Study the Impact of Thickness on Electrical Properties of Spin Coated CuO Thin Films

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Abstract

Copper oxide (CuO) thin films are gaining significant attention in various technological applications due to their distinctive electrical properties. As a p-type semiconductor with a narrow bandgap, CuO is particularly valuable in the development of electronic devices such as transistors, diodes, and sensors. In this study, we investigate the influence of film thickness on the electrical properties of spin-coated CuO thin films. Thin films were prepared using a spin coating technique on glass substrates, with thicknesses ranging from 53 nm to 64 nm. The thickness of films was measured by low cost weight difference method. The electrical properties such as resistivity, activation energy and TCR were evaluated using a half bride technique. Obtained results reveal a systematic decrease in resistivity with increasing film thickness. This study underscores the vital role of film thickness in modulating the electrical behavior of CuO thin films, highlighting their potential for applications in electronic devices and sensors.

Keywords: Copper oxide, thin films, glass substrates, thicknesses, weight difference method.

1. Introduction:

Metal oxide semiconductors (MOS) are pivotal in modern electronics, owing to their unique electrical properties, chemical stability, and wide-ranging bandgaps [1]. These materials, which include oxides such as titanium dioxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), and copper oxide (CuO), are integral to the development of various electronic devices. Unlike traditional semiconductors like silicon, metal oxides offer greater flexibility in tuning their electrical properties through doping, defect engineering, and nanostructuring [2, 3]. This versatility allows for the fabrication of devices that operate under diverse conditions, including high temperatures and harsh environments. The ability to modify their electrical, optical, and chemical properties makes metal oxide semiconductors indispensable in the advancement of semiconductor technology [4]. One of the most significant applications of metal oxide semiconductors is in sensing technologies. Metal oxide semiconductors are particularly well-suited for gas sensors due to their high sensitivity to various gases, such as carbon monoxide, nitrogen dioxide, and volatile organic compounds. The electrical conductivity of these materials changes in response to gas adsorption on their surface, enabling the detection of low gas concentrations [4, 5]. For instance, zinc oxide (ZnO) is widely used in gas sensors for detecting toxic gases, while tin oxide (SnO_2) and CuO both are common in commercial gas sensors for detecting pollutants. Additionally, metal oxide semiconductors are employed in humidity sensors, where the change in electrical resistance with varying moisture levels enables precise environmental monitoring. Metal oxide semiconductors also play a critical role in the field of photovoltaics and energy harvesting. Titanium dioxide (TiO_2) and CuO are a prominent materials used in dye-sensitized solar cells (DSSCs), where it serves as the photoanode. The wide bandgap and excellent electron mobility of CuO facilitate efficient light absorption and electron transport, enhancing the overall efficiency of the solar cell. Moreover, metal oxide semiconductors are explored in perovskite solar cells as electron transport layers, contributing to the high power conversion efficiencies of these next-generation photovoltaic devices. Beyond solar energy, metal oxides like zinc oxide are also employed in piezoelectric nanogenerators, where they convert mechanical energy into electrical energy, showcasing their potential in energy harvesting applications [5-7]. Transparent electronics is another

emerging field where metal oxide semiconductors have made significant contributions. Materials like indium tin oxide (ITO) and CuO are transparent conductors, crucial for fabricating devices like transparent displays, touch screens, and transparent transistors [8, 9]. The combination of optical transparency and electrical conductivity in these metal oxides allows for the development of invisible electronic circuits that integrated into windows, flexible displays, and wearable devices [8, 10]. The potential for high mobility, environmental stability, and the ability to be processed at low temperatures make metal oxide semiconductors ideal for next-generation transparent electronics [11, 12].

CuO nanoparticles exhibit unique properties that make them highly valuable in various scientific and industrial applications. These nanoparticles are characterized by their p-type semiconducting behavior, high thermal and electrical conductivity, and significant catalytic activity [13, 14]. With a narrow bandgap of approximately 1.2–1.9 eV, CuO nanoparticles are highly effective in absorbing visible light, making them suitable for photocatalytic and photovoltaic applications [13, 14]. The synthesis of CuO nanoparticles could be achieved through various methods, including sol-gel, hydrothermal, co-precipitation, and chemical vapor deposition techniques. Each method allows control over the particle size, shape, and surface area, which are crucial factors in determining their performance in different applications [14, 15]. CuO nanoparticles are extensively used in gas sensors due to their high sensitivity to gases like hydrogen and carbon monoxide. They also play a crucial role in catalysis, particularly in environmental remediation processes such as the degradation of organic pollutants [16-18]. Additionally, CuO nanoparticles are explored in biomedical applications, including antimicrobial agents and drug delivery systems, due to their bioactivity and ability to interact with biological molecules. The versatility and wide-ranging applicability of CuO nanoparticles continue to drive research and innovation in various fields [18, 19].

The spin coating technique is a widely used method for the preparation of thin films, offering a simple, cost-effective, and highly controllable process for fabricating uniform layers on various substrates. In this technique, a solution containing the desired material is deposited onto the center of a substrate, which is then rapidly rotated at high speeds [20, 21]. The centrifugal force generated by the spinning motion spreads the solution evenly across the surface, while excess liquid is expelled, resulting in the formation of a thin film. The final thickness of the film is primarily determined by the spin speed, spin time, and the viscosity of the solution. Spin coating is particularly advantageous for producing thin films with well-defined thicknesses and smooth surfaces, making it ideal for applications in electronics, optics, and nanotechnology. It is commonly used to fabricate thin films of semiconductors, dielectrics, and organic materials for devices such as transistors, solar cells, and sensors [21, 22]. The versatility of spin coating allows for the integration of various materials into complex multilayer structures, enhancing the performance and functionality of thin-film devices [23].

The major aim of the current research work is to prepare CuO thin films at different RPM using spin coating technique and study the impact of thickness on electrical properties of prepared CuO thin films.

2. Experimental work

2.1 Synthesis and preparation of CuO thin films

All AR grade chemicals were used without further purification for synthesis and preparation of CuO thin films. $CuCl_2.2H_2O$ was used as source of CuO. The $CuCl_2.2H_2O$ (0.1 M) was dissolved in 100 ml in cleaned Beaker. 1 ml of glacial acetic acid is added to above aqueous solution of $CuCl_2.2H_2O$. Prepared solutions were mix through the constant stirring using magnetic stirrer at 60 ºC 8 M. After that, 0.1 M NaOH solution was added to above heated solution till $_PH$ reaches to ~ 10.30. The colour of solution turned from blue to black instantly and then large amount of black precipitate gel was formed [24, 25]. The obtained gel was used to prepare thin films of CuO at different RPM (revolutions per minute). After synthesizing the gel containing CuO precursors via the sol-gel method, the obtained gel was utilized to prepare thin films of CuO using the spin coating technique. The gel was first diluted to achieve the desired viscosity, ensuring smooth application onto the glass substrates. This solution was then carefully deposited onto the surface of cleaned glass substrates. To explore the effect of rotational speed on the film properties, the substrates were spun at various rotation speeds (1000, 2000, 3000 and 4000 RPM) during the spin coating process. Because in spin coating, RPM is a key parameter that directly influences the thickness of the thin film being applied. Selected different RPMs were employed to control the thickness of the resulting CuO thin films. The coated films were

subsequently dried under IR lamp for 30-40 minutes and then annealed at range of 400 ºC temperature using muffle furnace then used further characterizations [25, 26].

2.2 Electrical characterizations of CuO films by half-bridge technique

The electrical characterizations of prepared CuO thin films were investigated by using the half-bridge technique [27]. The schematic of half-bridge technique and circuit diagram is revealed in Fig. 1.

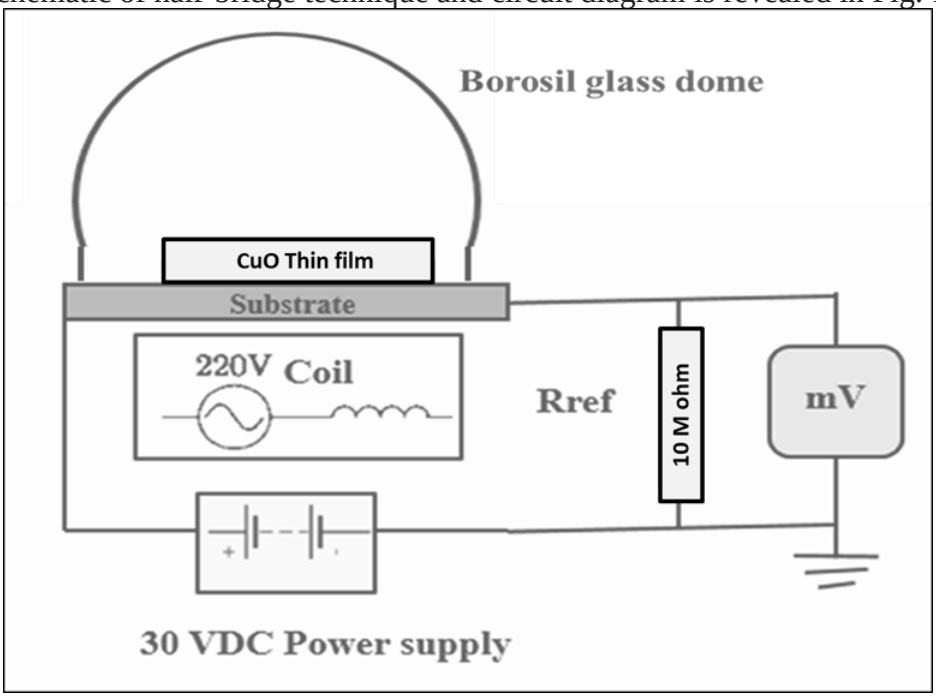

Figure 1: Schematic of half-bridge technique

Result and Discussion

The prepared CuO thin film samples at 1000, 2000, 3000 and 4000 RPM are labelled as Cu1, Cu2, Cu3 and Cu4 in this section. The thickness of the CuO thin films was estimated using the weight difference technique (Eq. 1), a straightforward and reliable method commonly employed in thin film studies. In this approach, the substrate is weighed before and after the deposition of the film. The difference in mass is attributed to the mass of the deposited film. To calculate the thickness, the mass of the film is divided by the area of the substrate and the density of the material [27, 28]. The estimated thickness of CuO films is shown in Fig. 1.

$$\text{Thickness} = \text{Mass difference}/\text{Area} \times \text{Density} \quad (1)$$

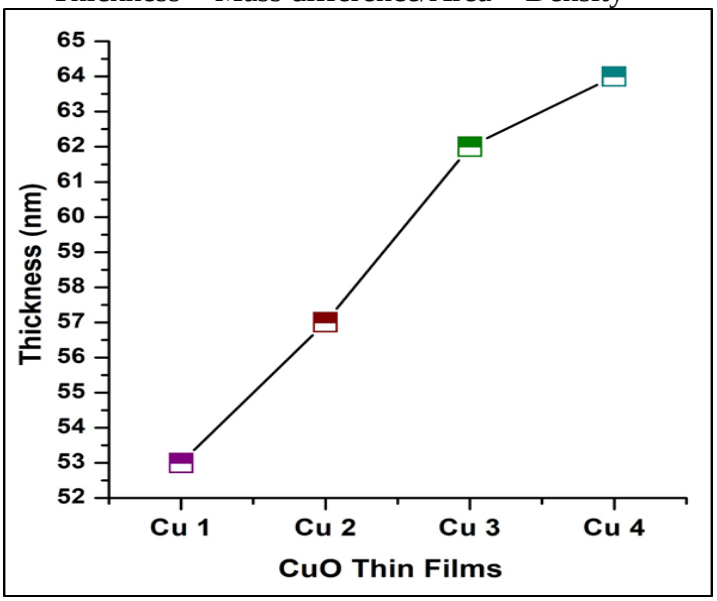

Figure 2: Thickness of CuO thin films

From Fig. 2, it is found that as the RPM increases the thickness of films is increases. It could be because of a solution with higher viscosity lead to a thicker film. A more viscous solution has a higher resistance to flow and spreads less easily during spinning, resulting in a thicker deposit on the substrate [24, 25]. Higher RPMs generally result in thinner films because the increased centrifugal force spreads the coating solution more thinly across the substrate.

The resistance versus temperature plot is shown in Fig. 3. The resistance of film is calculated by using Eq. 2.

$$R_{sample} = R_{ref}\left[\left(\frac{V_{supply}}{V_{ref}}\right)-1\right] \quad (2)$$

Where, R sample –film resistance, Vsupply – Applied voltage, and Vref – Voltage across external resistor R_L. Fig. 3 shows that the resistance of the film found to be decreases as surrounding temperature raised. This nature of films suggesting the semiconductor behaviour of films. As the temperature increases, the thermal energy provided to the charge carriers (holes in the case of p-type CuO) increases their mobility. Higher mobility allows charge carriers to move more freely through the material, thereby reducing the film's electrical resistance. As temperature rises, thermal activation promote more charge carriers into the conduction band. This increase in the number of charge carriers enhances the material's conductivity, resulting in lower resistance [27, 29].

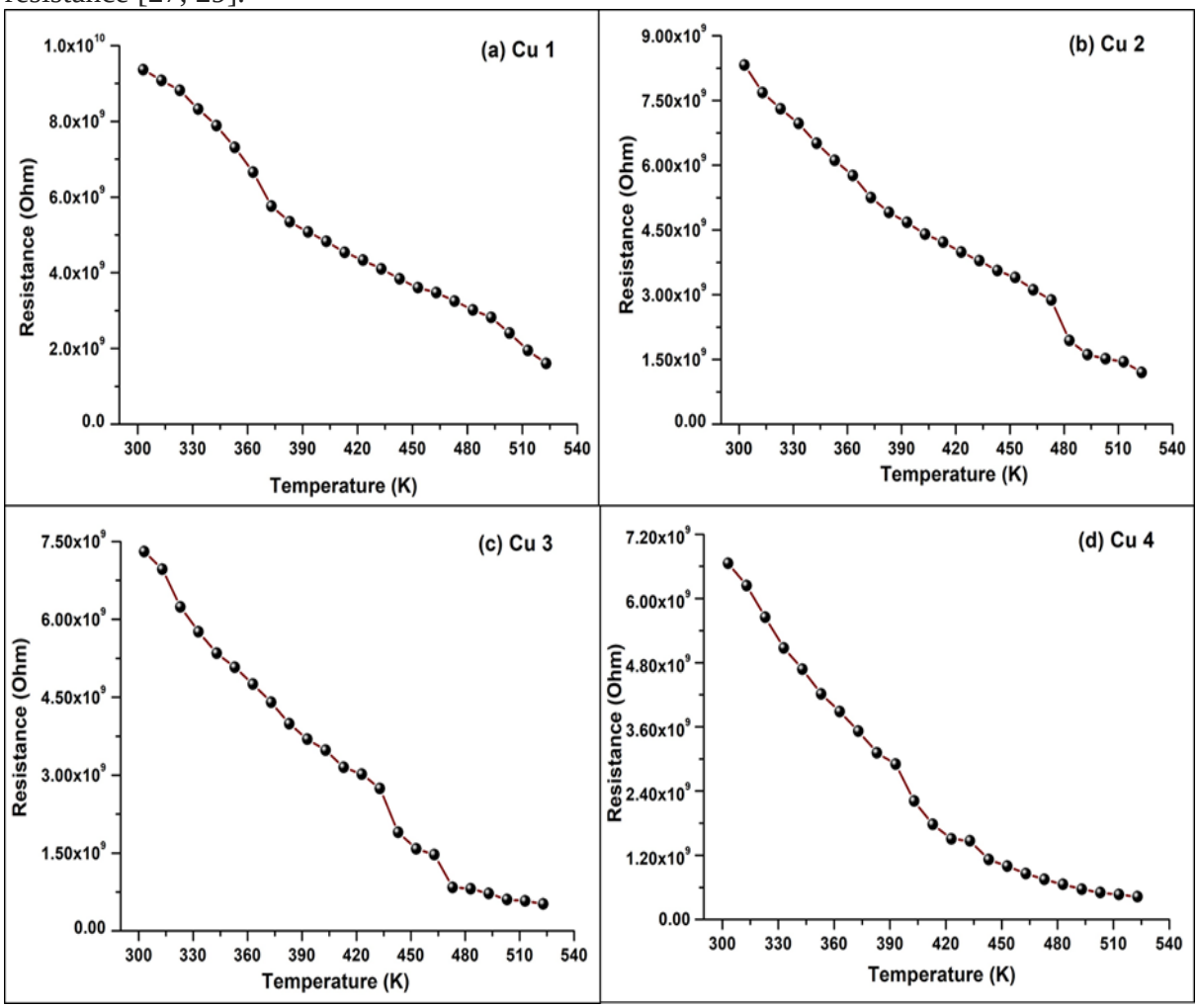

Figure 3: Resistance versus temperature plot of CuO thin films

Equation 3 was used to determine resistivity of prepared films.

$$\rho = \left(\frac{R \times b \times t}{l}\right)\Omega - m \quad (3)$$

Where, ρ = Resistivity of prepared film, R = resistance at normal temperature, b = breadth of film, t = thickness of the film, L = length of the film.

Fig. 4 illustrate the resistivity versus thickness (CuO thin films sample) plot. The resistivity of spin coated CuO thin films is increased as thickness increased. It may be an increased probability of charge carrier recombination, especially if the film is not well-optimized. Recombination of charge carriers reduces the number of free carriers available for conduction, leading to higher resistivity [29, 30].

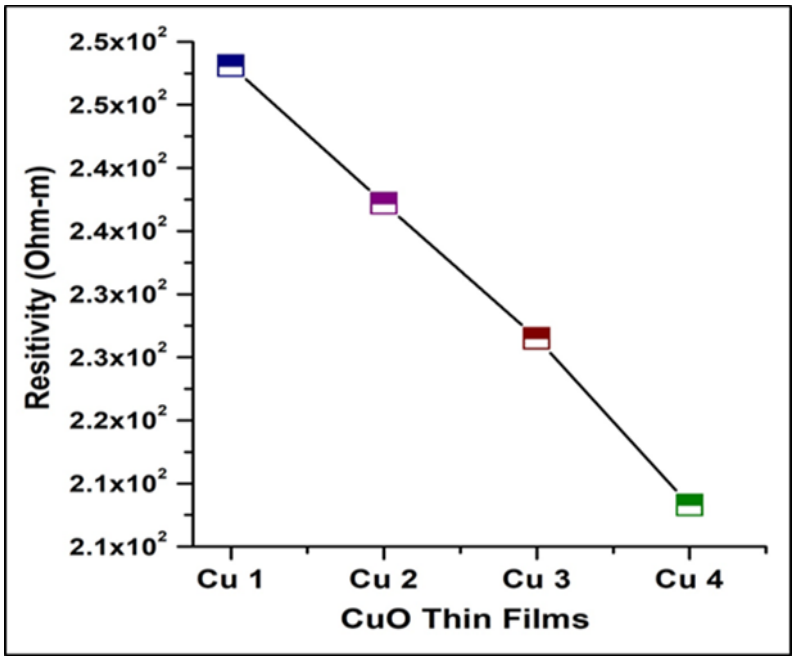

Figure 4: Resistivity versus CuO thin film

Also the distance that charge carriers must travel through the material is longer. As they traverse this increased path length, they are more likely to encounter scattering centers and other obstacles that contribute to increased resistivity. The TCR of films calculated by Eq. 4.

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right) \ /^{O} C \qquad (4)$$

Where, ΔR = change in resistance between temperature T_1 and T_2, ΔT = temperature difference between T_1 and T_2 and R_o = room temperature resistance of the film.

The activation energy of spin-coated CuO thin films is a key parameter that describes how the film's resistivity changes with temperature [27]. It provides valuable information about the charge transport mechanisms and is crucial for the practical application and optimization of CuO thin films in electronic and optoelectronic devices. Eq. 5 is used to calculated activation energy of prepared CuO films.

$$\Delta E = Ae^{-Ea/kBT} \quad \text{eV} \qquad (5)$$

Where, ΔE = Activation energy, T = Temperature in Kelvin and A = Arrhenius prefactor.

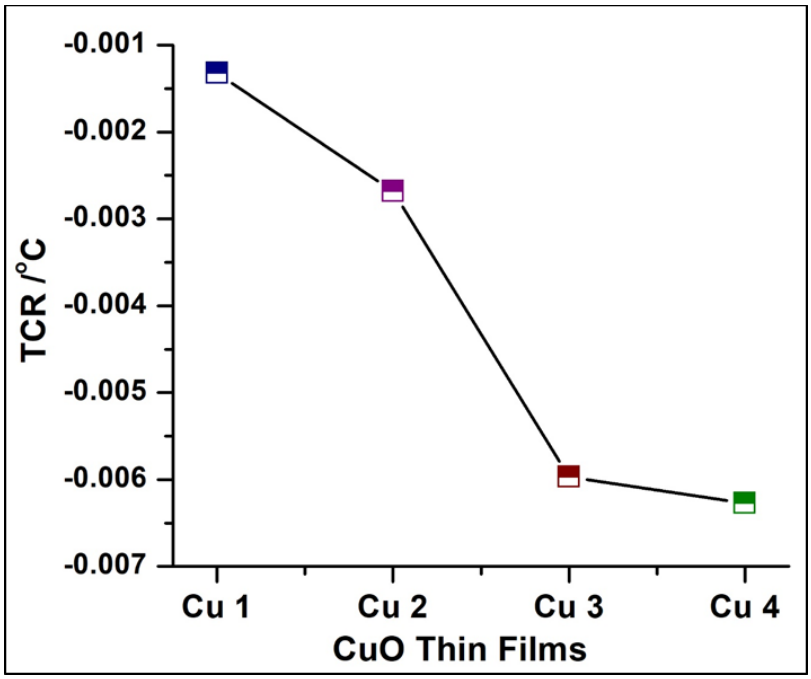

Figure 5: TCR versus CuO thin film

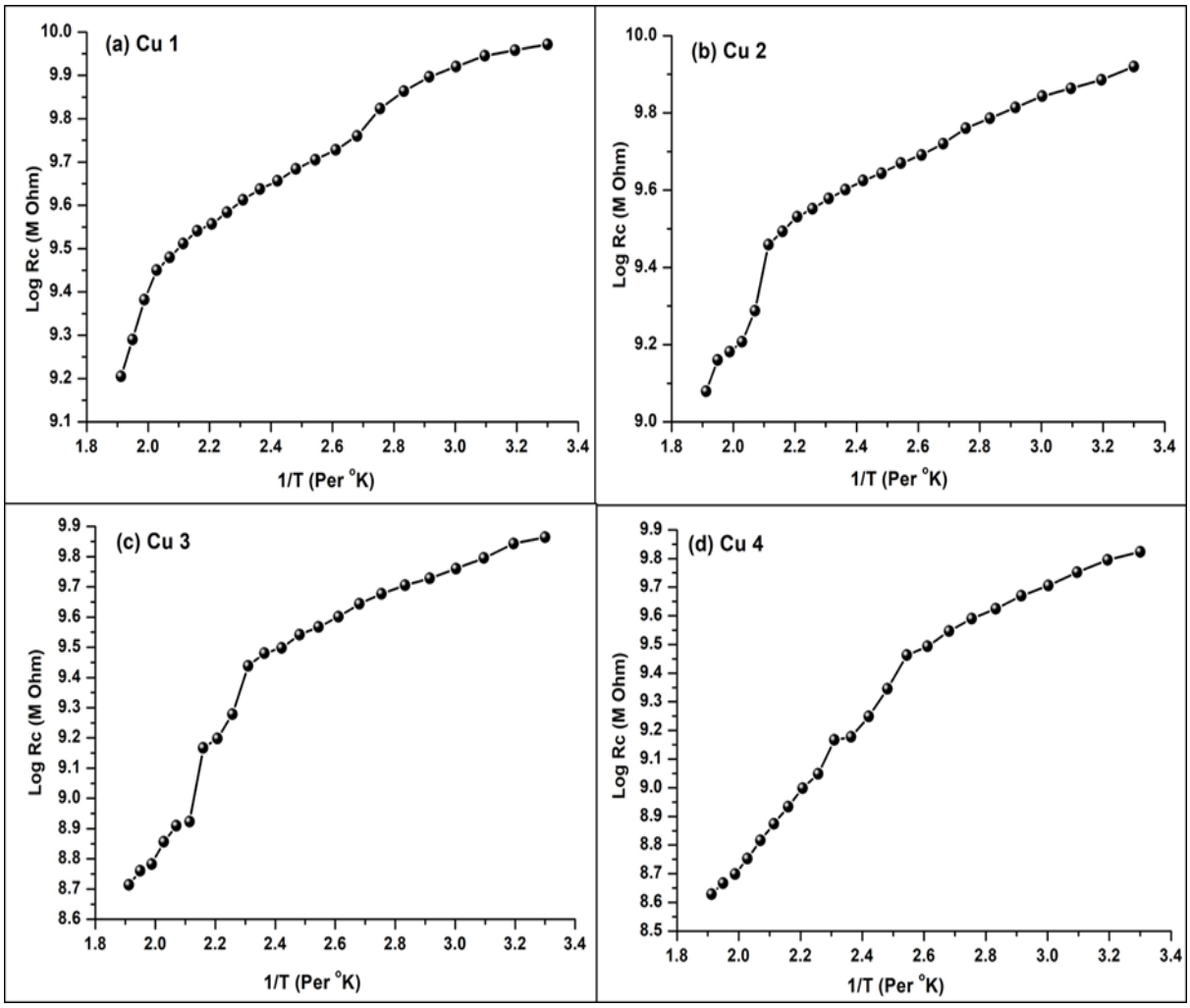

Figure 6: Log Rc versus 1/T plot of CuO thin films

It is observed that, as the thickness of the CuO thin films increases, the defect density often rises, including grain boundaries, dislocations, and voids. These defects impact the charge carrier transport mechanisms and, consequently, the activation energy. Higher defect densities decrease the activation energy depending on whether they act as traps or scattering centers. The activation energy of spin-coated CuO thin films is influenced by thickness through changes in defect density, microstructure, carrier transport mechanisms, and film quality [27-29].

The estimated electrical parameters of CuO thin films are tabulated in Table 1.

Table 1: Electrical outcomes of CuO thin films

Sample	Thickness (nm)	Resistivity (Ω.m)	TCR (/°C)	Activation Energy (eV)	
				HTR	LTR
Cu 1	53	248.1	-0.00132	0.3116	0.0532
Cu 2	57	237.2	-0.00268	0.2086	0.0551
Cu 3	62	226.5	-0.00597	0.2447	0.0738
Cu 4	64	213.3	-0.00627	0.2449	0.0903

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Conflicts of Interest:

The author declare no conflict of interest.

References:

1. Gao, X. and Zhang, T., 2018. An overview: Facet-dependent metal oxide semiconductor gas sensors. *Sensors and Actuators B: Chemical*, *277*, pp.604-633.
2. Sundaram, G.A., Muniyandi, G.R., Ethiraj, J., Parimelazhagan, V. and Kumar, A.S.K., 2024. Introduction and Advancements in Room-Temperature Ferromagnetic Metal Oxide Semiconductors for Enhanced Photocatalytic Performance. *ChemEngineering*, *8*(2), p.36.
3. Goel, N., Kunal, K., Kushwaha, A. and Kumar, M., 2023. Metal oxide semiconductors for gas sensing. *Engineering Reports*, *5*(6), p.e12604.
4. Yang, B., Myung, N.V. and Tran, T.T., 2021. 1D metal oxide semiconductor materials for chemiresistive gas sensors: a review. *Advanced Electronic Materials*, *7*(9), p.2100271.
5. Riente, P. and Noël, T., 2019. Application of metal oxide semiconductors in light-driven organic transformations. *Catalysis Science & Technology*, *9*(19), pp.5186-5232.
6. Zhang, J., Qin, Z., Zeng, D. and Xie, C., 2017. Metal-oxide-semiconductor based gas sensors: screening, preparation, and integration. *Physical Chemistry Chemical Physics*, *19*(9), pp.6313-6329.
7. Al-Ahmadi, N.A., 2020. Metal oxide semiconductor-based Schottky diodes: a review of recent advances. *Materials Research Express*, *7*(3), p.032001.
8. Jo, J.W., Kang, S.H., Heo, J.S., Kim, Y.H. and Park, S.K., 2020. Flexible metal oxide semiconductor devices made by solution methods. *Chemistry–A European Journal*, *26*(42), pp.9126-9156.
9. Bright, C.I., 2018. Transparent conductive thin films. In *Optical Thin Films and Coatings* (pp. 741-788). Woodhead Publishing.
10. Abbas, H.A., Youssef, A.M., Hammad, F.F., Hassan, A.M.A. and Hanafi, Z.M., 2014. Electrical properties of nano-sized indium tin oxide (ITO) doped with CuO, Cr 2 O 3 and ZrO 2. *Journal of nanoparticle research*, *16*, pp.1-11.
11. Banerjee, A.N. and Chattopadhyay, K.K., 2005. Recent developments in the emerging field of crystalline p-type transparent conducting oxide thin films. *Progress in Crystal Growth and Characterization of materials*, *50*(1-3), pp.52-105.
12. Kimura, M., 2019. Emerging applications using metal-oxide semiconductor thin-film devices. *Japanese Journal of Applied Physics*, *58*(9), p.090503.
13. Grigore, M.E., Biscu, E.R., Holban, A.M., Gestal, M.C. and Grumezescu, A.M., 2016. Methods of synthesis, properties and biomedical applications of CuO nanoparticles. *Pharmaceuticals*, *9*(4), p.75.
14. Ighalo, J.O., Sagboye, P.A., Umenweke, G., Ajala, O.J., Omoarukhe, F.O., Adeyanju, C.A., Ogunniyi, S. and Adeniyi, A.G., 2021. CuO nanoparticles (CuO NPs) for water treatment: A review of recent advances. *Environmental Nanotechnology, Monitoring & Management*, *15*, p.100443.
15. Singh, J., Kaur, G. and Rawat, M., 2016. A brief review on synthesis and characterization of copper oxide nanoparticles and its applications. *J. Bioelectron. Nanotechnol*, *1*(9).
16. Naz, S., Gul, A., Zia, M. and Javed, R., 2023. Synthesis, biomedical applications, and toxicity of CuO nanoparticles. *Applied Microbiology and Biotechnology*, *107*(4), pp.1039-1061.
17. Waris, A., Din, M., Ali, A., Ali, M., Afridi, S., Baset, A. and Khan, A.U., 2021. A comprehensive review of green synthesis of copper oxide nanoparticles and their diverse biomedical applications. *Inorganic Chemistry Communications*, *123*, p.108369.
18. El-Trass, A., ElShamy, H., El-Mehasseb, I. and El-Kemary, M., 2012. CuO nanoparticles: synthesis, characterization, optical properties and interaction with amino acids. *Applied Surface Science*, *258*(7), pp.2997-3001.
19. Phiwdang, K., Suphankij, S., Mekprasart, W. and Pecharapa, W., 2013. Synthesis of CuO nanoparticles by precipitation method using different precursors. *Energy procedia*, *34*, pp.740-745.
20. Birnie III, D.P., 2004. Spin coating technique. *Sol-gel technologies for glass producers and users*, pp.49-55.
21. Tyona, M.D., 2013. A comprehensive study of spin coating as a thin film deposition technique and spin coating equipment. *Adv. Mater. Res*, *2*(4), p.181.
22. Lun, T.T., Liu, C.Q., Wang, N., Zhai, X.N., Song, M.S., Ge, Q., Zhang, X.Y., Liu, S.M., Wang, H.L., Jiang, W.W. and Ding, W.Y., 2019. Preparation of compact CuO films by sol-gel spin coating technique. *Materials Letters*, *257*, p.126745.

23. Al Armouzi, N., El Hallani, G., Liba, A., Zekraoui, M., Hilal, H.S., Kouider, N. and Mabrouki, M., 2019. Effect of annealing temperature on physical characteristics of CuO films deposited by sol-gel spin coating. *Materials Research Express*, *6*(11), p.116405.
24. Dörner, L., Cancellieri, C., Rheingans, B., Walter, M., Kägi, R., Schmutz, P., Kovalenko, M.V. and Jeurgens, L.P., 2019. Cost-effective sol-gel synthesis of porous CuO nanoparticle aggregates with tunable specific surface area. *Scientific reports*, *9*(1), p.11758.
25. Kayani, Z.N., Umer, M., Riaz, S. and Naseem, S., 2015. Characterization of copper oxide nanoparticles fabricated by the sol–gel method. *Journal of Electronic Materials*, *44*, pp.3704-3709.
26. Jyoti and Kumar, R., 2023. Investigation of effect of spinning speed on structural, electrical and optical properties of CuO thin films prepared by sol–gel spin coating technique. *Journal of Optics*, *52*(3), pp.1065-1073.
27. Tupe, U.J., Zambare, M.S., Patil, A.V. and Koli, P.B., 2020. The binary oxide NiO-CuO nanocomposite based thick film sensor for the acute detection of Hydrogen Sulphide gas vapours. *Material Science Research India*, *17*(3), pp.260-269.
28. Koli, P.B., Kapadnis, K.H., Deshpande, U.G., Tupe, U.J., Shinde, S.G. and Ingale, R.S., 2021. Fabrication of thin film sensors by spin coating using sol-gel LaCrO3 Perovskite material modified with transition metals for sensing environmental pollutants, greenhouse gases and relative humidity. *Environmental Challenges*, *3*, p.100043.
29. Wagh, S.L., Tupe, U.J., Patil, A.B. and Patil, A.V., 2022. Influence of Annealing Temperature on Structural and Electrical Properties of Screen Printed Lanthanum Oxide Thick Films. *Iranian Journal of Materials Science & Engineering*, *19*(4).
30. Lad, U.D., Kokode, N.S. and Tupe, U.J., 2022. Study of pn Heterojunction Thin Films for Reducing Gas Sensing Application Fabricated by Thermal Evaporation Technique. *Advanced Materials Research*, *1172*, pp.67-82.