

Structural and Optical Properties of P-Type Cuprous Oxide (P-Cu₂O) Thin Films Prepared by Chemical Deposition

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Received: February 23, 2026; Accepted: March 02, 2026; Published: March 8, 2026

ABSTRACT

In the presented paper, p-type cuprous oxide (p-Cu₂O) thin films of various thicknesses ($d = 2 \mu\text{m}$; $3 \mu\text{m}$ and $5 \mu\text{m}$) were obtained by chemical deposition method. The mechanisms of the influence of the thickness of the obtained p-Cu₂O thin films on the optical transmission and absorption spectra were analyzed. A systematic red shift of the fundamental optical absorption edge toward lower photon energies, within the range of $E = 0.37\text{--}0.44 \text{ eV}$, has been observed with increasing sample thickness. This phenomenon is primarily attributed to the enhancement of crystalline quality, accompanied by a reduction in the density of surface defects and a suppression of sub-bandgap optical transitions associated with localized defect states.

Keywords: Debye Diffraction Pattern, Face-Centered Cubic, Absorption Edge

Introduction

The development of nanotechnology and solar energy has led to increased interest in thin films of semiconductor materials [1,2]. This has spurred the search for new composite materials for energy storage applications [3]. Thin films inherently possess a high degree of defectiveness, which is attributed to their non-equilibrium nature, the extensive boundaries of crystallites, and a significant proportion of surface states. New studies show that, Cu₂O thin film covering on a carbon network has flexible composite characteristics [4]. It was proven in the mentioned article that, P-type Cu₂O thin film with dominated (111) orientation was successfully deposited on the surface of the carbon network via an electrochemical method [4]. On the other hand, in p-Cu₂O/ZnO/AZO flexible heterojunction solar cell was prepared by electrodeposition of Cu₂O thin film on a plastic substrate and sputtering of ZnO:Al layer [5]. As a result of the experiments conducted, it was determined that such the solar

cell device exhibits a power conversion efficiency of $0.897 \pm 0.005\%$ [5]. So, mentioned approach to fabricate a flexible solar cell is promising for fabrication flexible and also cost solar cells. Research into nanocrystalline materials based on transition metal oxides indicates that their specific properties are linked to the manifestation of the quantum size effect [6]. Studies show that the production technology of cuprous oxide (Cu₂O) thin films and the thickness of these films significantly affect the efficient energy conversion of solar cells based on them [7]. It has been established that the surface of a thin films obtained by various deposition methods and having only a certain optimal thickness has an ideal morphological structure without pinholes, and also leads to the most efficient energy conversion in solar cells [7]. Based on the analysis of numerous articles, it was concluded that by varying the thickness of thin films based on p-type cuprous oxide (p-Cu₂O) using various deposition technologies, it is possible to purposefully control the optical band gap (E_g) and analyze its physical mechanisms, which is necessary both from a scientific point of view and to determine the possibilities of successful application of these films in solar cells. The aim of

the presented article is to investigate the physical mechanisms of the correlation between the fundamental optical absorption edge of p-type cuprous oxide (p-Cu₂O) thin films obtained by the chemical deposition method and the thickness of films and also their application possibilities in solar cells.

Experiment

The objective of this work was to obtain high-quality, thin films of the transition metal oxide (Cu) - Cu₂O - with practically unlimited area, using a relatively inexpensive and simple technology. We also aimed to investigate the structure and optical absorption and transmission spectra of these films in the region of the fundamental absorption edge. Transmission and absorption spectra were measured using a Hitachi-557 spectrometer at room temperature. Typically, the specific properties of nanocrystalline materials derived from a broad class of initial crystalline systems are primarily linked to the manifestation of the size effect. It should also be noted that real nanocrystalline materials are highly defective, with defect concentrations significantly greater than those in equilibrium mono- and polycrystals. This factor is determined not only by the method and conditions of material preparation but also by the specifics of their electronic structure. p-Cu₂O thin films were obtained using the chemical deposition method. The Debyeogram of cuprous oxide films was taken with a Debye-Scherrer X-ray camera at specific parameters: Radiation: CuK α ($\lambda = 1.5418 \text{ \AA}$), Filter: Ni, 55 kV, 14 mA, Exp. 16 h. The chemical deposition method allows for the preparation of thin Cu₂O films on any type of substrate that is unreactive with the solutions. For the deposition of Cu₂O films glass plates made from photographic plates were used. These plates were pre-cleaned with a mixture of chromic and sulfuric acid (chromic acid mixture), then thoroughly rinsed in distilled water, dried, and degassed. The choice of this substrate for deposition is not accidental, as photographic plates have good polishing; compared to other substrates, the orientation and structure of films deposited on them are less defective. For the deposition of p-Cu₂O films, two solutions, A and B, were used. Solution A consists of 100 cm³ of 1M CuSO₄ solution and 400 cm³ of 1M Na₂S₂O₃ solution, which is added to the CuSO₄

solution until it becomes colorless. This process yields a complex solution of 3Cu₂S₂O₃·2Na₂S₂O₃, which is then diluted to 1000 cm³. Solution A easily decomposes, so film deposition should be performed with a fresh solution. Solution B consists of 2M NaOH, heated to 60-80°C. Cleaned glass substrates are first immersed in solution B, held there for 1-2 seconds, and then immersed in solution A. This entire procedure is then repeated. After 3-5 consecutive immersions, a visible yellow deposited film becomes apparent on both sides of the glass. With further immersions, the film turns orange, and then brown. The film thickness is proportional to the number of consecutive immersions; for the given solution concentrations, every ten immersions result in a 0.1 μm increase in film thickness. Depending on the number of immersions, the thickness of the obtained films reached up to 5 μm . The films had a yellow-brown color.

Results and Discussions

Figure.1 Illustrates the Debye Diffraction Pattern of p-type Cu₂O Thin Films Obtained via Chemical Deposition.

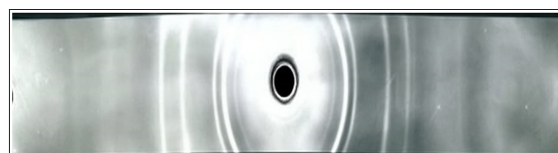


Figure 1: Debye Diffraction Pattern Of P-Type Cu₂O Thin Films Prepared by Chemical Deposition Method

The pattern reveals six distinct diffraction rings corresponding to 2θ angles of $14^{\circ}42'$, $18^{\circ}12'$, $21^{\circ}00'$, $30^{\circ}36'$, $36^{\circ}36'$, and $38^{\circ}36'$. Among these, the ring at $2\theta = 18^{\circ}12'$ exhibits the highest intensity and is attributed to the (111) crystallographic plane of face-centered cubic (FCC). The calculated lattice parameter for Cu₂O p is 4.2797 \AA , which is in good agreement with values reported for Cu₂O synthesized through high-temperature oxidation methods, indicating the reliability and structural integrity of the chemically deposited films. The corresponding diffraction data and calculated structural parameters derived from the Debye pattern are summarized in Table 1.

Table 1: Result According to the Debye Pattern: (2θ)-the Angle Between the Incident X-ray Beam and Reflected, (J/J_0)-Ratio of Scattering Intensities (d)-Distance Between Planes for a Cubic Crystal, (hkl)-Miller Indices

Experimental Data						
	2θ	$\sin 2\theta$	J/J_0	d	hkl	Lattice parameter
1.	$14^{\circ}42'$	0.2538	3	3.0374	110	4.2797 \AA
2.	$18^{\circ}12'$	0.3123	10	2.4685	111	
3.	$21^{\circ}00'$	0.3584	8	2.1509	200	
4.	$30^{\circ}36'$	0.5090	7	1.5145	220	
5.	$36^{\circ}36'$	0.5962	5	1.2930	311	
6.	$38^{\circ}36'$	0.6239	2	1.2356	222	

X-ray phase analysis of Cu₂O films prepared by chemical deposition confirmed their identity with the single-phase composition of polycrystalline cuprous oxide Cu₂O obtained via high-temperature oxidation. Fig.2 shows the optical absorption spectra of p-Cu₂O thin films of various thicknesses obtained by chemical deposition.

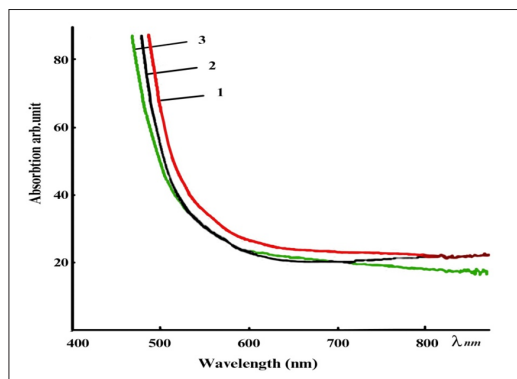


Figure 2: Absorption Spectra of p-Cu₂O Films of Various Thicknesses Obtained by Chemical Deposition: 1-5 μm ; 2-3 μm ; 3-2 μm .

As seen in Figure 2, the absorption edge of thin p-Cu₂O films is shifted towards shorter wavelengths compared to the band gap (E_g) for single-crystal Cu₂O [8,9]. On the other hand, the “red shift” of the optical absorption edge is observed as a result of the increase in thickness of sample. The experiment shows that, in samples of p-Cu₂O with a smaller thickness, a more noticeable red shift of the optical absorption edge occurs. As a result of the analysis of optical absorption spectra (Figure.2), it is concluded that at relatively small thicknesses, a $\sim d=3 \mu\text{m}$ decrease in thickness causes the fundamental absorption edge to shift towards higher energies by about $\sim 0.08 \text{ eV}$. However, the results of optical experiments conducted on polycrystalline p-Cu₂O films of relatively large thickness prove that the opposite result is observed [10]. Thus, in the absorption spectra of polycrystalline p-Cu₂O ($d=238\mu\text{m}, 268\mu\text{m}$) obtained by our high-temperature oxidation method, a slight shift of the absorption edge from 1.985 eV to 1.988 eV was also observed [10]. Studies also show that the above-mentioned results are also significantly affected by the method of obtaining thin films samples. That is, in the case of thin fine-grained p-Cu₂O films obtained by chemical means, the absorption edge is located at higher energies compared to polycrystalline p-Cu₂O obtained by high-temperature oxidation, specifically $2.36 \div 2.44 \text{ eV}$. Furthermore, with decreasing film thickness for samples 1, 2, and 3, the absorption edge shifts by approximately 0.08 eV towards higher energies (Figure.2). A comparable shift with nanocrystalline n-Cu₂O obtained by gas-phase condensation of metal (copper) vapor indicates the high quality of our chemically prepared films. This is further supported by X-ray phase data confirming their identity with single-phase samples obtained via high-temperature oxidation [10]. As the thickness of p-Cu₂O films decreases to $d=2\mu\text{m}$, transmittance increases, meaning the films become more transparent. This is crucial for their practical application as selective coatings and as the upper optical window in solar converters [11]. As evident from Figure 3, with decreasing film thickness, the transparency of the films increases up to 60%, and the transmission edge also shifts towards higher energies. Various approaches were applied to explain the results obtained in the article. Fine-grained oxides possess a high level of point and surface defects, which are associated with deviations from stoichiometry and the extensive nature of crystallite boundaries [5]. As is known, Cu₂O has a fully occupied shell, making it impossible for charge-transfer-type phase instability to exist here. In such systems, the features of the nanostate are solely related to size effects and the influence of defectiveness. Alongside the contribution of the quantum size

effect to the blue shift, it is important to point out the possibility of spectral density redistribution as a consequence of the high defectiveness of the obtained thin films. At first glance, it may be inferred that the observed “blue shift” of the fundamental absorption edge in thin Cu₂O films, approximately within the range of 0.37 to 0.44 eV, is attributable to quantum confinement effects.

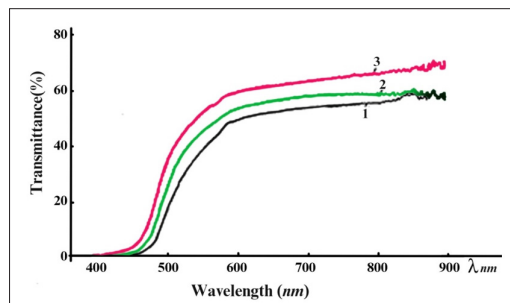


Figure 3: Transmission Spectra of Cu₂O Films of Various Thicknesses Obtained by Chemical Deposition: 1-5 μm ; 2-3 μm ; 3-2 μm .

However, the comparative analyses conducted herein provide clear evidence that a different underlying mechanism is responsible. Experimental and theoretical studies have shown that various factors affect the width of the optical band gap in Cu₂O films [12]. It was found that the complexing agent triethanolamine plays a key role in the formation of crystalline films. Moreover, increasing the pH shifts the preferred orientation from the (111) plane to the (200) plane, which promotes the formation of compact thin films and, consequently, enhances their conductivity. Finally, increasing the temperature leads to greater thickness and stimulates the formation of a well-defined morphology, which improves transmittance and narrows the band gap [12]. The XRD and X-ray photoelectron spectroscopy (XPS) analyses of the Cu₂O thin films treated by rapid thermal annealing (RTA) demonstrated an increase in crystal size with increasing RTA time and temperature, along with a reduction in copper oxidation states from Cu²⁺ to Cu¹⁺ [13]. Additionally, RTA treatment led to a decrease in the energy band gap to 2.38 eV and a reduction in electrical resistivity to 102 $\Omega\cdot\text{cm}$. The initially high energy band gap values of the Cu₂O thin films were attributed to quantum confinement effects resulting from their small crystal sizes in the range of 3.6–8.6 nm [13]. Analyses of various studies similar to the mentioned articles show that when the thickness of Cu₂O thin films becomes ultrathin (typically less than about 20 nm), quantum confinement is observed. As a result, the energy levels become discrete rather than continuous, which leads to a blue shift of the optical absorption edge (i.e., a shift to shorter wavelengths or higher energies). Thus, due to the spatial confinement of charge carriers, the effective band gap energy increases. However, despite this, in thin films with thicknesses greater than $\sim 20 \text{ nm}$, a decrease in thickness still causes a blue shift of the optical absorption edge (i.e., a shift to shorter wavelengths or higher energies) [13]. From this, it can be concluded that even in samples with micron-scale thickness, crystal sizes varying within the range of a few nanometers can form, which may lead to the observation of quantum confinement. However, since the study presented in the article was performed on samples with thicknesses of several microns, the occurrence of quantum confinement can be largely excluded. As a result of the research, it is concluded that in most cases, as the thickness

approaches the micron scale, significant changes occur in terms of crystallinity and microstructure. In this case, the improvement in crystallinity leads to a reduction in the concentration of surface defects and the associated sub-bandgap optical transitions. This results in a red shift of the optical absorption edge, i.e., a shift toward lower energies.

Conclusions

A comprehensive examination of the Debye diffraction pattern obtained from p-type Cu₂O thin films obtained by chemical deposition reveals that the diffraction ring observed at $2\theta = 18^{\circ}12'$ exhibits the highest intensity. This prominent reflection is unequivocally indexed to the (111) crystallographic plane of the face-centered cubic (FCC) Cu₂O structure, indicating a pronounced preferential orientation along this plane and suggesting a high degree of structural order and crystallinity within the chemically deposited films. The observed systematic red shift of the fundamental optical absorption edge toward lower photon energies ($E = 0.37\text{--}0.44$ eV) with increasing film thickness reflects an enhancement in crystalline quality, characterized by a decreased surface defect density and the attenuation of sub-bandgap optical transitions associated with localized defect states.

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