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Study of the Effects of Thermal Annealing on the Optical Band Gap of Nanocrystalline CoO Thin Films Prepared by Chemical Bath Deposition.

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Abstract

Nanocrystalline films of cobalt oxide have been prepared on glass slides by chemical bath deposition process. For deposition of CoO thin films, cobaltous chloride [$CoCl_2.6H_2O$] was used as cationic and ammonia [NH_3] as anionic precursor in aqueous medium. In this process NaOH was used as complexing agent. X-ray diffraction, scanning electron microscopic [SEM] analysis have been used to study the films' crystal structures, optical and solid state properties. We hereby present the effects of thermal annealing on the optical band gap of CoO thin films. The optical transition in the films is direct one. For the as- deposited film, the band gap is 2.1eV. This later decreased to 2.08eV, so that increased thermal annealing reduces the optical band gap of CoO. However,the energy gap cannot be said to be dependent on the annealing temperatures. These films could be used as photovoltaic cells, sensors light emitting diodes and also in biomedical imaging.

Key Words: Nanocrystalline CoO, Chemical Bath Deposition, Band Gap and Thermal Annealing.

1. Introduction

Oxide materials have been attractive topics in physics and material science in recent time. Though most oxides are good insulators, some of them like TiO_2, ZnO, CuO, Cu_2O, Co_3O_4, and

NiO etc are well-known semiconductors [1-6] Nanocrystalline materials have opened a fresh chapter in the field of electronic applications because changing the grain size and/or thickness of the film could change material properties drastically [7] The importance of oxide thin films in various technological and electronic fields cannot be overemphasized. For instance pure CaO with a wide band gap of 7eV was proved to be very useful for applications where electrical insulation is required such as cooling blankets for nuclear reactors, and can also be used as a magnetic semiconductor since it has an associated magnetic moment. [8]

With the control of the nanostructured morphology, metal oxides are believed to act as promising alternatives as the electron accepter and transporter in bulk-heterojunction solar cells [9]. Among the metal oxides, TiO_2 is a very good candidate for this purpose because, the use of nanocrystalline TiO_2 as electron accepting electrode for dye-sensitized solar cells has shown an overall power conversion efficiency as high as 10% [10]. Nickel oxide [NiO] thin film is an attractive material because of its excellent chemical stability as well as its optical, electronic and magnetic properties. It has been used as antiferromagnetic material, material for electrochromic display devices and functional layer material for chemical sensors [6]. Recently,some transition metal oxides have been reported to be very useful as shells or cores of core-shell thin films which can be applied as solar absorber material for photovoltaic architecture[11].

Cobalt oxide [CoO] is one of the transition metal oxides which in recent years, is more suitable in high power energy storage systems. For instance, it is used in acceleration and charge storage during regenerative braking [12]. Cobalt oxide [CoO] thin films have been proved to exhibit capacitance in negative potentials and can also serve as suitable positive electrodes in devices. The charge storage mechanism in CoO films was identified and proved to be similar to NiO films [13]. However, capacitance studies of cobalt oxide films indicated that an asymmetric device with NiO as a positive electrode and CoO as a negative electrode would give an adequate capacitance with a large potential window (0.9V) at a reasonably low cost [14]. CoO thin films can be deposited with a variety of methods such as electrochemical precipitation, sol-gel technique and chemical bath deposition technique [14-16] Transition metal oxide semiconductors in thin film form have unique properties of good electrical conductivity and high optical transparency [17]. Here we study cobalt oxide thin films prepared using the chemical

bath deposition [CBD] technique, with emphasis on the effects of thermal annealing on the films' optical band gaps.

2. Experimental Method

The glass substrates for the thin films were first given surface pre-treatment by cleaning with deionised water and detergent, followed by ammonia acid and finally rinsed with acetone. This ensured uniform coating. The synthesis and deposition of cobalt oxide thin films using chemical bath deposition technique, was done by using cobaltous chloride [$CoCl_2.6H_2O$] as cationic and ammonia [NH_3] as anionic precursor in aqueous medium. In this process NaOH was used as the complexing agent. The bath temperature was 65^oC and the deposition time was 3 hours. Four specimens were obtained once in the bath in order to ensure uniformity in the bath temperature, concentration and deposition time. Lastly the deposited CoO thin films were annealed in an oven from 373 to 673k temperature range for 1 hour per sample.

3. Results and Discussion

3.1 XRD Studies

The crystalline nature of CoO films in this study was obtained from the XRD patterns. Figure 1 shows the typical spectral obtained for CoO film annealed at 373K, for 1 hour. It can be observed that the sample exhibit good crystallinity corresponding to Rhombohedral Heterogenite Structure [JCPDS 07 0169]. The observed XRD peaks for this sa mple are at 19.5^0 [003], $28.5^0[002]$, $39.5^0[202]$, and $64.5^0[009]$ The average grain size for the samples was calculated to be 76nm, using the Scherrier's formula [18]

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

where β is the observed angular line width at half maximum intensity in radians; θ is the Bragg's angle and λ is the wavelength used [1.5406Å]. The high intensity XRD peaks, and absence of the noisy background observed in Fig 1, clearly indicate the presence of ordered fine grains and further buttressed the fact that these films are nanocrystaline in nature [16,19]

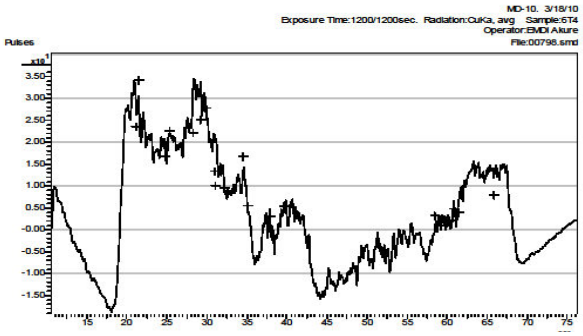

Fig. 1 XRD for CoO annealed at 373K

3.2 Surface Morphological Studies

The surface morphological studies of these oxide films were done using scanning electron microscopy [SEM] analysis, which is a convenient method for studying the microstructure of thin films. The SEM of CoO films annealed at 373K and 473K respectively are shown in Figs. 2 and 3. The SEM image for this sample reveals that the film is uniform and the substrate is well covered with nano-size grains. The grain sizes were observed to increase with increase in annealing temperatures.

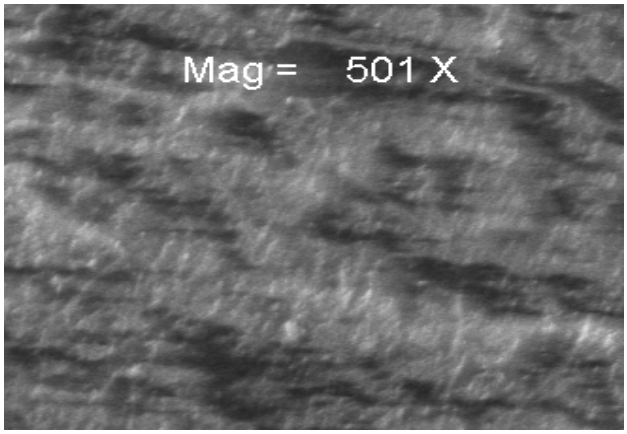

Fig. 2 SEM for CoO Film annealed at

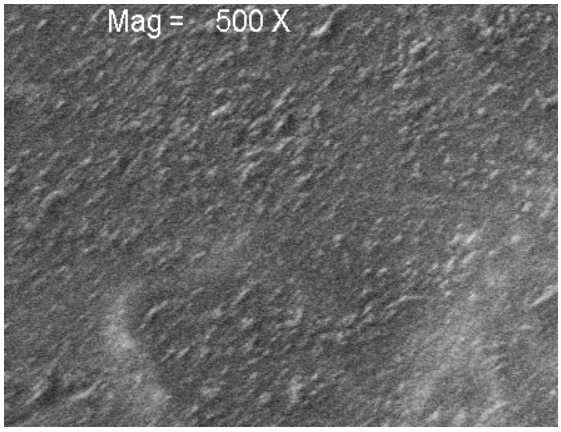

Fig. 3 SEM for CoO Film annealed at

3.3 Optical Studies

The optical absorbance studies were done at room temperature for the CoO thin films [as-deposited and annealed] in the range of 200-1500nm. The plot of $[\alpha h\nu]^2$ against photon energy $h\nu$ for the [as-deposited and annealed] CoO films are shown in Fig 4. The plot is a straight line, indicating that the transmittance is direct one. The absorption spectra were used in evaluating the optical band gap [Eg] of the films by extrapolating the straight portions of Fig.4, [annealed at different temperatures] The optical absorption theory is given by the equation.

$$\alpha = A\frac{[h\nu - Eg]^n}{h\nu} \qquad 2$$

where A is constant and n is also a constant equals to ½ for direct optical band gap semiconductors and n equals 2 for indirect optical band gap semiconductors [20]

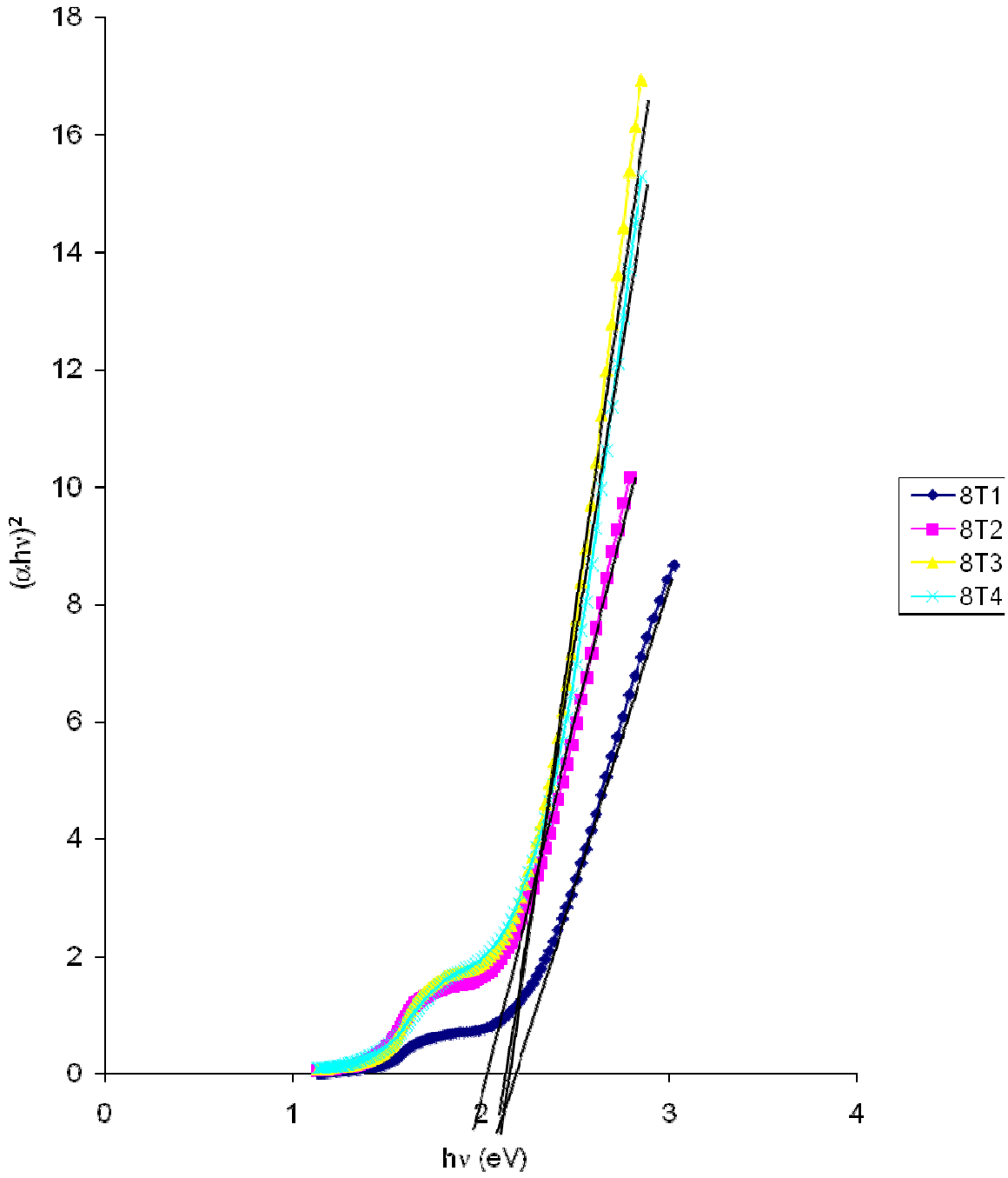

Fig. 4. Plot of $[\alpha h\nu]^2$ versus νh for CoO thin films [as-deposited and annealed]

The optical band gap for the as-deposited CoO film is determined to be 2.1eV. The energy gap for the sample annealed at 373K is 2.01eV. This resulted to a band gap shift of 0.09eV, after annealing. The optical band gap later increased from 2.01eV to 2.07eV and finally reached 2.08eV for the samples annealed at 473 and 573K respectively, leading to a further band gap shift of 0.07eV approximately. These changes may be attributed to grain size dependent properties of the energy band gap. The decrease in band gap shows that annealing the film causes a strong red shift in the optical spectra, due to the agglomeration of the nanocrystallites in larger crystiallites [7,21] Neverthless, energy gap cannot be said to be dependent on the annealing temperatures.The CoO thin films studied could be used as sensors in the violet and ultraviolet region, light emitting diodes, photovoltaic cells and biomedical imaging.

4 Conclusions

The chemical bath deposition [CBD] technique was used successfully to deposite CoO thin films from cobaltous chloride [$CoCl_2.6H_2O$] as cationic precursor and NH_3 as anionic precursor while NaOH acted as a complexing agent. XRD studies show that the prepared films have Rhombohedral structure. High intensity XRD peaks and absence of noisy background show that the films are crystalline in nature. The optical band gaps decreased and later increased gradually with increase in annealing temperatures. The optical transmittance of CoO film is a direct one. The band gap range for the CoO films studied is 2.08-2.1eV. The band gap decreases and increases with the annealing temperatures,and cannot therefore be said to be a function of the annealing temperatures.These thin films could have potential applications in sensors in light emitting diodes in the violet and ultraviolet region, photovoltaic cells and biomedical imaging.

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