

Production of Al³⁺ Doped Cobalt Oxide Thin Films by Solution Growth Technique

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Abstract

CoO:Al³⁺ were fabricated on glass substrates using solution growth deposition technique. Sample A is chosen as a representative sample for other fabricated ones. The Rutherford Backscattering Spectroscopy analysis shows that sample A annealed for 2 hours at the temperature of 250°C has thickness of 160nm. The elemental compositions of sample A, shows that: O: 94.33%, Al: 5.22%, Co: 0.55%. The transmittance of sample A(0.24-0.75) with increasing wavelength from UV to near infrared regions of electromagnetic spectrum which suggests that the material can be used as transparent material for solar heating applications. The band gap of the material is 3.40±0.05eV. Its high energy band gap makes it a good material for FPDs for optoelectronics applications and also a possible material applicable as heat and cold windows.

Keywords: Transmittance; Band gap; Cobalt oxide; Thin film; Extrapolating; Cold window

Introduction

Solution growth deposition technique has attracted great interest due to its self-limiting nature of growth and exceptional coating pattern on three-dimensional structures with high aspect ratios. The solution growth technique (SGT) is inexpensive and needs simple containing vessels and substrates mounting devices. The advantages of CBD are adherent, uniform and large scale deposition of thin films and reproducibility. The preparative parameters such as surface morphology and thickness of the thin film can be easily controlled by varying preparative parameter such as reaction time, pH, temperature and concentration of precursor. The disadvantages of this method is the wastage of solutions, excess of ionic product than solubility product, requires more time to obtain films due to slow growth rate.

Cobalt forms the two stable oxides CoO and Co₃O₄. These oxides have gained great interest due to their possible application as catalyst, *e.g.* for the combustion of hydrocarbons[1],[2] or as sensitive materials in gas sensors [3],[4]. Both amorphous and crystalline cobalt oxide layers are a promising anode material for thin film lithium-ion batteries enabling lighter batteries compared to standard graphite electrodes [5],[6],[7],[8]. Furthermore Co₃O₄, is an ideal material for absorber layers in solar thermal collectors due to its high absorption across the complete solar spectrum[9],[10]. Various processes are available for the deposition of cobalt oxides such as molecular beam epitaxy, [4] sputtering,[11] spray pyrolysis, [12] electrochemical deposition, [13],[14] thermal oxidation [14] and chemical vapor deposition.[15] Thermal oxidation of pre-deposited metallic cobalt is not feasible in terms of temperature and rate requirements, since temperatures above 375 °C are required to accelerate diffusion for a sufficiently fast oxidation. [16]. The aim of this work is to synthesis and study the thickness, composition and the optical properties of CoO doped with Al³⁺ using chemical bath deposition technique.

Materials and Method

The following materials are required to deposit successfully layers of CoO: Al³⁺ thin films. Cobalt Chloride (CoCl₂), Aluminum sulphate (Al₂(SO₄)₃ Ammonia NH₃ (as complexing agent), glass substrates, de-ionized water.

Preparation of Substrates

The substrates were soaked in concentrated solution of hydrochloric acid HCl and Nitric acid HNO₃ in the ratio of 3:1 for 24 hours and were washed with detergents and rinsed in de-ionized water and hanged in slanting order to air-dry. This is done in order to remove unwanted substances such as oil and grease and also to create the nucleation centers for easy and adherent deposition.

Experimental Procedure

The Deposition of Manganese Oxide Thin Films Doped with Aluminum

The synthesis of CoO thin films doped with 0.06M solution of Al³⁺ using solution growth technique (SGT) method constituted: 4ml of 3M solution of ammonia as complexing agent, 0.13M solution of CoCl₂ and was made to react with H₂O₂ solution forming CoO:Al as depicts in Figure 1.

Theory

4ml of 3M solution of ammonia was made to react with the solution of CoCl₂, forming cobalt tetra-ammine complex ion as given in equations (1).



De-ionized water was added up to 50ml and the solution was stirred vigorously in order to achieve uniformity in the mixture.

CoO:Al³⁺ thin films were deposited on substrates for 4 hours, by dipping the substrates into the beaker containing the cationic precursor of cobalt complex ion and anionic precursor of H₂O₂ at room temperature, the substrates were rinsed in de-ionized water and finally dipped in a beaker containing aluminum complex ion for 5 seconds and was rinsed in de-ionized water, The reactions are given in equations (2) and (3).

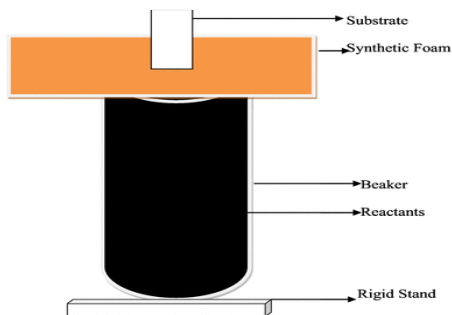
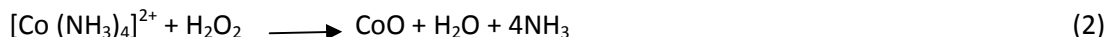


Figure 1 SGT Experimental Setup

Results and Discussion

Thickness and Composition measurements

In this work, atomic compositions were determined, by Rutherford backscattering Spectroscopy (RBS) analysis. The Rutherford backscattering analysis shows that the sample A has thickness 160nm. Figure 2 revealed that samples A annealed at 250°C has 94.33% of oxygen, 5.22% of aluminum, 0.55% of cobalt.

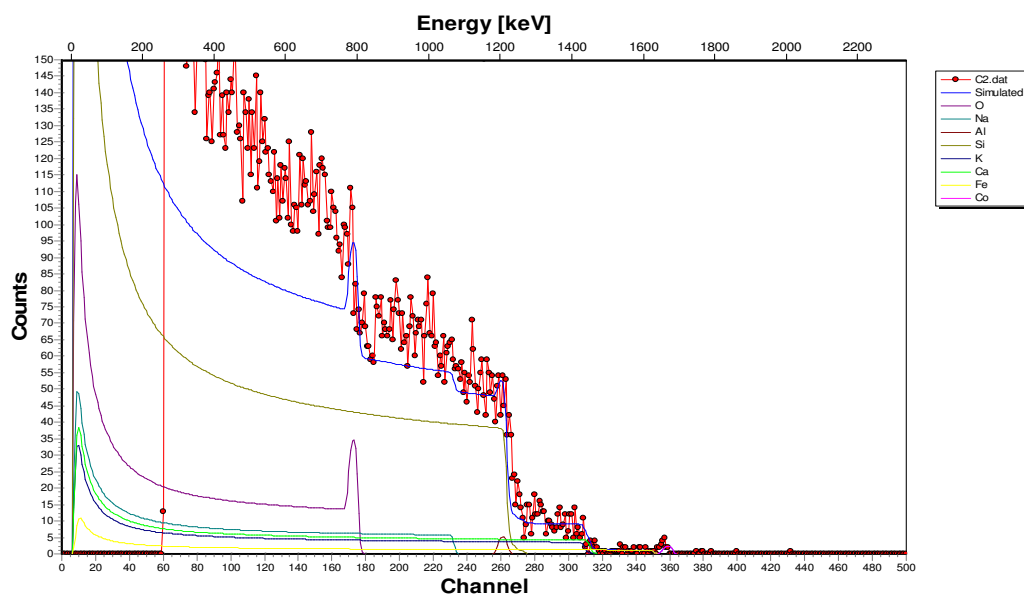


Figure 2 Elemental Composition of Sample A

LAYER 1: THICKNESS 160.0 nm

Compo: Co 0.55% Al 5.22 % O 94.33%

LAYER 2: THICKNESS 5000.0 nm

Compo: Si 35.19% O 51.02% Na 9.81% Ca 2.16% Al 0.02%
 K 1.41% Fe 0.39%

Table 1 Transmittance of Sample A

Wave Length	Sample A
300	0.2383
350	0.53137
400	0.61528
450	0.64369
500	0.67104
550	0.69646
600	0.71735
650	0.73077
700	0.74214

750	0.74635
800	0.74724
850	0.74612
900	0.74353
950	0.73994
1000	0.73543
1100	0.72729

Transmittance

The optical transmission data in the wavelength range 300nm to 1100nm as given in Table 1 was measured using UVI double beam Spectrophotometer with serial number 1800. The sample A has transmittance range (0.24-0.75), with high transmittance at the visible and near infrared regions and low transmittance at the UV as depicts in Figure 3. With the this feature, it can be a good material for cold and heat windows and also can be made use as sensor material for detection of harmful gases. .

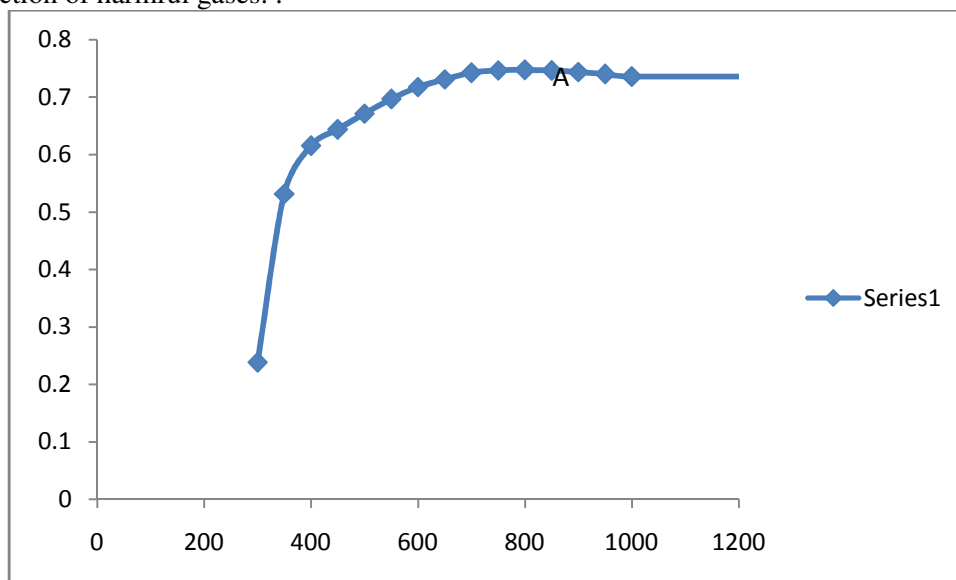


Figure 3 graph of transmittance against wavelength.

Table 2 of $(\alpha h\nu)^2$ (eV/m)² against photon energy $h\nu$ (eV) for sample A

$h\nu$ (eV)	$(\alpha h\nu)^2$
4.144	8.03516E+13
3.552	1.56172E+13
3.108	9.21418E+12
2.763	7.58101E+12
2.486	6.2165E+12
2.26	5.11169E+12
2.072	4.31059E+12
1.913	3.84298E+12
1.776	3.47397E+12
1.658	3.34343E+12
1.554	3.31624E+12
1.463	3.35047E+12
1.381	3.43051E+12
1.309	3.54348E+12
1.243	3.6888E+12
1.13	3.96085E+12

Energy band gap

The band gap of sample A is determined in the graph of $(\alpha h\nu)^2$ against $h\nu$, by extrapolating the linear portion of the curve where $\alpha h\nu = 0$ as shown in Figure 4. The band gap of sample A is found to be 3.4 ± 0.05 eV. It can be used as good material for optoelectronic applications, smart windows and also a possible material for super-magnetic applications.

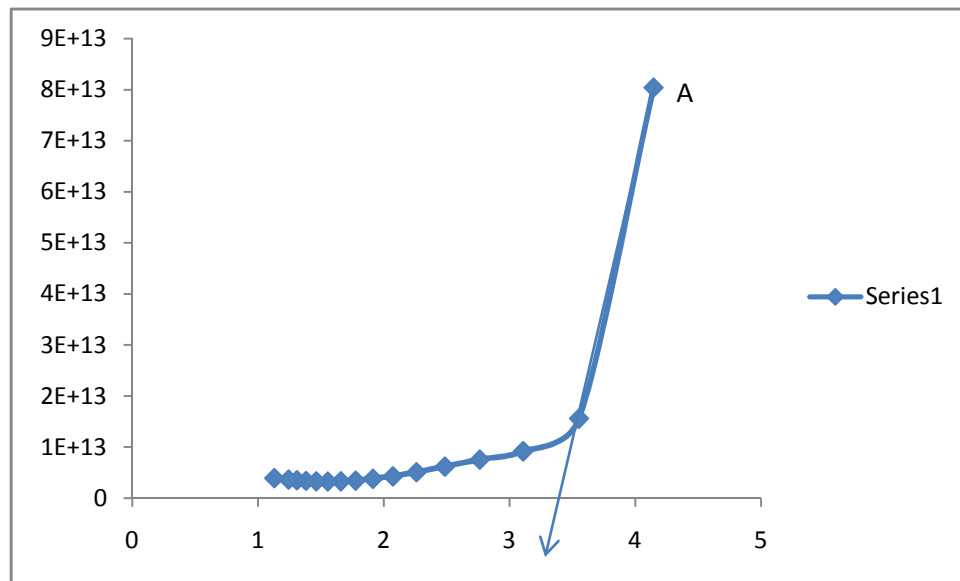


Figure 4 graph of $(\alpha hv)^2$ (eV/m)² against hv (eV) for sample A.

Conclusion

Al³⁺ doped CoO thin films were deposited successfully at room temperature onto glass substrates by SGT method. The deposition of the samples, shows that the films are uniform and adherent to the substrates. Annealing shows strong effects on the samples by removing moisture and volatile substances in the course of deposition. Rutherford back scattering was used in determining the atomic composition and the thicknesses of the samples. The optical properties were measured using UV1800 series double beam spectrophotometer. The optical band gap of CoO:Al³⁺ has been found to be 3.40 ± 0.05 eV. Thus the obtained results indicate that Al³⁺ doped CoO modifies the optical properties of the CoO thin films significantly with abundant applications ranging for electronic/optoelectronic, solar conversions and sensor uses.

Reference

1. N. Bahlawane *Appl. Catal., B*, 2006, **67**, 168 -176 .
2. M. M. Natile and A. Glisenti , *Chem. Mater.*, 2002, **14** , 3090 -3099.
3. H. Yamaura , J. Tamaki , K. Moriya , N. Miura and N. Yamazoe , *J. Electrochem. Soc.*, 1997, **144** , L158.
4. J. Wöllenstein , M. Burgmair , G. Plescher , T. Sulima , J. Hildenbrand , H. Böttner and I. Eisele , *Sens. Actuators, B*, 2003, **93** , 442 -448
5. H. J. Qiu , L. Liu , Y. P. Mu , H. J. Zhang and Y. Wang , *Nano Res.*, 2015, **8** , 321 -339.
6. G. X. Wang , Y. Chen , K. Konstantinov , M. Lindsay , H. K. Liu and S. X. Dou , *J. Power Sources*, 2002, **109** , 142 -147 .
7. M. E. Donders , H. C. M. Knoops , W. M. M. Kessels and P. H. L. Notten , *J. Power Sources*, 2012, **203** , 72 -77.
8. D. Barreca , M. Cruz-Yusta , A. Gasparotto , C. MacCato , J. Morales , A. Pozza , C. Sada , L. Sánchez and E. Tondello , *J. Phys. Chem. C*, 2010, **114** , 10054 -10060.
9. G. McDonald *Thin Solid Films*, 1980, **72** , 83 -87.

10. K. Chidambaram , L. K. Malhotra and K. L. Chopra , *Thin Solid Films*, 1982, **87** , 365 -371.
11. L. C. Schumacher , I. B. Holzhueter , I. R. Hill and M. J. Dignam , *Electrochim. Acta*, 1990, **35** , 975 -984.
12. V. R. Shinde , S. B. Mahadik , T. P. Gujar and C. D. Lokhande , *Appl. Surf. Sci.*, 2006, **252** , 7487 -7492 .
13. E. Barrera , I. González and T. Viveros , *Sol. Energy Mater. Sol. Cells*, 1998, **51** , 69 -82.
14. G. B. Smith , A. Ignatiev and G. Zajac , *J. Appl. Phys.*, 1980, **51** , 4186 -4196 .
15. T. Maruyama and T. Nakai , *Sol. Energy Mater.*, 1991, **23** , 25 -29 .
16. H. G. Tompkins and J. A. Augis , *Oxid. Met.*, 1981, **16** , 355 -369 .