result of the fine-crystalline structure and/or the availability of microstresses. Because, as noted above, the maximum observed at the angle of $2\theta \approx 36^\circ$ is the only one, it is not possible to divide these two contributions into the peak widening. The heat treatment of the films usually results in relaxation of macro- and microstresses, as well as to the increase in sizes of crystallites, which can clarify an issue of the phase composition of the produced films.

After the heat treatment in the vacuum of 10^{-4} Torr at the temperature of 600°C, the maximum intensity increases with decrease in its width, which can be indicative of recrystallization processes and the growth of crystallite size. At the same time, the maximum position does still match neither to the CoO phase, nor the Co₃O₄ phase, which can be the result of nonstoichiometry and extreme defectiveness of the produced films. On the other hand, the position of the maximum between the (111) CoO and (311) Co₃O₄ peaks can be indicative of simultaneous availability of these two phases in the produced film.

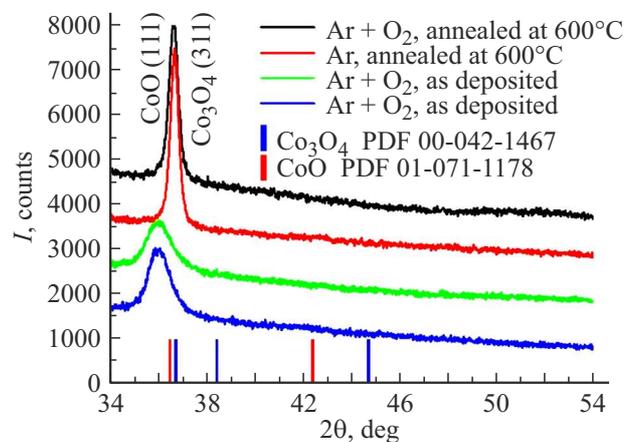


Figure 1. X-ray diffraction images for the cobalt oxide thin films synthesized in the argon atmosphere (Ar) and the mixed atmosphere (Ar + O₂).

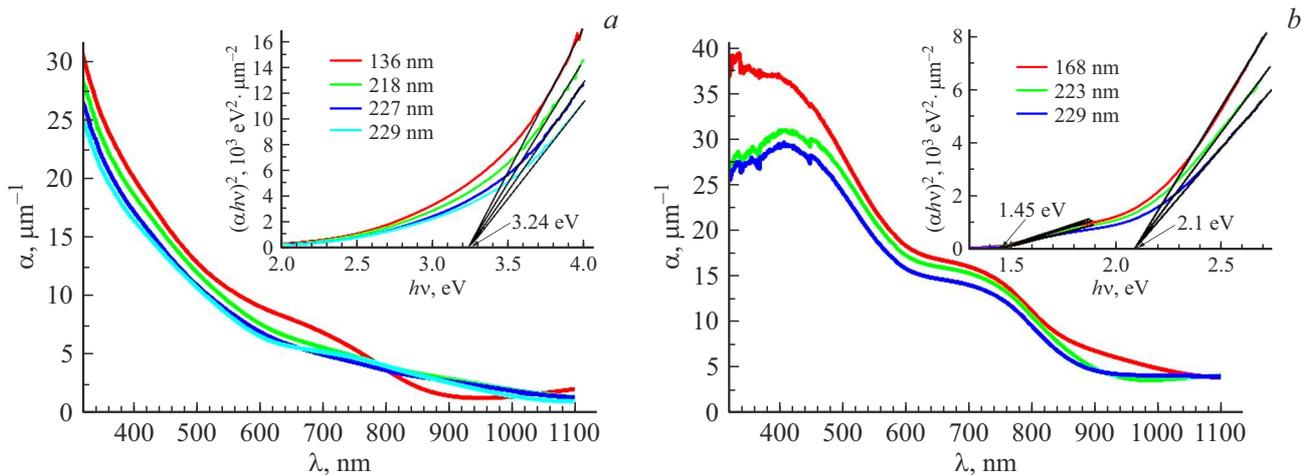


Figure 2. Spectra of the optical absorption coefficient α in dependence on the wavelength of the incident radiation for the cobalt oxide films produced in the atmosphere of Ar (a) and Ar + O₂ (b). The inserts show the dependences of the optical absorption coefficient on the photon energy in the coordinates $(\alpha h\nu)^2 \propto f(E)$.

3. Optical properties of the cobalt oxide thin films

In order to investigate the optical properties and determine the band gap of the cobalt oxide thin films, light transmission spectra within the wavelength range from 300 to 1100 nm were measured at the room temperature. The spectra of the optical absorption coefficient $a = -\ln T/d$ (T — the optical transmittance, d — the film thickness) of the films studied in the work are shown on Fig. 2.

In general, the edge of the fundamental absorption can be described by the Tauc formula [4]:

$$\alpha h\nu = A(h\nu - E_g)^n, \quad (1)$$

where α — the absorption coefficient, $h\nu$ — the photon energy, E_g — the optical band gap, A — the constant depending on the effective masses of electrons in the conductivity band and holes in the valence band, n determines the type of the electron or optical transition and takes the values 1/2, 2, 3/2 or 3. If $n = 1/2$, then the transition is a direct allowed one, $n = 3/2$ — a direct unallowed, $n = 2$ — an indirect allowed and $n = 3$ — an indirect unallowed.

It is known from the literature sources that both for the CoO phase, and for the Co₃O₄ phase, the direct allowed optical transitions are characteristic [4], thereby estimating the optical band gap of the studied cobalt oxide films (the inserts of Fig. 2) from the curves $(\alpha h\nu)^2 \propto f(h\nu)$ by the method of extrapolation of the dependence linear portion until intersecting the $h\nu$ ($\alpha h\nu = 0$) axis around the edge of the fundamental absorption.

The estimations have shown for the cobalt oxide films produced in the argon atmosphere the optical band gap did not depend on the film thickness and was 3.24 eV, thereby laying within a range of values specified in the literature for the CoO phase [14]. For the cobalt oxide films produced in the atmosphere Ar + O₂, the two direct

optical transitions with the energies of 1.45 and 2.1 eV have been found. As per [15], the availability of the two direct allowed optical transitions is caused by features of the Co₃O₄ band structure, which are due to the availability of the two valence states Co²⁺ and Co³⁺ in this compound. Thus, the Co₃O₄ valence band is formed by the 2p oxygen orbitals, so is the conductivity band — by the 3d orbitals of the Co²⁺ cobalt. The Co³⁺ atoms form a narrow subband in the band gap. Thus, the direct allowed O²⁻ → Co³⁺ transitions correspond to the optical transitions with the energy of $E_{g1} = 1.45$ eV. The energy of the O²⁻ → Co²⁺ transitions provide for the value of the „true“ band gap, which is $E_{g2} = 2.1$ eV in our case. The obtained values fully comply with the literature data [15,16].

It follows from the studies of the optical properties that the optical band gap of the cobalt oxide films produced in the atmosphere of argon is determined by the direct allowed transitions of the CoO electrons. When adding the oxygen of the partial pressure of $1.1 \cdot 10^{-5}$ Torr into the atmosphere of argon, the edge of the fundamental absorption of the produced thin films is determined by the direct allowed transitions in the Co₃O₄ phase.

4. Influence of the strong electric field on the conductivity of the cobalt oxide thin films

The preliminary results of investigation of the electric properties of the cobalt oxide thin films have shown that the latter have high electric resistance. That is why the thin film samples have been synthesized for the studies in the perpendicular geometry and it included investigation of the strong electric field on the conductivity thereof. Figure 3 shows the current-voltage characteristics (current-voltage curves) of the studied samples.

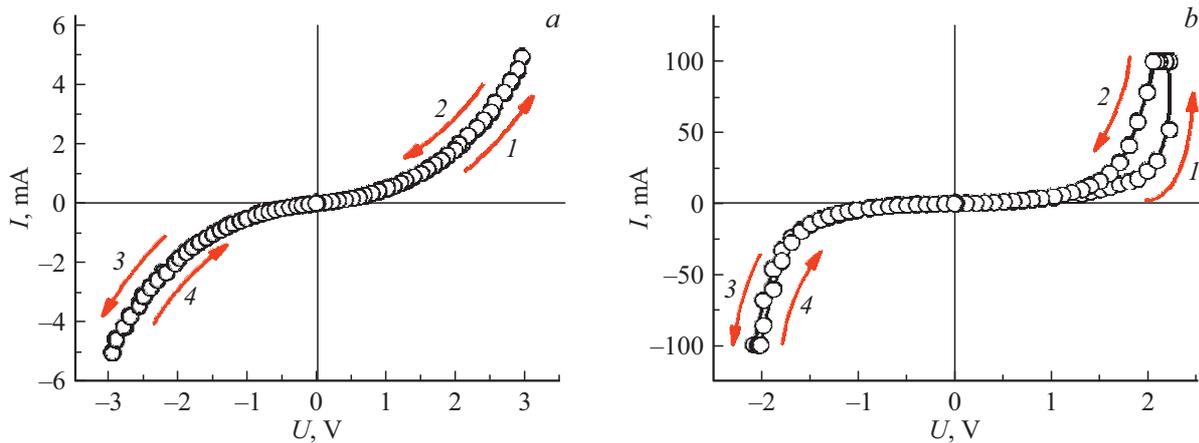


Figure 3. Current-voltage curve of the cobalt oxide thin films of the thickness of 230 nm produced in the atmosphere of Ar (a) and Ar + O₂ (b).

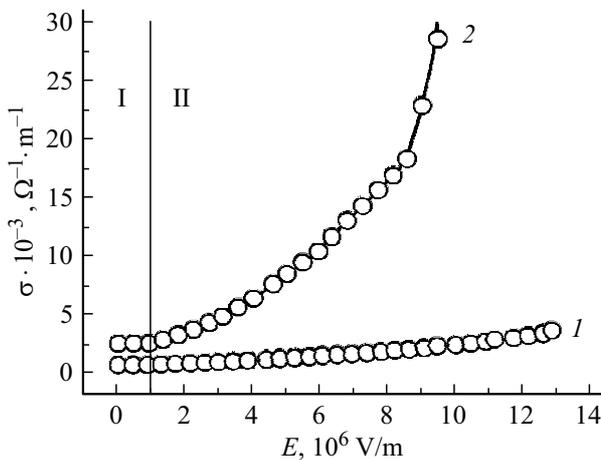


Figure 4. The dependences of the electric conductivity on the value of the external electric field for the cobalt oxide thin film samples produced in the atmosphere Ar (1) and Ar + O₂ (2).

The digits 1–4 designate the sequence of the change of the sample voltage, where 1 — the increase in the positive voltage at the upper electrode, 2 — the decrease in the positive voltage at the upper electrode, 3 — the increase in the negative voltage at the upper electrode, 4 — the decrease in the negative voltage at the upper electrode. As it is clear from Fig. 3, a, the current-voltage curve of the cobalt oxide films produced in the Ar medium is symmetrical relative to zero and non-linear. The dependences measured at the increase and decrease in the electric field are the same. For the cobalt oxide films produced in the Ar + O₂ medium, the current-voltage curve is non-linear and unsymmetrical relative to zero (Fig. 3, b). The dependences measured at the increase and decrease in the electric field are not the same, i.e. for the current-voltage curves of the cobalt oxide films produced in the Ar + O₂ atmosphere, there is evidently hysteresis.

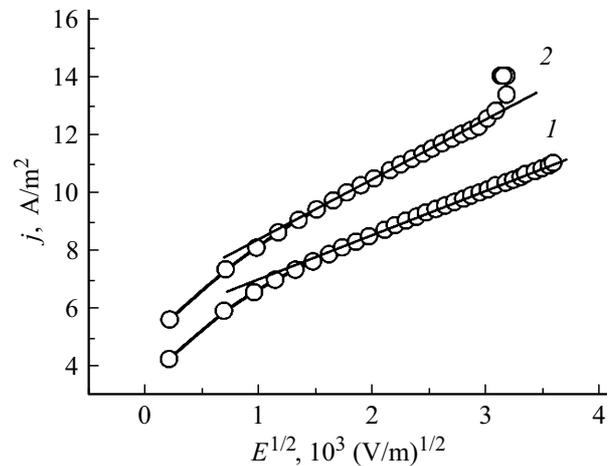


Figure 5. Current-voltage curves when injecting the charge carriers from chromium into the cobalt oxide in the coordinates, which correspond to the Schottky injection mechanism for the cobalt oxide thin film samples produced in the atmosphere Ar (1) and Ar + O₂ (2).

Because, when applying high-strength electric fields, the oxide semiconductors can exhibit shifting of the oxygen vacancies, i.e. the change of the distribution of the electrically active impurities, then in order to analyze the produced dependences, the positive parts of the current-voltage curve have been selected (they are designated by the digits 1 on Fig. 3), whose data were used to calculate the values of the specific electric conductivity. The dependences of the conductivity of the studied films shown on Fig. 4 can be conditionally divided into two portions. The first portion I corresponds to the linear current-voltage curve at the electric field strength not exceeding $E = 10^6$ V/m (the ohmic conductivity portion), so does the second one II to the non-linear dependence of the current on the applied voltage. The values of the specific electric conductivity determined by the ohmic conductivity portions

were $5.3 \cdot 10^{-4}$ and $2.4 \cdot 10^{-3} \Omega^{-1} \cdot \text{m}^{-1}$ for the films produced in the atmosphere of Ar and Ar + O₂, respectively. When applying the higher field with $E > 10^6$ V/m, the conductivity starts rising non-linearly (the region II).

In order to explain the influence of the electric field strength on the conductivity of the thin-film cobalt oxide included in the structure Cr/Cu/Cr–cobalt oxide–Cr/Cu/Cr, we will analyze the processes limiting the electrotransport within the cobalt oxide thin film bulk and the processes limiting the carrier injection at the metal–semiconductor contact.

The influence of the metal contacts was taken into account within the three models of the carrier injection mechanisms through the metal–semiconductor barrier: the Fowler–Nordheim effect, the thermally facilitated tunneling and the Schottky thermionic emission. For this, the current-voltage curves of the cobalt oxide thin films shown on Fig. 3 have been restructured in the coordinates $\ln(j/E^2) = f(1/E)$, $\ln(j/E) = f(E^2)$ and $\ln(j) = f(\sqrt{E})$, respectively [17]. The experimental data have been analyzed to show that for the studied films the charge carrier injection from the contact into the bulk can satisfy the Schottky thermionic emission mechanism, which is confirmed by the linear portions of the experimental curves plotted in the coordinates $\ln(j) = f(\sqrt{E})$ at the electric field strength from $E = 3 \cdot 10^6$ to $8 \cdot 10^6$ V/m (Fig. 5).

If in our case the carriers are injected from the metal into the semiconductor as per the Schottky mechanism, then the current density is expressed as follows [17]:

$$j = AT^2 \exp\left(-\frac{\Phi_0 - \beta_{\text{Sn}} F^{1/2}}{kT}\right), \quad (2)$$

where $A = (4\pi n^* k^2 e)/(m_e h^2) = \frac{120m^*}{m_e} \text{A} \cdot \text{cm}^{-2} \cdot \text{deg}^{-2}$ — the Richardson–Dushman, $\beta_{\text{Sn}} = (e^3/(4\pi\epsilon_\infty\epsilon_0))^{1/2}$ — the Schottky constant, ϵ_∞ — the dynamic permittivity. Then, by a slope of the straight lines in the coordinates $\ln(j) = f(\sqrt{E})$ we can obtain the values $\epsilon_\infty = 5$ for the films produced in the Ar atmosphere and $\epsilon_\infty = 2.9$ for the films produced in the Ar + O₂ atmosphere. Assuming that the effective tunnel mass of the electrons in the produced films insignificantly differs from the value $m^* \approx 0.5m_e$ [17], then based on values of the intersection point coordinates of the linear approximations $\ln(j) = f(\sqrt{E})$ with the abscissa axis, we have evaluated a height of the potential barrier to be $\Phi_0 = 0.59$ eV for the films produced in the Ar atmosphere and $\Phi_0 = 0.58$ eV for the films produced in the Ar + O₂ atmosphere. The obtained evaluations of the dynamic permittivities and the potential barrier heights are reasonable and it can indicate the influence of the carrier injection from the metal to the semiconductor as per the Schottky mechanism in the structures Cr/Cu/Cr–the cobalt oxide–Cr/Cu/Cr at the electric field strengths from $E = 3 \cdot 10^6$ to $8 \cdot 10^6$ V/m. At the same time, the non-linearity of the current-voltage curve of the produced structures not complying with the above-described models of the contact phenomena is observed at the lesser electric field strengths

$E > 10^6$ V/m. Thus, despite successful linearization of the obtained results in the Schottky coordinates, it is unlikely that the contact phenomena play a decisive role in the electrotransport of the structures Cr/Cu/Cr–the cobalt oxide–Cr/Cu/Cr. In order to explain the current-voltage curve non-linearity, let us analyze the results of Fig. 3 by applying the models describing the influence of the strong electric fields on the electrotransport within the bulk of the semiconductor cobalt oxides.

First of all, taking into account the availability of the two oxide nanocrystalline phases of cobalt, one can expect a hopping conductivity of the charge transport at the room temperature. As per the hopping conductivity theory, the semiconductor conductivity under the strong electric field complies with the law [18]:

$$\sigma = e^2 R^2 \nu_{\text{ph}} N(E_F) \exp\left(-\frac{B}{T^{1/4}}\right) \exp\left(\frac{eE\gamma R}{kT}\right), \quad (3)$$

where e — the elementary charge, ν_{ph} — the multiplier depending on the phonon spectrum, $N(E_F)$ — the density of the electron states at the Fermi level, $B = 16/(a^3 k N(E_F))$, a — the localization radius of the electron wave function, k — the Boltzmann's constant, R — the hopping length in the weak electric field, E — the electric field strength, $\gamma = 0.17$ in the three-dimensional system and $\gamma = 0.18$ in the two-dimensional system.

Taking the logarithm of the expression (3), we find

$$\ln[\sigma(T, E)] = \frac{eE\gamma R}{kT} + \text{const.} \quad (4)$$

If plotting the dependence $\ln \sigma = f(E)$, then the slope angle tangent

$$\frac{\Delta \ln \sigma}{\Delta E} = \frac{e\gamma R}{kT} = A. \quad (5)$$

Using this dependence, it is possible to determine the charge carrier hopping length

$$R = \frac{AkT}{e\gamma}. \quad (6)$$

By rebuilding the dependences of the conductivity of the studied samples on the field strength as shown on Fig. 4 into the coordinates $\ln(\sigma) = f(E)$, we obtain the linear portions at the experimental curves within the region II for the studied films at the electric field strength from $E = 10^6$ to $3 \cdot 10^6$ V/m (Fig. 6). As per the expression (6), the angle of the slope of the straight lines (Fig. 6) is proportional to the charge carrier hopping length in the weak electric field. At the higher electric field strengths, there is an evident deviation from the dependence of the equation (3). It probably can be correlated to the change of the dominant mechanism of transport ($E = 3-8 \cdot 10^6$ V/m), so at the higher strengths can be correlated to the beginning of the motion of the charged oxygen vacancies.

It is clear from the dependences of Fig. 6 that for the cobalt oxide films synthesized in the mixed atmosphere

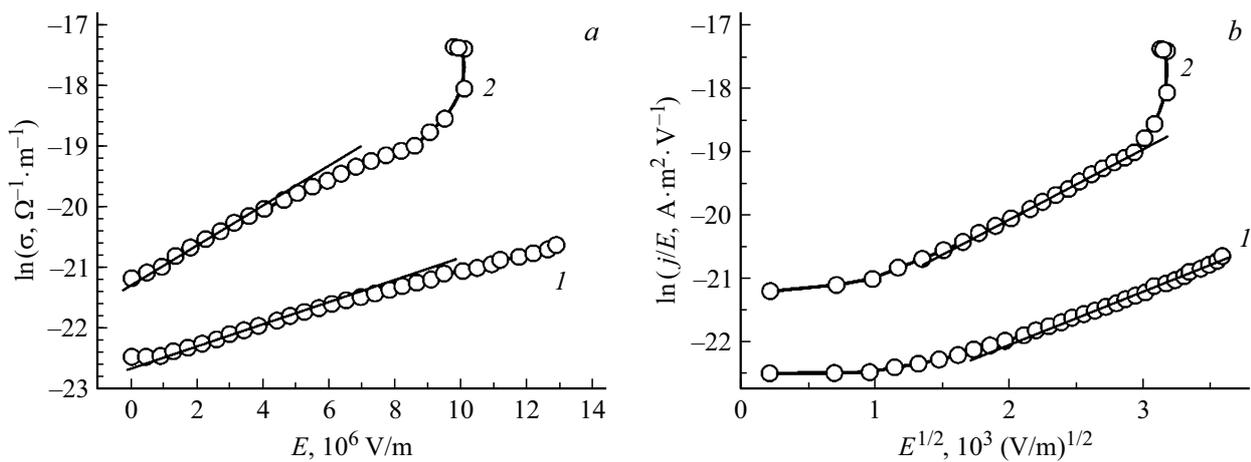


Figure 6. Dependences of the electric conductivity logarithm on the external electric field strength (a) and the current-voltage curve in the coordinates corresponding to the Poole-Frenkel mechanism (b) for the cobalt oxide thin film samples produced in the atmosphere of Ar (1) and Ar + O₂ (2).

the angle of the slope of the straight line $\ln[\sigma(E)]$ is noticeably higher than for the films synthesized in the argon atmosphere, thereby meaning the increased hopping length with increase in the cobalt oxidation degree and explaining it by the decreased density of the localized states. This experimental fact confirms that the conductivity of the produced films is realized as per the conductivity hopping mechanism with a variable hopping length across the localized states correlated to the availability of the oxygen vacancies.

In order to estimate the hopping length from the dependences of the logarithm of the specific electric conductivity of the synthesized samples on the electric field strength, the formula (6) has been used to calculate the slope angle tangents and the charge carrier hopping lengths have been determined to be equal to $R_1 = 26.6 \text{ nm}$ for the films synthesized in the argon medium and $R_2 = 47.7 \text{ nm}$ for the films synthesized in the mixed Ar + O₂ atmosphere.

However, despite the fact that the proposed conductivity mechanism allows obtaining certain information about the structure of the synthesized cobalt oxide films, there are doubts about the hopping conductivity with a variable length at the room temperature. That is why for explanation of the experimental results efforts have been made to describe the obtained dependences within the Poole-Frenkel models and the current limited by the space charge, which describe the electrotransport in the semiconductors with traps [17–20]. The linearization of the current-voltage curves of Fig. 3 in the coordinates $(\ln(j/E) = f(\sqrt{E}))$ and $\ln(j) = f(\ln(E))$ [17]), which correspond to these mechanisms has satisfactorily resulted only in the Poole-Frenkel coordinates when $E > 3 \cdot 10^6 \text{ V/m}$.

As per the Frenkel mechanism's trap ionization model, the current density is expressed as [21]:

$$j = DE \exp\left(\frac{\Phi_0 - \beta_{PF} T^{1/2}}{kT}\right), \quad (7)$$

where $D = e\mu N_C$, μ — the mobility of charge carriers, N_C — the effective density of the trap states, $\beta_{PF} = (e^3 / (\pi\epsilon_\infty\epsilon_0))^{1/2}$ — the Poole-Frenkel constant, ϵ_∞ — the dynamic permittivity. Then, by a slope of the straight lines in the coordinates $\ln(j/E) = f(\sqrt{E})$ we can obtain the values $\epsilon_\infty = 12$ for the films produced in the Ar atmosphere and $\epsilon_\infty = 7$ for the films produced in the Ar + O₂ atmosphere. The obtained dynamic permittivities are also reasonable, but higher than those determined from the Schottky mechanism's carrier injection model. It probably can be explained by superposition of the contact and bulk mechanisms of conductivity.

Thus, with the increase in the electric field strength, the synthesized cobalt oxide thin film samples exhibit replacement of the dominant mechanism of electrotransport from the one limited by the hopping electrotransport processes with the variable hopping length across the localized states near the Fermi level within the bulk of the semiconductor ($E < 3 \cdot 10^6 \text{ V/m}$) to the Frenkel's trap ionization mechanism ($E > 3 \cdot 10^6 \text{ V/m}$).

Conclusion

The cobalt oxide thin films produced in the work contain two nanocrystalline CoO and Co₃O₄ phases. The studies of the optical properties of the synthesized films have shown for the cobalt oxide films produced in the argon atmosphere the optical band gap did not depend on the film thickness and was 3.24 eV, thereby laying within a range of values specified in the literature for the CoO phase. For the cobalt oxide films produced in the atmosphere Ar + O₂, the two direct optical transitions with the energies of 1.45 and 2.1 eV have been found. The availability of the two direct allowed optical transitions is correlated to features of the Co₃O₄ band structure, which is caused by the mixed-valence of

cobalt in this compound and the availability of the two valence states Co^{2+} and Co^{3+} .

The current-voltage curves of the synthesized films have been investigated and it has been established that the electric conductivity did not depend on the electric field strength until $E = 10^6$ V/m. At $E = 1-3 \cdot 10^6$ V/m, the conductivity is determined by the hopping electrotransport with the variable hopping length, and with the increase in the electric field strength it is replaced by the Frenkel's trap ionization mechanism at $E > 3 \cdot 10^6$ V/m.

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Conflict of interest

The authors declare that they have no conflict of interest.

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