# CuO Thin Film Prepared by Chemical Bath Deposition Technique: A Review

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## Abstract

This paper critically reviewed the preparation of Copper Oxide thin films by Chemical Bath Deposition method. The important results obtained from XRD, SEM, FTIR, Uv-Vis Spectrometer, AES and photoluminescence measurements are discussed. The films deposited by this technique have possible applications as thin film transistors, photovoltaic's, smart windows, IR detector, optical limiters etc. It has been seen that properties of the film are highly influenced by the basic ingredients used in reaction, bath temperature, pH of solution, annealing and substrate material.

Keywords: Thin film, Chemical bath deposition, Copper Oxide

## **INTRODUCTION:**

In recent years, nano-structured transition metal oxides (TMO) have gained a great interest from scientific community due to different properties compared with corresponding bulk counterparts, which in turns provides promising applications in the various fields of technology [1]. CuO, categorized as a TMO, is a p-type, narrow band gap semiconductor. Copper Oxide has two common forms; cupric oxide (CuO) with band gap in the range 1.2-2.1eV and cuprous oxide (Cu<sub>2</sub>O), with band gap of 2.1-2.6 eV [2]. In CuO the lattice structure has monoclinic symmetry, where as Cu<sub>2</sub>O has cubic structure [3]. The CuO and Cu<sub>2</sub>O thin films are widely used in several device applications such as thin film transistors, photovoltaic's, smart windows, IR detector, optical limiters etc [4-8]. A number of reports have been made on CuO thin films preparation by various techniques including magnetron sputtering[9], microwave[10], sol-gel[11], chemical vapour deposition[12], spray pyrolysis [13], pulsed laser deposition [14] and chemical bath deposition [15] etc. All these techniques offer distinct advantages depending on the kinds of applications. Among these techniques, Chemical bath deposition (CBD) which is also known as solution growth at controlled precipitation technique. The reaction takes place between the dissolved precursors generally in aqueous solution at low temperature  $(30\pm80^{\circ}C)$ . The solution chemistry must choose such that a spontaneous reaction from the liquid phase is possible.

CBD method is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipments. The simple equipments like hot plate with magnetic stirrer are sufficient for deposition needed. The starting chemicals are commonly available and cheap. With this method a large number of substrates can be coated in a single run. No electrical conductivity of the substrate is required for deposition. The low temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical deposition results in pin hole free and uniform deposits are easily obtained since the basic building blocks are ions instead of atoms [16]. In this review, we would like to summarize the preparation of CuO and Cu<sub>2</sub>O thin film by CBD method. The effect of precursor solution on its structural, morphological, electrical and optical properties has been discussed.

# LITERATURE REVIEW:

Chemical bath deposited CuO thin films have been synthesised on glass substrate by Ramya et.al. [15]. They have studied the effect of pH of the solution on structural, optical and electrical properties of films. All the films have exhibited orthorhombic structure with preferred orientation along (111) plane. The morphological studies show that the average particle size increases as an effect of increases in pH of the solution. Optical absorption measurements indicate that the deposited films has direct band gap values of 1.89eV, 1.69eV, and 1.53 eV for solution pH 10.0, 10.5 and 11.0 respectively. Low resistivity has been observed for the films deposited with pH 11.0 which may be suitable for the solar cell applications.

Nasser et al [17] have been deposited copper oxide on glass substrate by CBD alternate immersion method at room temperature for 20 second intervals. They have studied the effect of annealing on the properties of the films. The significant improvement in structure by annealing at different temperature was discussed. The SEM image so obtained showed that porous structure was distinctive materials for the manufacture of gas sensors.

Cetinkaya et al.[18] has deposited CuO interlayers in the CuO/p-Si Schottky diodes were fabricated by using CBD and sol-gel methods. Deposited CuO layers were characterized by SEM and XRD techniques. From the SEM images, it was seen that the film grown by CBD method is denser than the film grown by sol-gel method. The XRD results show that the crystallization in CBD method is higher than that is in sol-gel method. In this paper author has concluded that, producing CuO interlayer via chemical bath deposition method is convenient and effective way to modify the device parameters of the diode.

Sultana et al [19] has been deposited thin films of CuO on Si substrate. The special emphasis is given on the varying thickness of grown copper oxide with different reaction time and its subsequent impact on chemical composition on CuO, surface morphology, phase formation and grain size of the nanostructures. The electrical and optical properties of the CBD grown thin film varies significantly with thickness. The result conforms that the films with 110nm thickness are promising to use for anti-reflection coating and solar energy harvesting.

Bayansal et al [20] has reported a simple route for the synthesis of dense, continuous and stable nano structured CuO films by two methods. The first method is immersing glass, quartz, silicon and Cu foil substrate in an aqueous solution of Cu(II) chloride dehydrate and ammonia. And the other method is immersing Cu foil in an aqueous solution of ammonia and sodium hydroxide. The morphology of CuO nanostructures (plate, needle and wire) can be changed by using different types of substrate.

Direct deposition of cuprous oxide film with different particle shapes has been achieved by Hai Yan Xu et al.[21] through a simple one step and inexpensive CBD method with bargain glucose as reductant and trisodiumcitrate as complexant at low temperature (80°C). The particle morphology of the films was octahedral at copper ion concentration with excessive glucose; with the increased copper ion concentration at excessive glucose, the spherical particles were obtained.

Das et al. [22] has synthesised CuO nano-particles on boro-float glass by combination of sputter and chemical bath deposition method. CuO seeds were prepared by R.F. sputter and nanoparticles were prepared by CBD with varying molar concentration of solutes. The samples were annealed at 400°C for 1 hour. The as grown and annealed sample shows monoclinic structure with particle size ranging from 22 to 100nm.

The photoluminescence properties of CuO thin films deposited on glass substrate has been studied by Ahirrao et al.[23]. The structural studies shows that Cu<sub>2</sub>O films has mainly (111) and (200) crystalline orientations. The room temperature photoluminescence study showed a green band at 503nm, 540nm, and a strong red emission at 627nm.

Uniform and crake free CuO films have been prepared by CBD method simply using  $Cu(NO_3)_2$  and ammonia. Xu et al [24] synthesised nano-structured thin films with unique morphologies deposited on glass substrate at 40-80°C for 1-5 h with pH value ranging from 8.5-10. Unique elliptical sheet like morphology can be obtained at temperature  $\geq 70^{\circ}$ C, while corncob like nanostructure can be obtained at lower temperature  $\leq 60^{\circ}$ C.

Photoconductive copper oxide thin film has been prepared by Muhibbullah et al. [25]. The aqueous solution of  $CuSO_4$  and  $Na_2SO_3$  were used to key ingredients, and the deposition temperature was 70-80°C. The Auger electron spectroscopy measurements reveal that the samples have Cu/O ratio near the stoichiometric ratio of Cu<sub>2</sub>O. By bubbling oxygen in to the solution during the deposition, the oxygen content of the film increased. The films exhibit p-type conduction and photosensitivity, and thus useful as an absorber material in hetero-structure solar cells.

Study of annealing effects on the properties of copper oxide thin film prepared by chemical deposition has been carried out by Mohd Rafie Johan et al. [26]. The films were annealed in air at different temperature range of  $200 - 400^{\circ}$ C and as prepared sample was used as reference. The XRD results reveal that, the as prepared film and films annealed at 200°C were cuprite structure with Cu<sub>2</sub>O composition. Films annealed at 300°C consist of mixed phase of CuO and Cu<sub>2</sub>O, where as film annealed at 400°C completely converts in to CuO phase. The FTIR measurements also confirm the transformation of phase. The photoluminescence intensity is greatly improved with increase in annealing temperature.

## **CONCLUSION:**

The Copper Oxide thin films were successfully deposited by Chemical Bath Deposition (CBD) method. The obtained films were well studied and analyzed using XRD, SEM, AES, EDX, electrical measurement and UV-Vis spectrometer. The results show that the properties of the film are highly influenced by the basic ingredients used in reaction, bath temperature, pH of solution, annealing and substrate material.

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## **REFERENCES:**

- 1. Thi Ha Tran; Viet Tuyen Nguyen; International Scholarly Research Notices, Volume 2014, Article ID 856592.
- 2. Balamurugan B.; Mehta R., *Thin Solid Films*, **2001**, 396 (1-2), 90.
- 3. Ghijsen J.; Tjeng H. L; J.van Elp V.; Eskes H.; and Czyzyk T. M., *Physical review B*, **1988**, 38(16), 11322-11330.
- 4. Chen A.; Yang G.; Long H.; Li F.; Li Y. and Lu P., *Thin solid Films*, **2009**, 517, 4277.
- 5. Chen A.; Yang G.; Long H.; Lu P.; Zhang W. and Wang H., *Materials letters*, **2013**, 91,319.
- Wange B. S.; Hsiaoa H. C.; Changa J. S.; Lamb T. K.; Wenb H. K.; Hungc CV. S.; Youngd J.S. and Huange R.B.; *Sens. Actuators*, 2011, A 171, 207.
- 7. Nandy S.; Banerjee N. A.; Fortunato E.; and Martins R.; *Rev. Adv. Sci. Eng.*, **2013**, 2, 1.
- 8. Pattanasattayavong P.; Thomas S.; Adamopoulos G.; McLachlan A. M. and Anthopou los D. T., *Appl. Phy. Lett.*, **2013**,102,163505.
- 9. Wanjala S.K.; Njoroge K.W.; Makori E.N. and Ngaruiya M.J.; American Journal of Condensed Matter Physics, 2016, 6 (1), 1-6.

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- 10. Rejith G.S.; and Krishnan C.; *Material letters*, **2013**,106, 87-89.
- 11. Etefagh R.; Azhir E. and Shahtahmasebi N.; *Scientia Iranica*, **2013**, 20(3), 1055-1058.
- 12. Maruyama T.; Jpn. J. Appl. Phys, 1998, 37,4099.
- 13. Shabu R.; Moses Ezhil Raj A.; Sanjeeviraja C. and Ravidhas C.; *Material Research Bulletin*; **2015**, 68, 1-8.
- 14. Chen A.; Long H.; Li X.; Li Y.; Yang G. and Lu P., Vacuum, 2009, 83,927.
- 15. Ramya V.; Neyvasagam K.; Chandramohan R.; Valanarasu S.; Milton Franklin Benial A., *J Mater Sci: Mater Electron*, **2015**, 26, 8489.
- 16. Mane S. R.; Lokhande D. C., *Materials Chemistry and Physics*, 2000, 65, 1-31.
- 17. Nasser Saadaldin; Alsloum M. N.; Hussain N., *Energy Procedia*, **2015**, 74, 1459-1465.
- Cetinkaya S.; Cetinkara A. H.; Bayansal F. And Kahraman S.; The Scientific World Journal Volume, 2013, Article ID126982,6 pages
- 19. Jenifar Sultana, Somdatta Paul, Anupam Karmakar, Ren Yi, Goutam Kumar Dalapati, Sanatan Chattopadhyay; *Applied Surface Sciences*, **2016**.(Article in press)
- 20. Bayansal F.; Cetinkara A. H.; Kahraman S.; Cakmak M. H.; Guder S. H., *Ceramics International*, **2012**, 38,1859-1866.
- 21. Hai Yan Xu; Chen Chen; Ling Xu; Jin Kuang Dong; *Thin Solid Films*, **2013**, 527, 76-80.
- 22. Avishek Das; Ajay Kushwaha; Nakul Raj Bansal; Vignesh Suresh; Sanghamitra Dinda; Sanatan Chattopadhyay; Goutam Kumar Dalapati, *Adv. Mater. Letters*, **2016**, 7(8), 600-603.
- 23. Ahirrao B. P.; Gosavi R. S.; Patil R. D.; Shinde S. R. and Patil S.R., *Archives of Applied Sciences Research*, **2011**, 3(2), 288-291.
- 24. Ling Xu; Hai-Yan Xu; Shi-Biao Wu; Xu-Dong Wang; Tian Cao; Shao-Feng Zhu and Yan Li, *Asian Journal of Chemistry*, **2011**, 23 (5), 2295-2298.
- 25. Muhammad Muhibbullah and Masaya Ichimura; *Japanese Journal of Applied Physics*, **2010**, 49, 081102.
- 26. Mohd. Rafie Johan; Mohd Shahadan Mohd Suan; Nor Liza Hawari; Hee Ay Ching; *Int. J. Electrochem. Sci.*, **2011**, 6, 6094-6104.