

Gas Sensing Behaviour of Fe-Doped CuO Thin Films with Structural, Morphological and Optical Insights

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Abstract

In the present work, pure and Fe-doped CuO thin films were deposited on glass substrates by the spray pyrolysis technique to investigate the effect of Fe incorporation on their structural, morphological, optical, and H₂ gas sensing properties. XRD analysis confirmed the formation of monoclinic CuO without detectable secondary phases, while FESEM revealed significant morphological changes with Fe doping, including improved grain distribution and surface compactness. UV-visible analysis showed a variation in the optical band gap from 1.82 to 1.94 eV, indicating modifications in the electronic structure due to Fe incorporation. Gas sensing measurements demonstrated a significant enhancement in H₂ sensing performance, with the optimized Fe-doped CuO film exhibiting a maximum response of approximately 63%. The improved sensing behavior is attributed to Fe-induced modifications in crystallinity, surface morphology, defect states, and carrier-related properties, which enhance the interaction of H₂ molecules with the CuO surface. Overall, the results demonstrate that Fe incorporation effectively tailors the properties of CuO and improves its suitability for metal-oxide-based H₂ gas sensing applications.

Keywords: CuO, Fe, Spray pyrolysis, Thin film, XRD, FE-SEM, Gas sensing.

Introduction

Transition metal oxide semiconductors have become an important class of functional materials because of their excellent chemical and structural stability, adjustable electronic characteristics, and diverse potential for technological applications [1–3]. Within this group, copper oxide (CuO) is a particularly interesting p-type semiconductor, characterized by a relatively narrow band gap of approximately 1.5-2.2 eV, good chemical durability, low toxicity, and economic feasibility [4–7]. These inherent characteristics have encouraged extensive research on CuO for a variety of applications, including gas detection, heterogeneous catalysis, energy-storage systems, photovoltaic devices, antimicrobial surfaces, and optoelectronic technologies [8].

The properties of CuO are strongly dependent on its composition and microstructural features, which can be effectively regulated through the incorporation of foreign dopant species. Doping with transition metal ions is one of the promising approaches for controlling the structural arrangement, charge-transport behavior, optical response, and sensing performance of CuO-based thin films. Iron is particularly suitable as a dopant for CuO because the ionic size of Fe ions is relatively close to that of Cu²⁺, facilitating their incorporation at copper sites within the host lattice while minimizing substantial lattice deformation [9]. In addition to the choice of dopant, the method employed for thin-film fabrication plays a crucial role in determining the resulting film characteristics. Among the available deposition techniques, spray pyrolysis offers several advantages, including simple experimental requirements, low production cost, ease of scale-up, and the capability of producing films over comparatively large substrate areas. Moreover, important film parameters such as thickness, chemical composition, and surface texture can be regulated by controlling experimental variables including precursor concentration, substrate temperature, and spraying conditions [10].

Based on these considerations, the present investigation focuses on the preparation of CuO thin films containing different concentrations of Fe using the spray pyrolysis method. Particular emphasis is placed on understanding how the incorporation of Fe modifies the structural and surface morphological characteristics of the resulting films. The study is intended to establish a clearer relationship between Fe incorporation and the microstructural evolution of CuO, thereby

contributing to a better understanding of its potential for functional applications, particularly in sensing and optoelectronic technologies [11,12].

Experimental and methods

Materials

Copper (II) acetate monohydrate $(\text{CH}_3\text{OOH})_2\text{Cu}\cdot\text{H}_2\text{O}$ and ferrous acetate tetrahydrate $(\text{Fe}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O})$ ~99.00% purity, AR grade were treated as host and dopant precursors, procured from SD fine-chem. Ltd. India. Glass slides with dimension 75*25*1.35 mm from blue-star was used. For cleaning purpose, chromic trioxide and acetone were purchased from Global Nanotech, India. Before deposition, glass slides were cleaned with labolene and washed under running tap water. After drying, slides were dipped in chromic trioxide solution which is boiled at 175°C for 2 hours. Then slides are washed with Distilled water and kept for ultrasonic cleaning for 30 mins in the solution of acetone and Deionized water in 1:3 ratio. After using a dryer, slides become ready to use. Pure and Fe doped CuO (7 %) thin film preparation is carried out on soda lime glass substrate using spray pyrolysis setup. For host precursor, 0.1 m of copper acetate was added to 20 ml of DDW and stirred until a homogeneous solution was formed. Then this precursor solution is sprayed onto a glass substrate. Similarly, Dopant precursor solution is formed by mixing Cobalt acetate 0.1 molar into 20 ml DDW and added drop-wise into host precursor solution, to achieve desired doping concentrations. Characterization techniques were employed to investigate the structural, morphological, optical, and functional properties of the synthesized samples. The structural properties were analyzed using X-ray diffraction (Ultima IV, Rigaku, Japan) with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) in the 2θ range of 20–80°. Morphological features such as grain size and surface texture were examined using Field Emission Scanning Electron Microscopy (FE-SEM, SUPRA55, Zeiss).

Results and Discussion

XRD analysis

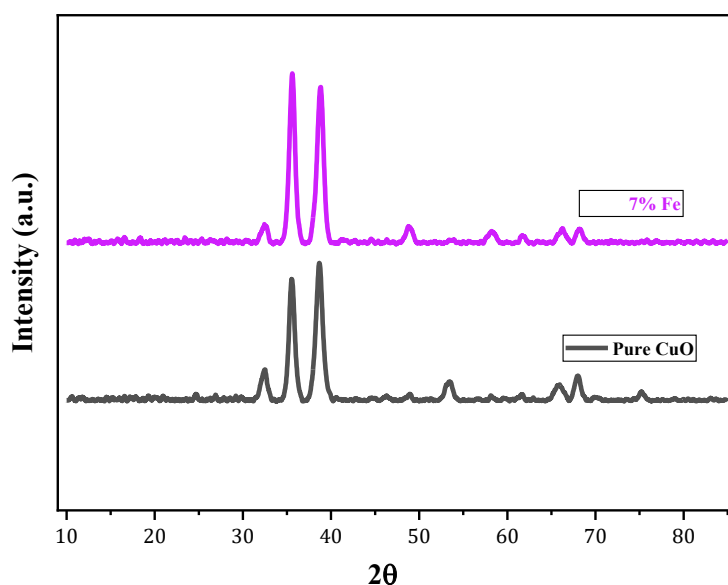


Figure 2: XRD pattern of CuO and Fe doped CuO thin films.

The crystalline structure of the Fe-incorporated CuO thin films was examined by X-ray diffraction (XRD) using Cu K α radiation within the 2θ range of 20°–80°. Figure 2 illustrates the diffraction profiles obtained for the undoped CuO and 7% Fe-doped CuO films prepared by spray pyrolysis. In both samples, distinct diffraction reflections are observed around 32.2°, 35.5°, 38.7°, 49.2°, and 61.6°, which can be attributed to the characteristic crystalline planes of CuO [13–16].

The presence of distinct and relatively intense reflections indicates the formation of a well-crystallized CuO phase. The positions of the detected peaks correspond closely to the characteristic reflections reported for monoclinic CuO, confirming the formation of the desired crystalline phase. Furthermore, no additional diffraction reflections associated with secondary or impurity phases are detected within the investigated angular range. The experimental

patterns are in good agreement with the reference diffraction data given by JCPDS card No. 48-1548 for monoclinic CuO [17].

Comparison of the diffraction patterns of pristine and Fe-doped CuO reveals that the fundamental monoclinic structure of CuO is retained following Fe incorporation. However, a noticeable variation in the relative intensity and/or sharpness of the diffraction reflections suggests that Fe addition has a measurable effect on the degree of crystallinity and crystal growth of the deposited films. Thus, the XRD results indicate that Fe can be incorporated into the CuO system while largely preserving its parent crystal structure.

FESEM analysis

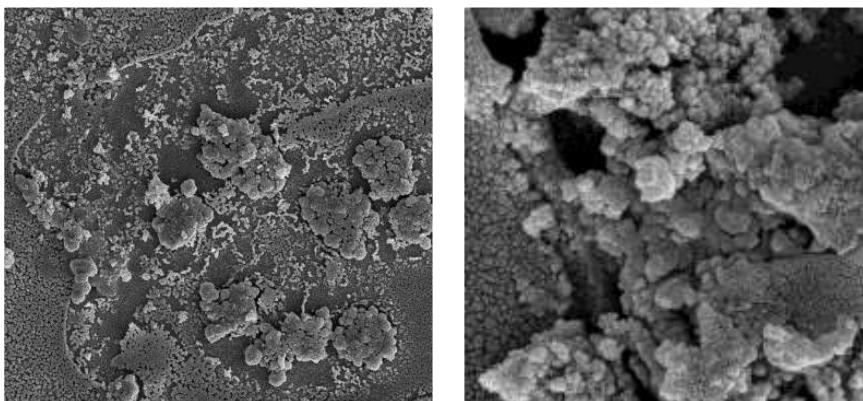


Figure 3: FE-SEM of CuO and Fe doped CuO thin films.

The surface characteristics of the synthesized CuO thin films were examined by field-emission scanning electron microscopy (FE-SEM). The corresponding micrographs of pristine CuO and CuO containing 7% Fe, deposited through the spray pyrolysis route, are shown in Figure 3. A clear variation in the surface morphology is observed upon the introduction of Fe into the CuO matrix, demonstrating the significant influence of doping on the film growth process. The undoped CuO film presents a relatively smooth but non-uniform surface, characterized by randomly distributed grains and the occurrence of fine cracks. The appearance of these surface cracks can be associated with the development of residual stresses during deposition, followed by thermal contraction during the cooling stage [18]. The grain arrangement in the pristine film also suggests that the nucleation and subsequent growth of CuO crystallites are comparatively less homogeneous.

A pronounced morphological evolution is observed after incorporating 7% Fe into the CuO lattice. The doped film exhibits predominantly spherical and clearly distinguishable grains, which are distributed more uniformly across the substrate. Compared with the pristine sample, the Fe-doped film shows a more compact surface with improved grain packing and considerably reduced surface cracking [19]. Such changes suggest that the presence of Fe influences the nucleation kinetics and subsequent crystallite growth during film formation, resulting in a more homogeneous microstructure [20].

The development of spherical grain features may further indicate enhanced grain coalescence and improved utilization of the available substrate surface [21]. Thus, the FE-SEM observations demonstrate that Fe incorporation substantially modifies the surface morphology and growth behavior of CuO thin films. The morphological features observed for the Fe-doped sample are consistent with the changes identified from the XRD analysis, supporting the influence of Fe incorporation on the crystallographic growth of CuO. Importantly, no distinct morphological or structural evidence of an additional secondary phase is observed, indicating that Fe incorporation occurs without significant alteration of the CuO host phase.

UV visible

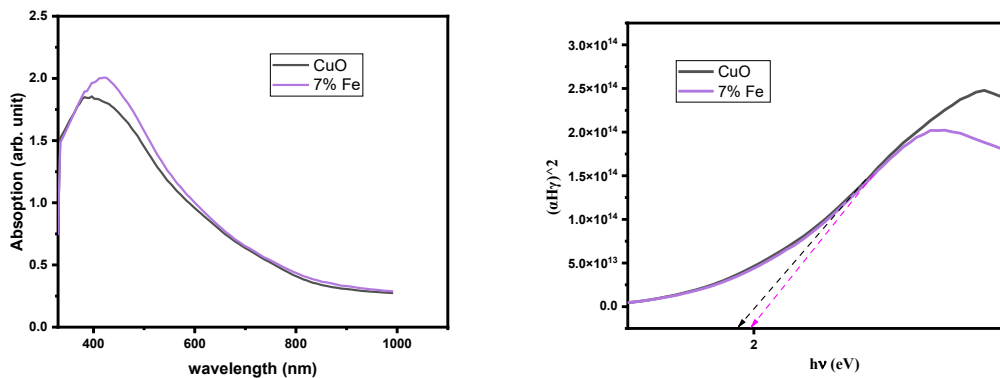


Figure 4: Absorption and Tau plot of CuO and Fe doped CuO thin films.

The optical transmittance spectra of pristine and Fe-doped CuO thin films were recorded in the wavelength range of 300–1000 nm using UV–Visible spectroscopy. Figure X shows the transmittance spectra of the prepared films. The pristine CuO film exhibits comparatively higher transmittance, while Fe incorporation leads to a reduction in optical transparency. This decrease in transmittance can be attributed to enhanced light absorption and scattering resulting from Fe-induced modifications in crystallite size, surface morphology, defect concentration, and optical density of the films [22]. The incorporation of Fe alters the nucleation and growth behavior of CuO crystallites, thereby modifying the interaction of incident radiation with the film surface. The resulting structural and morphological changes contribute to increased scattering and absorption, particularly at higher Fe concentrations.

The optical band-gap energy of the prepared films was determined from the absorption data using the Tauc relation, and the band-gap value was obtained by extrapolating the linear portion of the corresponding plot to the energy axis which is 1.84 eV and 1.93 eV for CuO and Fe doped CuO, respectively. The variation in band-gap energy with Fe concentration indicates that Fe incorporation modifies the electronic structure of CuO. This change may be associated with variations in carrier concentration, lattice disorder, defect states, and the local electronic environment produced by Fe incorporation [23]. Thus, the observed changes in optical transmittance and band-gap energy demonstrate that Fe doping provides an effective approach for tuning the optical and electronic properties of CuO thin films.

Gas sensing study

Gas sensing measurement were conducted by placing the prepared thin films into a sealed chamber and assessing its electrical resistance with a source meter under regulated conditions. A known concentration of hydrogen gas (25 ppm) was introduced into the chamber, and the dynamic change in resistance was recorded during exposure and subsequent purging with air. The response and recovery characteristics were analysed using the transient resistance curves to evaluate the sensing performance.

The CuO sensor's P-type semiconductor sensing mechanism is described in Fig. 5. It occurs in two phases: reduction and oxidation. Like the N-type semiconductor sensor, a hole-accumulation layer is created when atmospheric oxygen combines with metal oxide electrons. When the target gas strikes the sensor in the second step, the adsorbed electrons are returned to the metal oxide. These electrons eventually lower the charge concentration and raise the resistance when they mix with the hole in the accumulation. The response of the films was calculated using relation [24].

$$S = \frac{R_g - R_s}{R_a} \dots\dots\dots(6)$$

Where R_g and R_s is resistance of films in presence of target gas and air respectively.

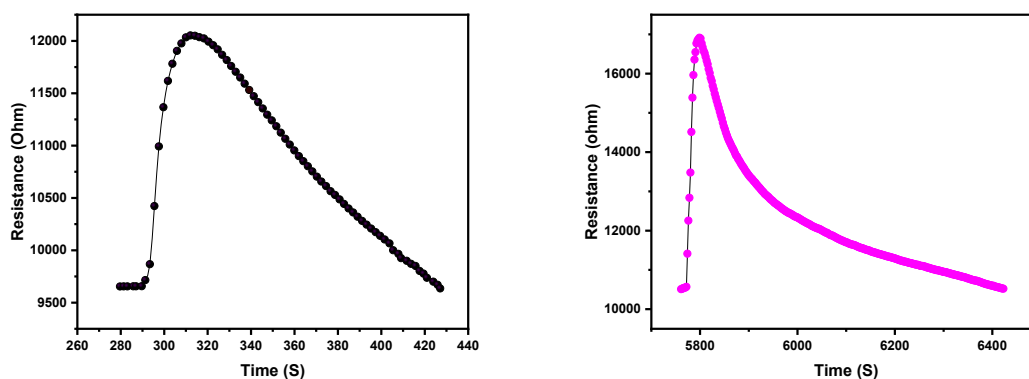


Fig. 7: The gas response of undoped and Fe-doped CuO thin films toward 25 ppm H_2 .

The dynamic sensing characteristics of the Fe-doped CuO thin film toward 25 ppm H_2 gas were investigated at an operating temperature of 300 °C [25]. The observed transient response clearly demonstrates the influence of Fe incorporation on the hydrogen-sensing behavior of CuO. As CuO is a p-type semiconductor, its electrical resistance increases upon exposure to hydrogen. This behavior can be explained by the interaction of H_2 molecules with chemisorbed oxygen species present on the film surface. During the initial exposure to air, oxygen molecules adsorb onto the CuO surface and capture electrons from the semiconductor, thereby increasing the hole concentration [26]. When H_2 is introduced, it reacts with the adsorbed oxygen species and releases the trapped electrons back into the sensing layer. The resulting electron–hole recombination decreases the hole concentration, leading to an increase in the resistance of the p-type CuO film [27].

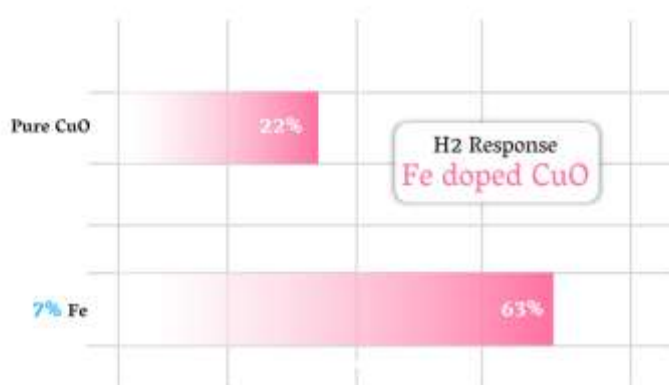


Fig. 7: Graphical gas response of CuO and Fe-doped CuO thin films toward 25 ppm H_2 .

The 7% Fe-doped CuO thin film exhibits a pronounced resistance variation upon exposure to 25 ppm H_2 , demonstrating its improved interaction with the target gas. A maximum gas response of approximately 63% is obtained at 300 °C. The enhanced sensing behavior can be associated with the incorporation of Fe ions into the CuO lattice, which modifies the surface and electronic properties of the host material. Fe incorporation can influence the defect concentration, carrier density, and adsorption characteristics of the CuO surface, thereby providing a greater number of energetically favorable sites for oxygen and hydrogen adsorption [28].

The pronounced transient response observed for the 7% Fe-doped CuO film indicates effective gas adsorption and surface reaction processes at the selected operating temperature. The elevated temperature facilitates the activation of surface reactions between hydrogen molecules and chemisorbed oxygen species, resulting in a substantial change in electrical resistance [29]. The improved sensing response may also be related to modifications in the microstructure produced by Fe incorporation, as observed from the structural and morphological investigations. The altered grain structure and surface characteristics can provide enhanced interaction between the sensing surface and H_2 molecules [30-32].

Thus, the obtained response of approximately 63% toward 25 ppm H₂ at 300 °C confirms that Fe incorporation significantly improves the hydrogen-sensing characteristics of CuO thin films. The results demonstrate the potential of Fe-doped CuO as an effective sensing material for hydrogen detection.

Results and discussion

In the present study, Fe-doped CuO thin films were successfully deposited by the spray pyrolysis technique, and their structural, morphological, optical, and gas sensing properties were systematically investigated. XRD analysis confirmed the formation of monoclinic CuO with improved crystallinity after Fe incorporation, without the formation of secondary phases. FE-SEM analysis revealed significant morphological modifications, with Fe doping leading to a more uniform and compact surface with well-defined grains. The UV study indicates an improved band gap by 0.9 eV. These structural, morphological and optical changes contributed to the improved gas sensing performance of the films. The Fe-doped CuO thin films exhibited an enhanced response toward H₂ gas, with a maximum gas response of 63%. The improved sensing behaviour can be attributed to Fe-induced modifications in the surface morphology, grain structure, and active surface sites, which enhance the interaction between the sensing layer and H₂ molecules. Thus, Fe incorporation is an effective approach for tailoring the properties of CuO thin films and improving their potential for H₂ gas sensor applications.

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