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Fabrication and characterization of nanocrystalline cobalt oxide thin films

Biljana Pejova*, Ardijana Isahi, Metodija Najdoski, Ivan Grozdanov

*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University,
POB 162, Arhimedova 5, 91000 Skopje, Republic of Macedonia*

(Refereed)

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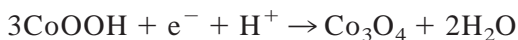
Abstract

A simple solution growth route has been employed to synthesize nanocrystalline cobalt oxide thin films on glass substrates. The obtained films were characterized by X-ray diffraction and FTIR spectroscopy. The as-deposited films were identified as a mixture of different phases of $\text{Co}(\text{OH})_2$, while the annealed ones as Co_3O_4 . The absorption of the annealed films gradually decreases with an increase of the wavelength in the 310–820 nm region. Upon annealing, the absorption coefficient decreases. The calculated band gap energy from optical absorption data for annealed films is 2.2 eV. The as-deposited thin films are dielectric, while the post-deposition heat-treated ones are characterized by resistivity of several $\text{M}\Omega/\text{cm}^2$ at room temperature. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The preparative aspects of cobalt oxide thin films have been a subject of investigations by various workers because of their numerous applications in various fields of technology. They are attractive in application to solar thermal energy collectors as selective absorbing layers [1]. Cobalt oxyhydroxide is an electrochromic material that exhibits anodic coloration [2]. It has been recognized that the electrochromic transition of cobalt oxide is based on the redox process [3]:



* Corresponding author. Tel.: +389-91-117-055; fax: +389-91-226-865.

E-mail address: biljana@iunona.pmf.ukim.edu.mk (B. Pejova).

where the green product is cobalt(III) oxyhydroxide having a slight stoichiometric excess of oxide [4], and the colored form of the electrochrome is dark brown/black Co_3O_4 (a mixed-valence material that is formally $\text{Co}^{\text{II}}\text{Co}_2^{\text{III}}\text{O}_4$) [5]. The phenomenon of anodic electrochromism of cobalt oxide allows potential application of this material as a counter electrode in electrochromic devices [2,6–8]. The interest in devices based on electrochromic materials is due to their potential application to energy efficient “smart windows,” glare-free and variable reflectance mirrors, high-contrast nonemissive information displays, switchable displays, devices for thermal control, semiconductor-based sensors [9], etc. A number of techniques have been developed for fabrication of cobalt oxide thin films such as sputtering [10], chemical vapor deposition [1], spray pyrolysis [11], dip-coating [12], electrolytic method in liquid phase [13–15], electrodeposition methods [7,8], and chemical bath deposition [16].

In our laboratory we continue to develop various solution growth techniques for deposition of thin films of inorganic materials [17–24]. In this paper, we describe our method to deposit thin cobalt oxide films. Some optical and electrical properties of the prepared films are discussed.

2. Experimental procedure

2.1. Preparation of the substrates

The thin films reported in this paper were deposited on standard microscope glass substrates, which were previously cleaned overnight in sulfochromic acid and afterwards well washed in deionized water. In order to achieve a uniform wetting of the substrate surface and improve film adhesion, the substrates were treated with fresh 0.3% aqueous solution of tin(II) chloride for a few minutes. As a result of the hydrolysis of tin(II) chloride, an ultra-thin film of $\text{Sn}(\text{OH})\text{Cl}$ was created on the substrate, which improved the film adhesion and allowed uniform wetting of the substrate surface. The substrates were rinsed with deionized water and annealed at 220–250°C for 20 min. Before use, the substrates were cooled to room temperature.

2.2. Deposition of the cobalt oxide thin films

The proposed methodology is similar to that previously used by us for deposition of iron(III) oxide and nickel oxide thin films [25,26]. The cobalt oxide films growth is based on a thermal treatment of an aqueous solution, which contains 0.02 mol/dm^{-3} cobalt (2+) ions and 0.06 mol/dm^{-3} urea. Upon heating at 100°C, the onset of turbidity is achieved after about one-half hour. At the bottom of the beaker a pink bulk precipitate of $\text{Co}(\text{OH})_2$ was formed and the same material was deposited as a homogeneous thin film on both sides of the substrates. As-deposited films were washed with deionized water and annealed at temperature of 350–400°C for about 48 h. The annealed films were dark brown/black, uniform and homogeneous.

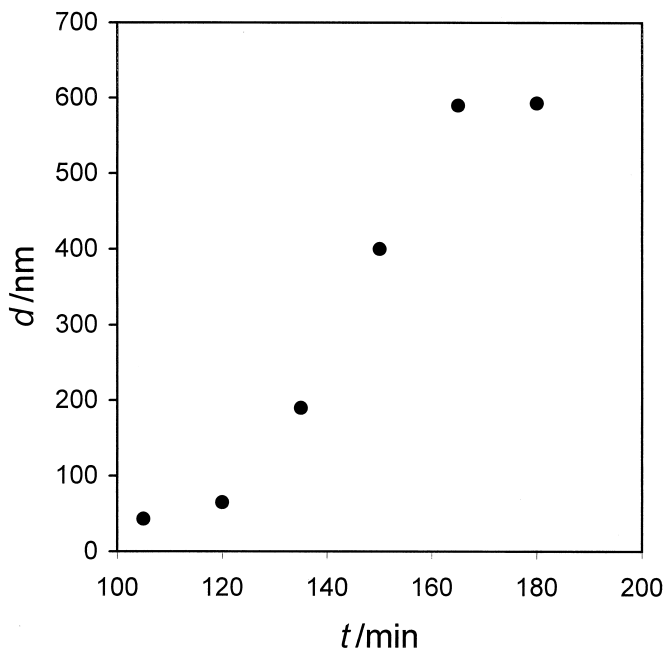


Fig. 1. The dependence of the film thickness on the deposition time.

In Fig. 1, the plot of film thickness vs. deposition time is presented. As can be seen, the deposition is practically completed after about 3 h. The terminal thickness is about 0.6 μm . Thicker films can be prepared by re-immersing the initially deposited thin films into a fresh bath.

2.3. Physical measurements

The identification of the as-deposited and the annealed materials was carried out by X-ray diffraction and FTIR spectroscopy. XRD patterns were recorded on a Philips PW1710 diffractometer (using nickel-filtered $\text{Cu K}\alpha$ radiation), while IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR interferometer. A Hewlett Packard 8452A spectrophotometer (UV-VIS spectral region) was used for optical investigations. The sheet resistance of the thin films was measured between two silver pasted electrodes 1 cm in length and 1 cm apart, using a Radio Shack Digital Multimeter model 22–168. The film thickness was determined gravimetrically.

3. Results and discussion

3.1. Chemical considerations

By analogy with the solution deposition of iron(III) oxide and nickel oxide thin films [25,26], the following reaction is proposed as a basis for the chemistry of solution growth route to cobalt oxide:

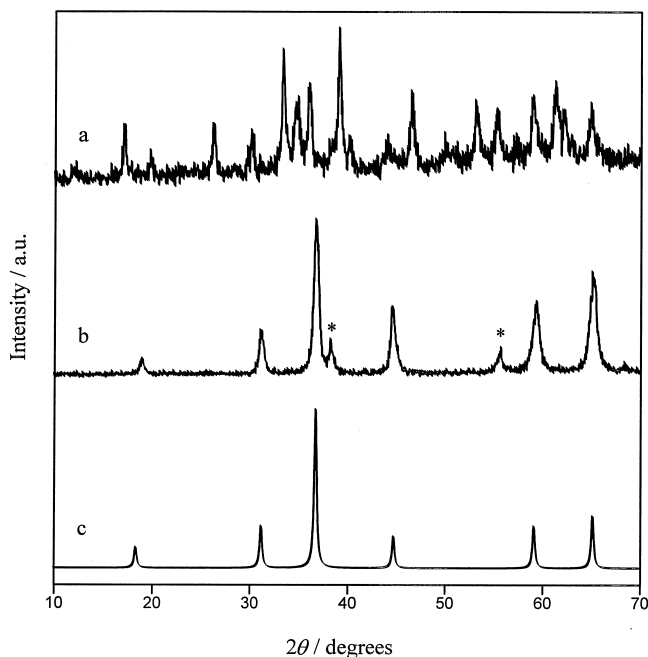
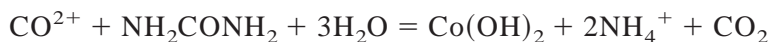
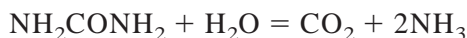


Fig. 2. X-ray diffractograms of the as-deposited material (a) post-deposition treated one at 350°C (b) and simulated Co_3O_4 pattern.



By heating at higher temperature (90–100°C), urea decomposes to CO_2 and NH_3 :



The Co^{2+} cations and the hydroxide ions (released by the protolytic reaction of ammonia) react, finally giving insoluble pink $\text{Co}(\text{OH})_2$. Upon annealing in air at 350–400°C, the as-deposited films converted to Co_3O_4 , accompanied by a color change to dark brown/black. It is known that $\text{Co}(\text{OH})_2$ decomposes to Co_3O_4 [27] upon annealing in air at 350°C. The decomposition of Co_3O_4 to CoO in air was found to take place above 800°C, while this transformation under vacuum occurs at 350°C. The direct decomposition of $\text{Co}(\text{OH})_2$ to CoO was possible under vacuum conditions even at 140°C [28]. The described changes upon annealing are established by the recorded X-ray diffractograms as well as from the FTIR spectra of the as-deposited and the post-deposition treated films.

For most of the film deposition process, a bulk precipitation is observed accompanied with scattering of the coherent laser light. This indicates that the predominant deposition mechanism is the cluster one (not excluding the ion-by-ion one at least at the end of the deposition) [29].

3.2. X-ray investigations

XRD patterns of obtained materials (as-deposited and annealed) are presented in Fig. 2a

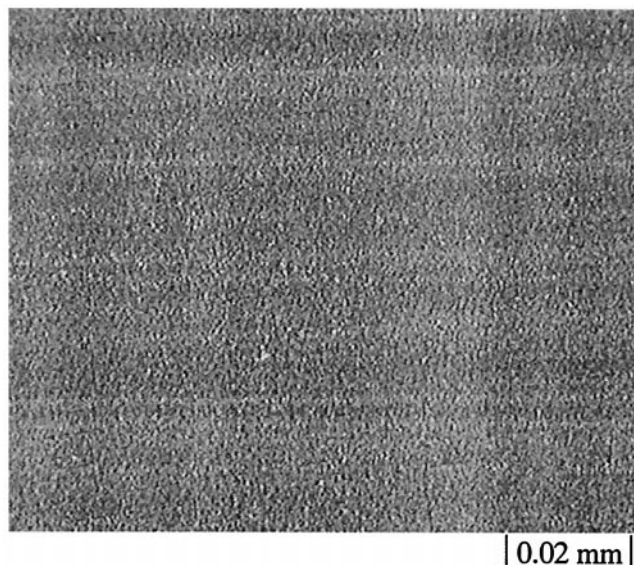


Fig. 3. The dark-field microphotograph of a Co_3O_4 thin film.

and b, correspondingly. The comparison of the recorded pattern of annealed material (in air at 350–400°C) with the simulated XRD pattern (Fig. 2c) [30] confirmed that the annealed material is polycrystalline Co_3O_4 . The as-deposited material was found to be a mixture of different phases of $\text{Co}(\text{OH})_2$ [30]. The annealed films are characterized by average crystal size of about 12 nm. This parameter was calculated by the Debye–Scherrer expression [31].

Fig. 3 shows the dark-field microphotograph of an annealed thin film. As can be seen from the microphotograph, the obtained films are characterized by uniform and homogeneous microstructure.

3.3. FTIR study

Fourier transform IR spectra were recorded for the initially obtained bath precipitate and films, as well as for the post-deposition treated materials at 350–400°C (Fig. 4). The appearance of the IR spectra of both the as-deposited and post-deposition treated materials fully supports the previously outlined discussion. However, some important aspects regarding the deposition process and the obtained materials are enlightened more deeply. The analysis of the recorded spectra further confirmed that the as-deposited material contains $\text{Co}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ (a mixture of different phases), while the post-deposition treated one is hydrated Co_3O_4 . The band appearing at $\sim 3630 \text{ cm}^{-1}$ in the FT IR spectrum of the as-deposited films (due to the $\nu(\text{OH})$ mode) reveals the presence of the weakly hydrogen bonded hydroxide ions. This band disappears upon thermal treatment, as can be seen from the spectra. However, the lower-frequency broad band corresponding to the hydrogen bonded $\nu(\text{HO}-\text{H}\cdots\text{O})$ mode (with centro-frequency of $\sim 3490 \text{ cm}^{-1}$) retains even upon annealing (shifted to 3440 cm^{-1}). It is interesting to note that the FTIR

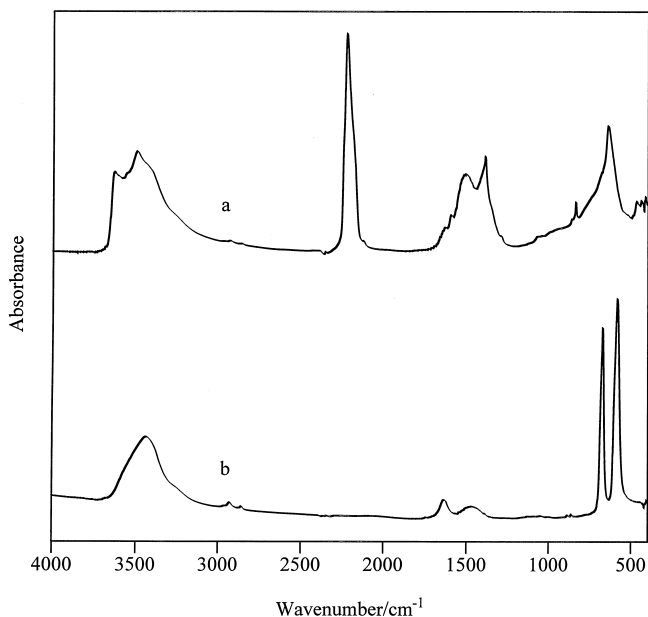


Fig. 4. FT-IR spectra of the bath precipitate (a) and post-deposition treated material (b).

study indicated the presence of the intercalated-NCO species in the as-deposited films. The very strong band appearing at $\sim 2220 \text{ cm}^{-1}$ (due to the $\nu_a(\text{NCO})$ mode), together with those appearing at 1385 cm^{-1} (due to the $\nu_s(\text{NCO})$ mode) and at 630 cm^{-1} (the $\delta(\text{NCO})$ mode), all of which disappear upon thermal treatment of the films, prove the presence of these species [32]. It may be reasonably postulated that the isocyanate anions, generated in the course of the hydrolysis of urea, partially fill the Co^{2+} coordination sphere, leading to growth of very homogeneous films (preventing the formation of larger agglomerates). Upon annealing, the intercalated species are obviously eliminated from the films, which reflects in the appearance of the FTIR spectra. It is worth noting at this point that the role of intercalated anions within the cobalt oxide films may be very important to their electrochromic properties. However, there are only a limited number of detailed studies devoted to this subject in general [33]. The appearance of two strong bands (due to the $\nu(\text{Co-O})$ modes) at ~ 670 and $\sim 580 \text{ cm}^{-1}$ in the FTIR spectra of the annealed films, is a clear evidence for the presence of the crystalline Co_3O_4 . The absence of the weakly hydrogen bonded hydroxide group stretching mode at $\sim 3630 \text{ cm}^{-1}$ in the FTIR spectra of the annealed films eliminates the possibility of simultaneous presence of phases with lower degree of crystallinity. The summarized band assignments for the most important bands in the FTIR spectra of the as-deposited and annealed films are presented in Table 1. Note that all of the previously outlined discussion regarding the FTIR study of the cobalt oxide films is quite similar to that in the case of nickel oxide films. A similar chemical behavior of these species with respect to the chemical bath deposition of the corresponding oxide phases is, however, expected.

Table 1

The assignments of the most important bands in the FTIR spectra of $\text{Co}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and $\text{Co}_3\text{O}_4 \cdot x\text{H}_2\text{O}$ thin films

$\text{Co}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ Wavenumber/ cm^{-1}	Assignment	$\text{Co}_3\text{O}_4 \cdot x\text{H}_2\text{O}$ Wavenumber/ cm^{-1}	Assignment
3630	$\nu(\text{OH})$		
3490	$\nu(\text{HO}-\text{H} \cdots \text{O})$	3440	$\nu(\text{HO}-\text{H} \cdots \text{O})$
2220	$\nu_a(-\text{NCO})$		
1637	$\delta(\text{HOH})$	1630	$\delta(\text{HOH})$
1385	$\nu_s(-\text{NCO})$		
630	$\delta(-\text{NCO})$	670	$\nu(\text{Co}-\text{O})$
		580	$\nu(\text{Co}-\text{O})$

3.4. Optical measurements

The optical characteristics of both the as-deposited and the annealed films were studied in the range 300–820 nm. In Fig. 5a and b, the absorption spectra for as-deposited and annealed films (with equal thickness, recorded against the glass substrate reference) are shown. It is clear that upon annealing process, the absorption of the films decreases. The comparison of the absorption spectra of annealed films with different thickness is given on Fig. 6. As can be seen, the film absorption gradually decreases with an increase of the wavelength in the region from 310–820 nm.

In Fig. 7, the dependence of $(\alpha h\nu)^2$ vs. $h\nu$ for annealed film is presented. It is known that for a large number of semiconductors, in both crystalline and amorphous forms, the depen-

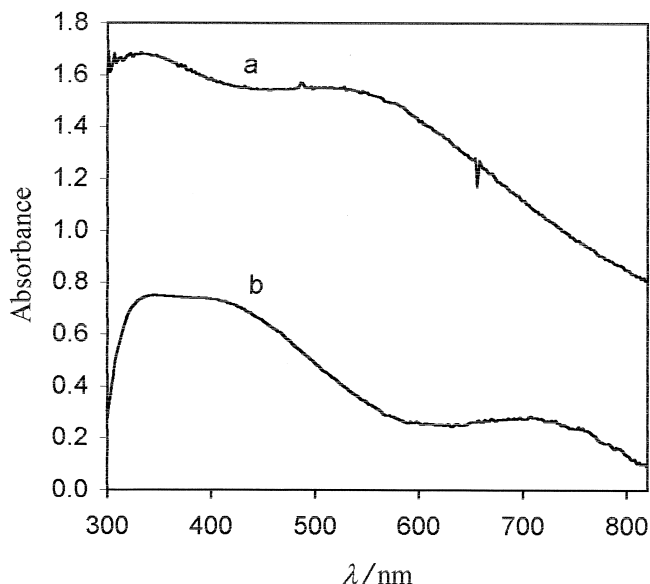


Fig. 5. Optical spectra for as-deposited film (a) and post-deposition treated one (b).

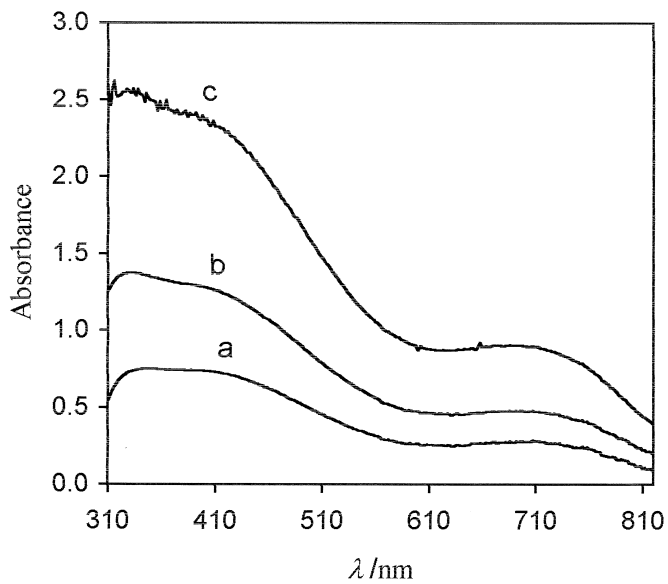


Fig. 6. Optical spectra for annealed films, with thickness of 117 (a), 168 (b), and 194 nm (c).

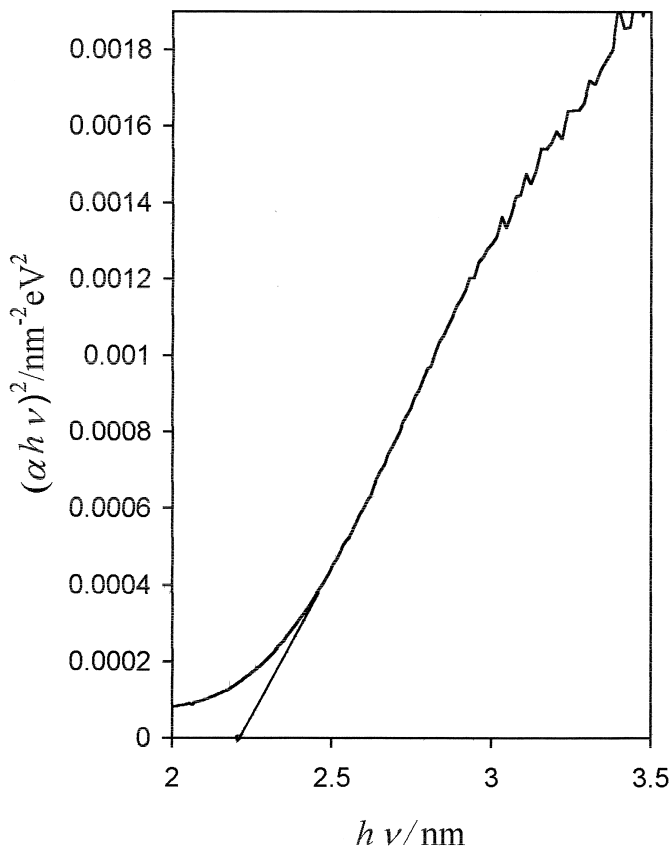


Fig. 7. The plot of $(\alpha h\nu)^2$ vs. the photon energy for post-deposition treated film at 350°C.

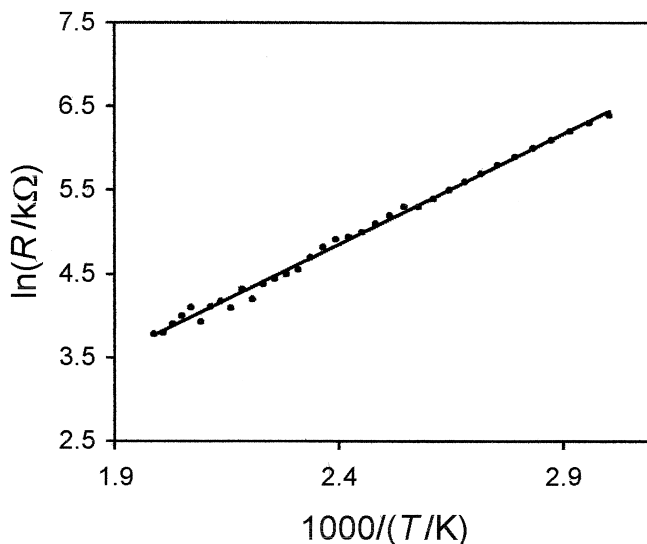


Fig. 8. The dependence of $\ln(R/\Omega)$ vs. $10^3/(T/K)$ for Co_3O_4 thin film.

dence of absorption coefficient α upon the photon energy $h\nu$, for optically induced transitions, takes the form

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

where E_g is the optical band gap, A is a constant, $h\nu$ is the photon energy, while n depends on the nature of the transition. For direct transitions $n = 1/2$ or $3/2$, while for indirect ones $n = 2$ or 3 , depending on whether they are allowed or forbidden, respectively. The dependence of $(\alpha h\nu)^{1/n}$ on the photon energy should result in a straight line intercepting the abscissa at $h\nu = E_g$. In our case, the best fit of $(\alpha h\nu)^{1/n}$ vs. $h\nu$ was obtained for $n = 1/2$. This exponent ($n = 1/2$), indicates that the obtained Co_3O_4 thin films are semiconductors with allowed direct transitions. The calculated value for optical E_g of the obtained Co_3O_4 thin films is 2.2 eV. This somewhat higher value compared to the previously reported one (1.65 eV [16]) may be attributed to the very small crystal size in our case, *i.e.*, size quantization effects [29].

3.5. Electrical investigations

The room temperature dark resistivity of annealed films deposited by the presented method is of the order of $10^7 \Omega/\text{cm}^2$. The resistivity of the solution grown films may be lowered by adding dopant impurities to the reaction mixture while depositing the films.

Fig. 8 shows the dependence of the logarithm of electrical resistance on the temperature in the range of 323–523 K (which corresponds to the intrinsic semiconduction mechanism). The measured resistance fitted the following expression:

$$R = C \cdot \exp(Ea/2kT)$$

where C is constant, k is Boltzman constant, T is temperature and E_a is the activation energy. Such trend indicates a classical semiconducting behavior. The slope of the curve is equal to $E_a/2k$. On the basis of this plot we have calculated the activation energy of 0.45 eV.

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