X-Ray Diffraction-Analytical Studies of Nanocrystalline Cobalt Oxide Thin Films via Solution Growth Technique.

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Abstract

Sail brand microscope glass slides Cat. No. 7102 were used in growing thin films of cobalt oxide [CoO] by using the solution growth technique, at 300K. X-ray diffraction was used to determine the structural properties of the film samples. Two samples of CoO thin films annealed at 373K and 573K, respectively were investigated. The particle size D[nm] and inter-planar spacing d[Å] of the film samples were calculated from Debye-Scherrer formula and Bragg's formula respectively, while the thickness t[nm] was determined from peak indexing. Both the thickness and d-spacing of CoO thin films decreased with the increase in annealing temperature. In contrast, the particle size of the thin film samples studied increased with the increase in annealing temperature. The ranges in the particle sizes determined are 18-23nm and 19-25nm for the samples annealed at 373K and 573K respectively.

Key words: Cobalt Oxide, X-Ray diffraction, Chemical Bath Deposition

1. Introduction

Preparation and study of nanacrystalline transition metal oxide thin films are becoming very important in the recent researches in thin films. This is because the characteristics of metal nano-particles such as optical, electrical, structural and solid state properties depend on their sizes and chemical surroundings. They also possess wide applications in various devices such as light emitting diodes, ultra violet detectors and gas sensors etc [1-3]. The high cost of Faradaic capacitors such as RuO_2 and IrO_2 [4] has necessitated the need to identify and study less expensive alternative materials with more or less similar characteristics and cobalt oxide films are among this later class of pseudo-capacitors [5]. The applications of oxide thin films are wide and the scope depends largely on the peculiar properties of a given oxide thin film. For instance, CoO thin films with energy gaps ranging from 2.08 to 2.01eV could be used as sensors in light emitting diodes in the violet and ultraviolet regions, and as direct energy gap materials, these films are good for electroluminescence [3, 6].

Nickel Oxide films [NiO] can be used in asymmetric devices with CoO films due to their potential applications and suitability as positive electrodes [7]. An asymmetric device with N_iO as a positive electrode and CoO as a negative electrode would give an adequate capacitance with a large potential window [0.9V] at reasonably low cost [5,8]. Cobalt oxide thin films can be prepared by using various deposition methods such as sol-gel [9], chemical vapour deposition [10] and electrochemical precipitation [5].

Recent development in the applications of oxide thin films is in the preparation of core-shell thin films or materials. In this regard, CoO has been used as a shell in TiO_2/CoO core-shell thin films. These thin films have band gaps ranging from 1.9 to 2.3eV, and are good materials for photovoltaic applications or solar cells [11]. Other oxide thin films that have been used as shells in core-shell oxide materials include nickel oxide [NiO] and iron oxide [Fe_2O_3], [12, 13].

2. Experimental Details

Cobalt oxide thin films were deposited onto sail Brand microscope glass substrates Cat No.7102, 25.4 x 76.2 x 1.1mm, using the chemical bath deposition method. This method was used in the deposition of CoO thin films because it does not require the presence of externally applied field [14]. It is cost effective and produces highly uniform thin films having the same composition and thickness [15]. The films produced using this technique, have good structural and optoelectronic properties when compared with those deposited with other methods [16]. The experimental set up and synthesis of CoO was done by using 6mls of 0.5M of cobaltous chloride [$CoCl_2.6H_2O$], 3mls of ammonia [NH_3], 5mls of sodium hydroxide [NaOH] and 25mls of water. The surface pre-treatment of the substrates and other experimental details were described and already published [3].

3. Results and Discussion

3.1 X-ray Diffraction Studies

The XRD analysis of cobalt oxide [CoO] thin films was done using Rigaku D/max – 2100 diffractometer equipped with a CuKα [λ = 1.5406Å] radiation source. X-ray diffraction [XRD] study is one of the most important and powerful tools used in nano-materials science. X-ray spectrometer works on the condition that when a bean of monochromatic X-rays falls on a crystal, each atom acts as a source of scattering radiations. With the values of glancing angles at which reflections occurred and known wavelengths of the X-rays used, the inter-planar spacing could be determined. X-ray diffraction technique was used in studying the CoO thin films' structural properties. Hence in this paper we present the X- ray diffraction studies of two samples of CoO thin films annealed at 373K and 573K respectively, with emphasis on the particle size [D], inter-planar spacing [d] and thickness [t].

3.2 Peak Indexing from d-spacing

The peak indexing is a process of determining the dimensions of the unit cell from peak positions. The XRD pattern analysis was used in determining the Miller index [hkl] for each peak. The peak indexing from d-spacing for CoO thin film sample A, annealed at 373K is shown in Table 1 while the peak indexing for CoO thin film sample B annealed at 573K is shown in Table 2.

Table 1: Peak indexing for sample A

2θ	D	$\frac{1000}{d^2}$	$\frac{\frac{1000}{d^2}}{50}.22$	Miller indices
23.73	3.4873	82.23	1.64	101
24.04	3.4413	84.44	1.68	011
24.73	3.3321	90.07	1.79	102

For the sample annealed at 373k, the three strong and prominent peaks were observed at 2θ values of 23.73, 24.04 and 24.73 degrees with [101], [011] and [102] preferred orientations respectively [3].

Table 2: Peak indexing for sample B

2θ	D	$\frac{1000}{d^2}$	$\frac{\frac{1000}{d^2}}{50}.22$	Miller indices
26.12	3.2772	93.12	1.85	110
27.33	3.1289	102.15	2.03	101
28.41	3.0168	109.88	2.18	011

For the sample annealed at 573K, three strong prominent peaks were observed at 2θ values of 26.12, 27.33 and 28.41 degrees with [110], [101] and [011] preferred orientations respectively [3].

3.3 Particle Size [D] Calculation

The average particle size was calculated by using Debye-Scherrer's formula, given in equation (1), [17] as:

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where D is the average particle [or grain] size, $\lambda(=1.5406\text{Å})$ is the wavelength of X-rays used, β is broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction.

3.3.1 Calculation of D, for the sample A, annealed at 373K

The particle size [D] for the thin film sample A, was calculated using the equation (1);

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

[i] When 2θ = 23.73,

$$\beta = \frac{.35 \times 3.14}{180} = 0.00611\, rad$$

$$D = \frac{0.9 \times 1.506 \times 10^{-10}}{0.00611 \times cos\, 11.87} = 23nm$$

[ii] When 2θ = 24.04

$$\beta = \frac{0.39 \times 3.14}{180} = 0.00680\, rad$$

$$D = \frac{0.9 \times 5406 \times 10^{-10}}{0.00680 \times cos\, 12.02} = 20nm$$

[iii] When 2θ = 24.73

$$\beta = \frac{0.4303.14}{180} = 0.00750\, rad$$

$$D = \frac{0.9 \times 1.540 \times 10^{-10}}{0.00750 \times \cos 12.37} = 18nm$$

For the sample annealed at 373K, the particle size D is less than 30nm and has a range from 18 – 23nm.

3.3.2 Calculation of D, for sample B, annealed at 573K

The particle size [D] for the thin film sample B, was also calculated using the equation (1);

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

[i] When 2θ = 26.12

$$\beta = \frac{0.36 \times 3.14}{180} = 0.00628\, rad$$

$$D = \frac{0.9 \times 1.5406 \times 10^{-10}}{0.00628 \times \cos 13.08} = 25nm$$

[ii] When 2θ = 27.33

$$\beta = \frac{0.4 \times 3.14}{180} = 0.00698\, rad$$

$$D = \frac{0.9 \times 1.5406 \times 10^{-10}}{0.00698 \times \cos 13.67} = 20nm$$

[iii] When 2θ = 28.41

$$\beta = \frac{0.42 \times 3.14}{180} = 0.00733\, rad$$

$$D = \frac{0.9 \times 1.5406 \times 10^{-10}}{0.00733 \times \cos 14.21} = 19nm$$

For the CoO thin film sample annealed at 573K, the particle size D is less than 30nm and has a range from 19 – 25nm. Particle size increased with increase in annealing temperature. Increase in the annealing temperature of thin films has been reported to give better crystallization and greater grain size. This trend applies to both halides and oxide thin films. The particle sizes of Co_3O_4, NiO and SnS:Ag thin films increased with increase in the annealing temperature [9, 17, 18].

3.4 Calculation of d-spacing

3.4.1 Calculation of d-spacing for sample A

The inter-planar spacing d, for CoO thin film sample annealed at 373K was calculated using Bragg's law or equation (2).

$$2d \sin\theta = n\lambda \qquad (2)$$

where n = 1, 2, 3 ... is a constant λ is wavelength of incident electromagnetic wave and θ is glancing angle.

$$d = \frac{\lambda}{2\,sin\theta}\ (n = 1)$$

$$d = \frac{1.5406 \times 10^{-10}}{2 \sin 11.87} = 3.7\text{Å}$$

3.4.2 Calculation of d-spacing for sample B

Calculation of d-spacing for CoO thin film sample annealed at 573K,

$$d = \frac{1.5406 \times 10^{-10}}{2 \sin 13.06} = 3.4\text{Å}$$

The value of d-spacing decreased as the annealing temperature increased.

3.5 Determination of Thickness (t) of CoO Thin Films

3.5.1 The thickness of CoO thin film sample annealed at 373K is calculated using equation (3), [19].

$$Thickness\ (t) - \frac{\lambda_1\lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad (3)$$

where n_1 and n_2 are the refractive indices corresponding to wavelength λ_1 and λ_2 respectively.

$$t = \frac{4.85 \times 10^{-7} \times 3.65 \times 10^{-7}}{2(4.85 \times 10^{-7} \times 1.74 - 3.65 \times 10^{-7} \times 1.51)} = 3.03 \times 10^{-7}m$$

$$\simeq 303nm$$

3.5.2 Thickness (t) of CoO thin film sample annealed at 573K, is

$$t = \frac{2.95 \times 10^{-7} \times 3.02 \times 10^{-7}}{2(2.95 \times 10^{\ 7} \times 2 - 3.02 \times 10^{\ 7} \times 1.8)}$$

$$t = 9.4 \times 10^{-8}m \simeq 95nm$$

The thickness of the CoO thin film decreased as the annealing temperature increased.

4 Conclusion

Studies of X-diffraction of cobalt oxide [CoO] thin films have been carried out. The average particle size, inter-planar spacing and thickness of the film samples annealed at 373K and 573K respectively, were calculated. It was noted that both the thickness and inter-planar spacing of CoO thin films decreased as the annealing temperature increased while the particle size increased with increase in the annealing temperature. The dependence of the particle sizes of thin films with annealing temperatures for halides and oxide thin films has been reported in literature [9, 17, 18].

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