

Effect of Post-Air Annealing on the Structural, Morphological, and Compositional Properties of Chemical Bath Deposited CuO Thin Films

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ABSTRACT

Copper oxide (CuO) thin films were deposited on silicon substrates by the chemical bath deposition (CBD) technique at 70 °C and subsequently subjected to post-air annealing at 450 °C to investigate the influence of thermal treatment on their structural, morphological, and compositional properties. X-ray diffraction studies confirmed the formation of monoclinic CuO with enhanced crystallinity after annealing, as evidenced by sharper diffraction peaks and an increase in crystallite size from 10.46 nm to 13.41 nm. Raman spectroscopy revealed pronounced A_g and B_g vibrational modes in the annealed films, indicating improved phase purity and reduced defect concentration. SEM analysis showed densely packed nanoparticles with average grain sizes increasing from approximately 33 nm for the as-deposited film to 43 nm after annealing, demonstrating thermally assisted grain growth. EDS analysis confirmed the presence of copper and oxygen as the major constituents and indicated improved stoichiometry following air annealing. The Cu:O atomic ratio increased from 0.871 to 0.894, suggesting enhanced oxidation and phase stability. The results demonstrate that post-air annealing at 450 °C significantly improves the structural quality, morphology, and compositional homogeneity of CBD-grown CuO thin films, making them promising candidates for optoelectronic and sensing applications.

Key Words: Copper Oxide Thin Films, Chemical Bath Deposition, Post-Air Annealing, Structural and Morphological Properties

INTRODUCTION

Copper oxide (CuO) is a p-type semiconductor possessing a narrow band gap (1.2 to 2.2 eV), high optical absorption coefficient, low cost, and excellent chemical stability, making it a promising material for applications in gas sensors, solar cells, photocatalysis, and energy storage devices [1- 4]. Among various thin-film fabrication techniques, chemical bath deposition (CBD) has attracted considerable attention owing to its simplicity, low processing temperature, cost-effectiveness, and ability to produce uniform coatings over large areas.

However, as-deposited CuO films prepared at relatively low temperatures often exhibit poor crystallinity, high defect density, and incomplete oxidation, which adversely affect their physical properties and device performance. Post-deposition thermal treatment is an effective approach to overcome these limitations. In particular, air annealing provides an oxygen-rich environment that facilitates complete oxidation, promotes grain growth, reduces lattice imperfections, and enhances phase purity [5, 6].

In the present work, CuO thin films were deposited by the CBD technique at 70 °C and subsequently annealed in air at 450 °C. The influence of annealing on the structural, morphological, and compositional characteristics of the films was investigated using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The study aims to understand the role of post-air annealing in improving the quality of CuO thin films for their potential use in various functional device applications [7, 8].

MATERILS AND EXPERIMENTAL METHODS

CuO thin films were deposited by the chemical bath deposition (CBD) technique. Initially, 3.41 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 200 ml of distilled water to prepare a 0.1 M precursor solution, which was magnetically stirred for 5 min to ensure complete dissolution. The solution temperature was then raised to 60 °C, and 11 ml of 25% ammonia solution was added dropwise as a complexing agent to facilitate the controlled formation of CuO nanoparticles. Subsequently, the reaction mixture was heated to 70 °C under continuous stirring, during which the solution gradually changed to a dark blue color, indicating the formation of copper–ammonia complexes.

Silicon substrates, cleaned using the standard RCA1 and RCA2 procedures [9], were mounted on a glass substrate holder and immersed vertically in the reaction bath maintained at 70 °C for 2 h. After deposition, the stirring and heating were switched off, and the substrates were kept undisturbed in the bath for an additional 20 h to promote uniform film growth. The deposited films were removed from the bath and thoroughly rinsed with running distilled water to eliminate any loosely adhered or unreacted species, followed by drying with hot air. The silicon substrates were then carefully detached from the holder using acetone, and any residual adhesive on the backside was removed using acetone and a cotton earbud before a final drying step. To improve the crystallinity and structural quality of the films, the as-deposited samples were subsequently subjected to post-air annealing at 450 °C [10].

Thin films deposited on n-type Si substrates were employed for structural, morphological, and compositional characterization using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS).

RESULT AND DISCUSSION

XRD Structural Analysis

Figure 1 shows the X-ray diffraction (XRD) patterns of the as-deposited CuO thin film (C1) and the post-air-annealed film (C2) annealed at 450 °C. The as-deposited film exhibits broad and low-intensity diffraction peaks, indicating poor crystallinity and the presence of structural imperfections. Upon air annealing at 450 °C, the diffraction peaks become sharper and more intense, and the characteristic reflections corresponding to monoclinic CuO are clearly observed, indicating enhanced crystallinity and grain growth. The sharpening of the peaks further suggests a reduction in lattice strain and improved phase formation. All the observed diffraction peaks are in good agreement with the standard JCPDS Card No. 00-001-1117, confirming the formation of phase-pure monoclinic CuO. These results demonstrate that post-air annealing at 450 °C significantly improves the structural quality of the chemically bath deposited CuO thin films [5].

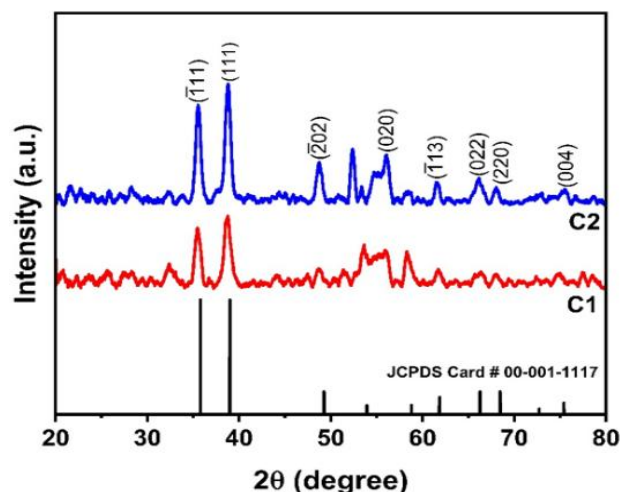


Figure 1: X-ray diffraction (XRD) patterns of as-deposited(C1) and post-air-annealed (C2) chemical bath deposited CuO thin films

Table 1: Structural parameters estimated from the most intense (111) XRD peak of as-deposited and air-annealed chemical bath deposited CuO thin films

Sample	2 θ degree	FWHM (β)	D nm	d nm	δ m ⁻²	ϵ	Crystallinity %
C1	38.71	0.907	10.46	0.2324	00.0091	00.0072	37.36
C4	38.81	0.728	13.41	0.2318	00.0056	00.0051	47.02

The structural parameters calculated from the most intense (111) diffraction peak of the chemical bath deposited CuO thin films are summarized in Table 1. The results reveal a significant improvement in the structural properties after post-air annealing [11]. The as-deposited film (C1), prepared at 70 °C, exhibits a relatively small crystallite size of 10.46 nm, high dislocation density, and low crystallinity (37.36%), indicating the presence of structural disorder and lattice imperfections. After air annealing at 450 °C (C2), the crystallite size increases to 13.41 nm, accompanied by a decrease in lattice strain and dislocation density. Furthermore, the crystallinity increases to 47.02%, indicating improved atomic ordering and enhanced phase formation. These observations suggest that air annealing promotes grain growth, relieves internal stress, and reduces structural defects, thereby significantly improving the crystalline quality of the CBD-grown CuO thin films.

Raman Spectroscopic Analysis

The Raman spectra of the chemical bath deposited CuO thin films (Fig. 2) reveal significant structural modifications induced by post-air annealing. The as-deposited film (C1), prepared at 70 °C, exhibits the characteristic A_g vibrational mode at approximately 283.9 cm⁻¹ with relatively low intensity, indicating poor crystallinity and the presence of structural defects. Upon air annealing at 450 °C (C2), the A_g mode shifts slightly to 278.9 cm⁻¹ and becomes more intense, accompanied by the appearance of the B_g mode around 334.88 cm⁻¹, which is a characteristic vibrational mode of monoclinic CuO [12]. The increased intensity and sharpening of the Raman peaks after annealing indicate enhanced crystallinity, grain growth, and reduced defect-induced phonon scattering. These observations are consistent with the XRD results and confirm that post-air annealing at 450 °C significantly improves the structural quality and phase purity of the CBD-grown CuO thin films.

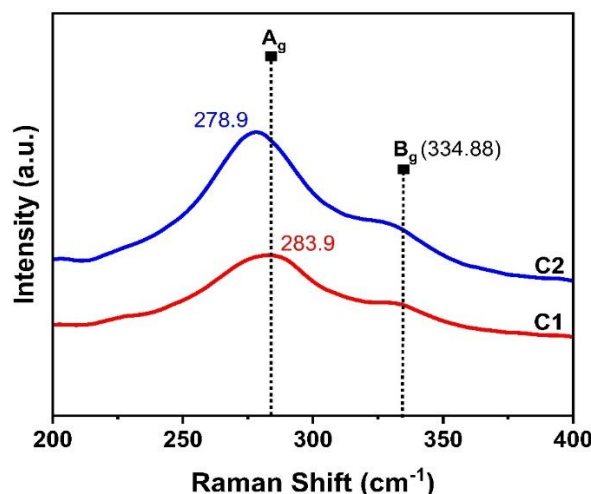


Figure 2: Raman spectra of as-deposited and post-air annealed chemical bath deposited CuO thin films

SEM Analysis

The surface morphology of the CuO thin films deposited by the chemical bath deposition (CBD) method was investigated using scanning electron microscopy (SEM), and the corresponding particle size distributions were obtained from Gaussian fitting of the SEM histograms, as shown in Fig. 3. The as-deposited film (C1), prepared at 70 °C, exhibits densely packed and irregularly shaped nanoparticles with an average particle size of approximately 33 nm, indicating the formation of fine granular clusters during the initial stage of film growth.

Upon post-air annealing at 450 °C (C2), a noticeable improvement in surface morphology is observed, characterized by enhanced grain coalescence and an increase in the average particle size to approximately 43 nm. The increase in particle size is attributed to thermally assisted grain growth and improved crystallization during annealing. Furthermore, the reduction in agglomeration and the development of well-defined grains suggest enhanced surface uniformity and compactness. The Gaussian-fitted particle size distributions also exhibit broadening after annealing, which is consistent with grain growth and improved crystallinity. Overall, post-air annealing transforms the fine and irregular grains of the as-deposited film into larger and more homogeneous CuO nanoparticles, thereby enhancing the structural quality of the CBD-grown CuO thin films [13].

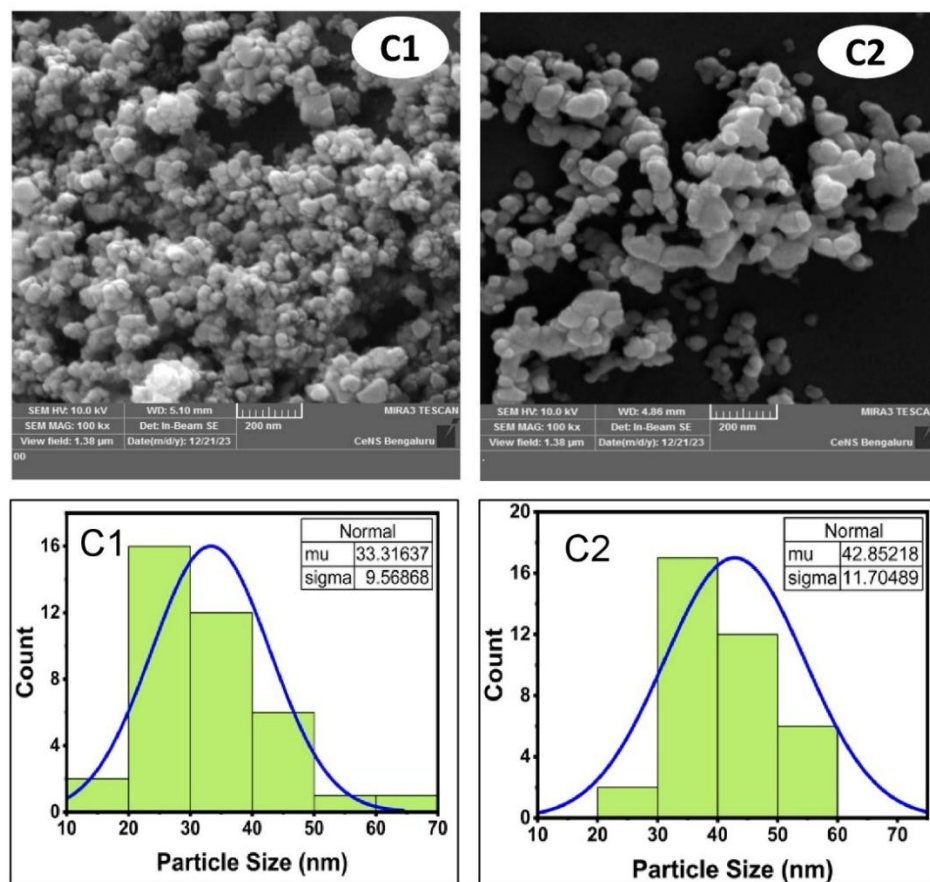


Figure 3: SEM images and Histograms of as-deposited (C1) and post-air annealed (C2) chemical bath deposited CuO thin films

EDS Analysis

The energy-dispersive X-ray spectroscopy (EDS) spectra of the as-deposited (C1) and post-air-annealed (C2) CuO thin films, shown in Fig. 4, confirm the presence of copper (Cu) and oxygen (O) as the major elemental constituents, indicating the successful formation of CuO [14]. The as-deposited film (C1) exhibits relatively lower intensities of the Cu and O peaks, suggesting incomplete oxidation and the formation of a less compact CuO phase. In contrast, the air-annealed film (C2) shows stronger and more distinct elemental peaks, indicating improved oxidation, enhanced crystallinity, and better compositional homogeneity.

The elemental composition obtained from EDS analysis is summarized in Table 2. The as-deposited film (C1) exhibits a Cu:O atomic ratio of 0.871, indicating a slightly copper-rich composition and the presence of oxygen deficiency. Following post-air annealing at 450 °C, the Cu:O atomic ratio increases to 0.894, approaching the stoichiometric composition of CuO. This improvement can be attributed to the enhanced incorporation of oxygen during thermal treatment in an oxygen-rich atmosphere. Overall, post-air annealing promotes better stoichiometry, improves phase stability, and facilitates the formation of chemically homogeneous and structurally superior CuO thin films [13].

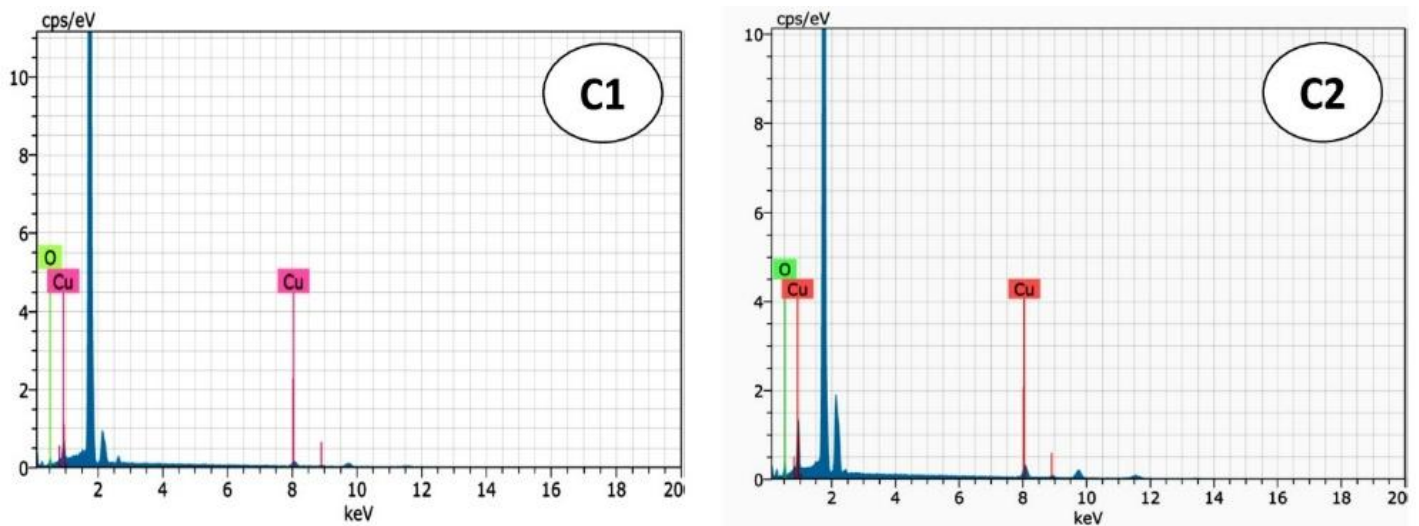


Figure 4: EDS spectra and elemental mapping of as-deposited and post-air annealed chemical bath deposited CuO thin films

Table 2: Elemental composition of as-deposited and air-annealed chemical bath deposited CuO thin films obtained from EDS analysis

Sample	Elements	Weight %	Atomic %	Cu:O Ratio
C1	Oxygen	22.42	53.44	0.871
	Copper	77.58	46.56	
	Copper	78.75	49.98	
C2	Oxygen	21.99	52.83	0.894
	Copper	78.01	47.17	

CONCLUSION

CuO thin films were successfully deposited by the chemical bath deposition method at 70 °C and further modified through post-air annealing at 450 °C. XRD analysis confirmed the formation of single-phase monoclinic CuO and revealed significant enhancement in crystallinity after annealing, accompanied by an increase in crystallite size and a reduction in lattice defects. Raman studies further supported the improved structural quality through the appearance of sharper and more intense characteristic CuO vibrational modes. SEM observations demonstrated thermally induced grain growth, with the average particle size increasing from about 33 nm to 43 nm and the film surface becoming more compact and homogeneous. EDS analysis verified the presence of Cu and O elements and indicated improved stoichiometry and oxidation after annealing. Overall, post-air annealing at 450 °C effectively enhances the crystallinity, morphology, and compositional uniformity of CBD-grown CuO thin films. These improvements suggest that air-annealed CuO films are suitable for advanced applications in optoelectronic devices, gas sensors, and energy-related technologies.

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