STRUCTURAL AND ELECTRICAL CHARACTERIZATION OF COBALT OXIDE SEMICONDUCTORS

ROMANA DRASOVEAN, SIMONA CONDURACHE-BOTA, NICOLAE TIGAU

"Dunarea de Jos" University of Galati, Faculty of Science, 800201, Galati, Romania

Abstract: In this work, it was investigated electrical and structural properties of porous cobalt oxide film that was grown on glass substrate via sol-gel method. The electrical parameters measurement was made using the Van der Pauw technique. Structural and morphological studies have been carried out by means of SEM, and AFM. As-deposited cobalt oxide films showed amorphous nature as confirmed from X-ray diffraction studies. It was shown that annealing influences the grain size of the nanosized cobalt oxide films were confirmed after annealing. Spherical grains were uniformly distributed over the substrate surface. In thicker films appears an improvement in crystallinity and grain size which induce higher conductivity. The conductivity of cobalt oxide based films exhibits ρ values between 10^{-3} - $10^{3} \Omega^{1}$ cm⁻¹, depending on the conditions of the annealing.

Keywords: cobalt oxide, crystallinity, conductivity.

1. INTRODUCTION

Cobalt forms two stable oxides: CoO and Co₃O₄. Thin films of cobalt oxide have been prepared from various deposition techniques such as spray pyrolysis, sputtering, chemical vapor deposition (CVD), pulsed laser deposition, sol–gel process, electrophoretic deposition (EPD), etc., on a variety of substrates [1–6]. These oxides present many applications as energy storage device or sensor for CO, NO, NO₂, C₄H₁₀, CH₄ etc. [7]. The crystalline Co₃O₄ film has been reported to be a good anodic coloration material for the EC application that shows comparable properties with electrochromic nickel oxide [8, 9]. The Co₃O₄ electrodes have been investigated for the electrochromic devices. The cobalt oxides films are used in the preparation of solar cell. Some of the applications include superconductivity in electronics, electrochemical properties in micro batteries and high density batteries [10].

In this work, we investigate electrical and structural properties of porous cobalt oxide film that was grown on glass substrate via sol-gel method.

2. EXPERIMENTAL

Cobalt oxide films were prepared on glass substrates by immersion technique, sol-gel method. The starting precursor was a methanolic solution of cobalt acetate $Co(CH_3COO)_2$ 4H₂O. After immersion into the cobalt solution, samples were dried at 90°C and calcinated at 300°C. The dried gels passed in to a solid oxide film. After drying and calcination, the films were heated at 500°C during 2 hours, half of them in air and half in forming gas (H₂/N₂).

The film thickness was varied by changing the deposition parameter as the withdrawal speed, cobalt oxide concentration, number of layers. The thickness was measured with a Sloan Dektak 3D surface profilometer. Structural analyses of cobalt oxide films were

performed by X-ray diffraction with a Rigaku diffractometer. An atomic force microscope (AFM) and a Scanning Electron Microscopy (SEM) were employed to analyze the surface morphology of the films. The electrical parameters measurement was made using the Van der Pauw technique.

3. RESULTS AND DISCUSSION

From the XRD patterns it was found that all the samples are polycrystalline. The films exposed 2h in air consist of Co_3O_4 phase. In the (a) XRD pattern (Fig.1) we can notice a major peak corresponding to (311) plane, which grows with increased film thickness. Two other peaks corresponding to (220) and (440) planes are also found to increase. The Co_3O_4 phase is stable because after film formation no structural changes have been noticed. The (b) XRD pattern revealed that the films exposed in H_2/N_2 consist of CoO phase and the crystallites have a preference growth to the (200) orientation [11].



Fig. 1. XRD patterns of cobalt oxide films annealed at 500°C: a) 2h in air; b) 2h in H₂/N₂.

The crystallite size, D_m , was calculated using Scherrer equation. The obtained values were compared with those obtained from AFM. The mean crystallite size grows both with the thickness of the film from 6.9 nm to 44.6 nm.

According to AFM measurements the films are crack-free and the grains are uniform in size and shape.

The mean crystallite size, D_m , grows when the film is exposed in H_2/N_2 . The film presented in the pictures below (Fig. 2) has a mean crystallite size of 12.8 nm when is treated in air and 23.77 nm when is exposed in H_2/N_2 .



Fig. 2. AFM pictures of cobalt oxide films annealed at 500°C.

The values of room temperature resistivity, ρ were obtained by using the Van der Pauw technique. The films heated in air have the resistivity values of order $10^2 \Omega \cdot \text{cm}$ while the films exposed in H₂/N₂ have these values in the range of $10^{-4} \Omega \cdot \text{cm}$. In both situations, the room temperature resistivity decreases with increasing film thickness (Table 1).

By measuring the Hall voltage, we could find also the type of carriers, the carrier density (p) and mobility (μ) and also the electrical conductivity (σ) of the films.

Type of the film	Thicknesses [nm]	ρ for 300 K [Ω·cm]
Films treated in air	166.1	227.595
	177.2	194.5672
	218.1	93.99
	225.9	62.1784
Films treated in H_2/N_2	100.6	$2.16 \cdot 10^{-4}$
	109.98	1.49.10-4
	118.78	1.14.10-4
	122.87	4.44.10-5

Table 1. The room temperature resistivity of cobalt oxide films with different thicknesses (t)

The conduction in both cases was attributed to holes. For the same value of the film thickness, the layers exposed in forming gas have the conductivity greater than those heated in air (Fig. 5). As the carrier mobility of the films does not appear to be influence by crystallite size (Fig. 3), the changed in conductivity may be due to that in carrier concentration (Fig. 4).



Fig. 3. Variation of carrier mobility with film thickness.



Fig. 4. Variation of carrier concentration with film thickness.

The carrier density increases with increasing thickness and it is greater for the films exposed in H_2/N_2 . The diffusion coefficient of hydrogen is higher, we assume that it get easily into the crystals inner space generating dislocations.

The impurities and the defects increase the carrier density and implicitly the conductivity of extrinsic semiconductors [14].

From our previous work [12, 13] we could see that in thicker films appears an improvement in crystallinity and grain size which induce higher conductivity.

For various thicknesses the activation energy, E_a , is between 0.41-0.59 eV. The activation energy decreases with increase in film thickness. Because E_a is larger than kT=0.026 eV (T=300K), these oxide films generate an extrinsic band or hopping conduction.



Fig. 5. Conductivity of cobalt oxide films with different thicknesses depending on the conditions of the thermal treatment.

4. CONCLUSIONS

Polycrystalline Co_3O_4 and CoO films have been synthesized from a methanolic solution of cobalt acetate.

The conduction in both cases was attributed to holes. The films are p- type semiconductors.

In thicker films appears an improvement in crystallinity and grain size which induce higher conductivity. The conductivity of cobalt oxide based films exhibits values between 10^{-3} - $10^{3} \Omega^{-1} \text{cm}^{-1}$, depending on the conditions of the thermal treatment.

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