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EFFECT OF PROCESS PARAMETERS AND SUBSTRATE MATERIAL ON OPTO-STRUCTURAL PROPERTIES OF CuO THIN FILM PREPARED FOLLOWING SOL-GEL SPIN COATING TECHNIQUE

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Abstract

Sol-gel spin coating is one of the finest facile techniques for thin films fabrication. Process parameter optimization is essential and incredibly crucial for quality thin films preparation. In this study, single phase monoclinic CuO thin films were prepared following sol-gel spin coating technique, and the process parameters were optimized. Here, the effect of solution spreading mode (static and dynamic) on substrate, rotation speed of spin coater and annealing temperature variation on film quality along with opto-structural properties of the films were investigated thoroughly. A remarkable effect of substrate type (soda-lime-silica, borosilicate, and quartz) on thin films structure has also been reported where soda-lime-silica substrate contaminated thin films and other two seems to be reasonably good. Finally, uniform CuO thin films were prepared on quartz substrate in static spin coating mode following two-step spin coating technique and by annealing at the optimized temperature of 500°C for one hour in a tube furnace. Opto-structural properties i.e., phase purity, crystallinity, crystallite size, transmittance and optical band gap of the films were characterized using X-ray diffraction (XRD) and ultraviolet visible spectroscopy (UV-Vis). For annealing temperature of 500°C at 1h on quartz substrate for static mode, single phase CuO films were prepared successfully having maximum crystallinity of 88.23% and minimum band gap of 1.98 eV.

Keywords: Sol-gel, Spin coating, Substrate, Band gap, Opto-structural.

1. Introduction

Cuprous oxide (Cu_2O) and cupric oxide (CuO) are the two stable phases of copper oxide. CuO is classified as a direct bandgap p-type semiconductor material [1].In recent years, CuO thin films are used in various applications e.g., solar cells, gas sensing devices, magnetic storage media, photocatalytic applications [2]. Among various synthesis routes, sol-gel spin coating has certain advantages over other processing techniques like simple setup, cost effectiveness, low processing temperature, and uniform coating. In this method, several crucial parameters including spin speed, spin time, solution viscosity, and substrate type control the characteristics of thin films [3]. These parameters affect the uniformity of film on the substrate. Annealing temperature is a major factor among these factors for sol-gel spin coating route. Phases present, crystallite size, crystallinity, film thickness, band gap of the films depends on annealing temperature to a great extent. A high-quality epitaxial film demands the use of a substrate that exhibits exceptional lattice matching, precise orientation, and little thermal expansion [4].

Here in this study, precursor solution was prepared by sol-gel route, and thin films were made by spin-coating onto various substrates (soda-lime-silica, borosilicate, and quartz). In additional, here authors explored the effects of solution spreading mode (static and dynamic) on substrate, rotation speed of spin coater and annealing temperature variation on the opto-structural properties of the thin films. Accordingly, thin films were characterized using X-ray diffraction and ultraviolet visible spectroscopy (UV-Vis).

2. Experimental Details

2.1 Materials

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Copper acetate monohydrate [Cu $(CH_3COO)_2$. H_2O], isopropanol [$(CH_3)_2CHOH$] and monoethanolamine (MEA) [$C_2H_7O_7$] were used as solute, solvent, and stabilizer respectively for solution preparation. Soda-lime-silica, borosilicate and quartz glass slides were used as substrate material.

2.2 Thin Films Synthesis

0.2 M copper acetate monohydrate was dissolved in isopropanol and stirred at the speed of 400 rpm at room temperature. After 15 minutes, MEA was added dropwise with continued stirring for the next 30 minutes at 60°C. 25 mm by 25 mm soda-lime-silica glass and 20 mm by 20 mm borosilicate glass substrates were prepared for film deposition. Cleaning procedure of the glass substrates consisted of five steps and were cleaned successively with detergent, deionized water, acetone, ethanol, and deionized water using ultrasonic cleaning bath. For film deposition process, static spin coating with two-step spinning as well as dynamic spin coating technique were used individually. For static mode, a rotational speed of 250 rpm for initial 10 seconds and 2000 rpm was used for later 30 seconds. Similar rotational parameters were used for dynamic mode as well. After deposition, five layered thin films were made, where each layer was dried for 10 minutes at 100°C temperature. Finally, the films were annealed at 200, 300, 400, and 500°C temperatures respectively for 1 hour using heating rate of 10°C/min using a Nabertherm tube furnace.

3. Characterization

Structure and phase of the thin films were examined using Rigaku X-ray diffractometer [SmartLab SE] with Cu $K_{\alpha 1}$ radiation of 0.15406 nm wavelength for Bragg's angle (2θ) range from 25 to 80° at 10°/min scanning rate. Crystallite size and micro strain were calculated from XRD analysis. Transmittance and absorbance spectra were measured with PerkinElmer Lambda 365 spectrometer and direct band gap was calculated from the absorbance spectra using Tauc's formula.

4. Results and Discussion

4.1 Effect of Solution Spreading Mode and Rotation Speed of Spin Coater

Solution spreading mode and rotation speed of the spin coater significantly controlled thin film uniformity. Rotation speed was optimized on trial-and-error basis. To achieve homogeneous solution spreading, both dynamic (Fig 1) and static modes (Fig 2) were attempted on quartz substrates and eventually later one showed superior spreading characteristics on the underlying substrates. This can be attributed to the more controlled surface nucleation and growth of crystals for static mode. Absence of substrate motion resulted in minimum strain in films; consequently, films were rather homogeneous and uniform. Lower rotational speed in initial stage at less than 500 rpm is frequently employed, as it ensures even dispersion throughout the film and reduce the amount of unused solution due to enhanced wetting characteristics. Moreover, two-stage solution spreading mode is advisable to prevent edge beads and voids in thin films. Therefore, static mode was selected for the subsequent film preparation.

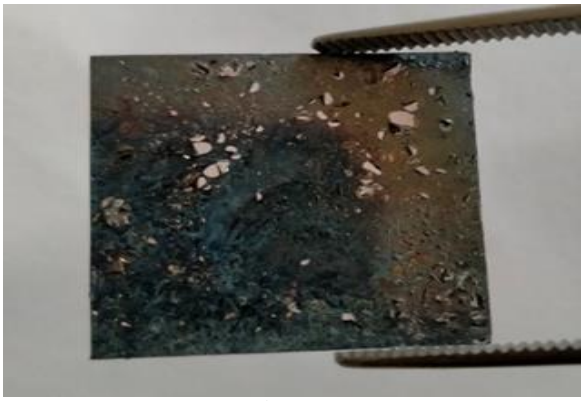

Fig 1: Film for dynamic mode.

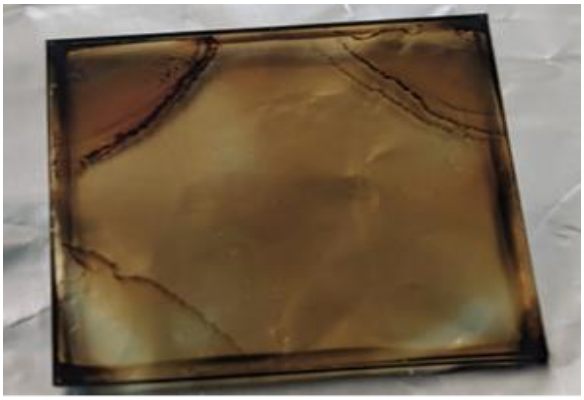

Fig 2: Film for static mode.

4.2 Structural Analysis

All the films were annealed at 200 to 500°C at 100°C interval for 1 h on quartz substrates. Prominent diffraction peaks in the normalised XRD spectra for annealing temperatures of 300, 400, and 500°C at 30.2°, 35.2°, and 38.6° for (110), (002), and (111) planes respectively verified the well-crystalline monoclinic structure of CuO thin films (JCPDS 48–1548) as shown in Fig 3. Peak intensities increased with increasing annealing temperature, and at 500°C, maximum intensity was observed revealing greater crystallinity with an increase in annealing temperature. XRD pattern for 200°C showed peaks at 43.3 and 61° for (200) and (220) planes that confirmed Cu_2O cubic structure (JCPDS 05-0667) as well as the peak at 50.5° for (200) plane verified the presence of

metallic copper. Diffusion of oxygen was facilitated at higher temperature facilitating the reaction $2Cu_2O + O_2 \rightarrow 4CuO$, as usually reported for temperature above 300°C [5].

From XRD data, crystallite size was measured using Debye-Scherer formula:

$$D(nm) = \frac{.9\lambda}{\beta cos\theta};$$

here, λ represents wavelength of X-ray radiation (1.5406 Å), β is full width at half maximum (FWHM), and θ is the diffraction angle. At 200°C, average crystallite size of Cu_2O was 9.5 nm and crystallite size increased up to 19.45 nm for CuO phase at 500°C. Slower growth rate of the copper oxide film resulted in such smaller crystallite size [6].

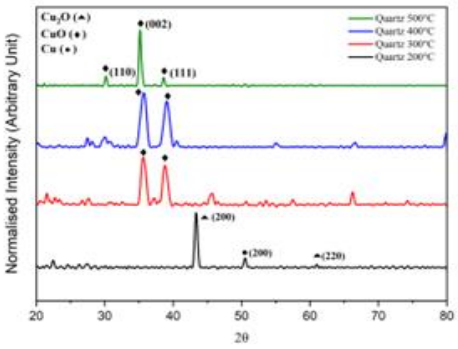

Fig 3: Normalised XRD spectra.

The W-H plot was used to calculate micro-strain (ε). From linear fit, slope of $\beta_{hkl}\cos\theta$ vs $4\sin\theta$ plot gave the micro-strain which is defined as $\varepsilon = \frac{\beta cos\theta}{4sin\theta}$; here, β is the full width at half maximum (FWHM) in radian. Reducing strain with increasing annealing temperature indicates a decrease in lattice imperfections by reduction of residual stress at higher annealing temperature (Table 1). To achieve such strain-relaxation, effectiveness of grain boundaries as sources and sinks for vacancies is considered as the key factor. Furthermore, these high-quality CuO thin films also showed better crystallinity with lower micro-strain [7].

Table 1. Crystallite size, crystallinity, micro-strain, and band gap with varying annealing temperature.

Annealing Temperature (°C)	Crystallite Size, D (nm)	Crystallinity (%)	Micro-Strain (ε)	Band Gap (eV)
200	9.50	46.87	-5.96×10^{-3}	2.39
300	12.55	68.13	4.72×10^{-2}	2.02
400	15.32	75.27	1.88×10^{-2}	1.99
500	19.45	88.23	1.09×10^{-3}	1.98

4.3 Optical Properties

As Fig 4 shows, all the films showed significant transparency between 850 and 1100 nm and transmittance dropped rapidly due to fundamental absorption between 600 and 850 nm [8] Direct band gap was calculated using Tauc's plot: $(\alpha h\nu)^2 = A(h\nu - E_g)$, here h, ν, and E_g are Planck's constant, wavelength, and direct band gap, respectively. Band gap values exhibited a gradual decrease with increasing annealing temperature (Fig 5). Thin films annealed at 200°C showed maximum band gap of 2.39 eV and at 500°C exhibited minimum band gap of 1.98 eV. This reduction can be attributed to the lower concentration of imperfections in lattice sites due to higher annealing temperature and larger crystallite size. With increasing annealing temperature, amount of amorphous phase decreased as more energy facilitated the crystallite growth [9]. The maximum crystallite size of 19.45 nm, and crystallinity of 88.23% were obtained for 500°C annealing temperature, which produced the best results.

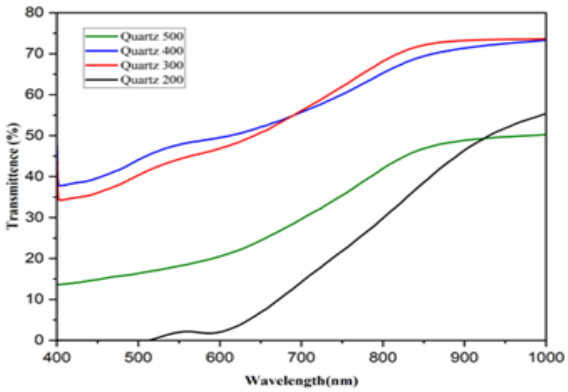

Fig 4: Transmission Spectra.

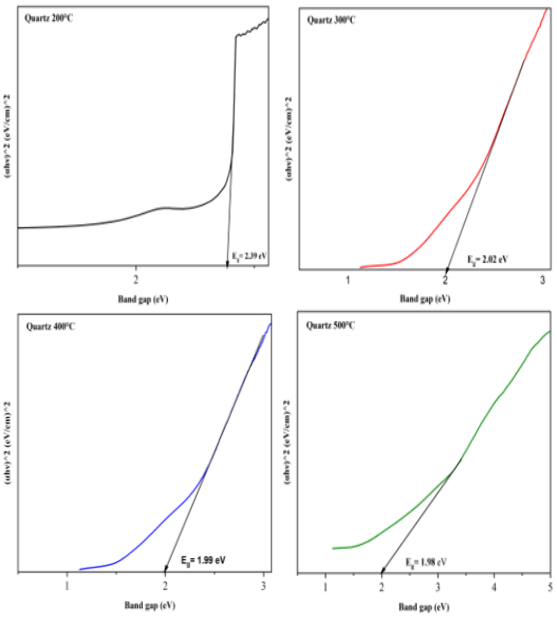

Fig 5: Tauc's plot for band gap estimation.

4.4 Effect of Substrate

For optimized parameters, thin films were deposited on three different (soda-lime-silica, borosilicate, and quartz) glass substrates and XRD was performed to analyse the phase structure. Diffraction peaks for quartz substrate appeared at 30.2, 35.2 and 38.6° for (110), (002) and (111) planes respectively verifying the monoclinic structure of CuO (Fig 6).

Similarly, diffraction peaks for borosilicate substrate appeared prominently at 32.64, 35.66 and 38.86° for (110), (002) and (111) planes respectively. On the other hand, a strong crystalline peak was observed at around 31° overlapping the peak for (110) plane for the film deposited on soda-lime-silica glass substrate).

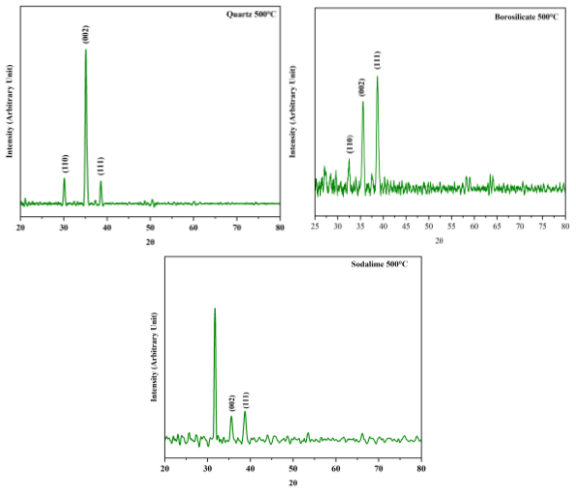

Fig 6: XRD spectra for thin films on various substrates.

The extra peak can be attributed to the leaching of soda-lime glass substrates since for high temperature annealing, elements (Na, Ca, Mg, Al, Si, F) from soda-lime-glass substrate can diffuse or leach into CuO thin film and contaminate. The current study illustrates such contamination of thin films and indicates the challenge of using widely available, low-cost glass substrate [10]. However, quartz substrates showed better structural stability for higher annealing temperature.

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