Investigation the electrical properties of CuO-ZnO thick films developed by screen printing technique

Devendra Bhikaji Sonwane

Department of Physics,
S. P. H. Arts, Science and Commerce College,
Nampur, Tal- Baglan, Dist.- Nasik, Affiliated to SPPU, Pune, and Maharashtra, India.

Abstract: The metals and metal oxide semiconductors (MOS) are classified on the energy band gap between conduction and valance bands. The energy band gap of any material indicating amount of energy required to charges to migrate from valance band to conduction band. In another way we can say that the band gap between to bands is nothing but a one type of barrier or resistance for charge carriers. The MOS thick or thin films has various applications like gas sensors, biosensors and others. The working principle of MOS based sensor is based on the change in resistance when particular material is in contact with particular gas molecules or enzyme. The electrical properties of any material is important parameter in any applications. Hence the current research work focused on the investigation of electrical properties of CuO-ZnO thick films. Thick films were prepared on glass substrate by screen printing technique. The electrical properties of prepared CuO-ZnO thick films were investigated by using resistivity, temperature coefficient resistance, and activation energy. The impact of wt. % ZnO additive on the electrical properties of CuO is described in the current research article.

Keywords: Energy band gap, CuO-ZnO thick films, charge carriers, electrical properties.

1. INTRODUCTION:

The mechanical, optical, electrical, catalytic, and magnetic properties of nanostructures make them special. These materials moreover have a high surface area per unit mass. Furthermore, when particles are nanoscale, new physical and chemical features appear. Gas sensing properties are also influenced by electrical characteristics like as resistivity, TCR, activation energy at high and low temperatures, and so forth. When the size of the material is reduced, both the specific surface area and the surface to volume ratio dramatically increase [1]. Additionally, the size and geometry of the materials have an impact on the motion of electrons and holes in nanostructured materials. Due to their characteristics, which may exceed the single phases by an order of magnitude, metal-oxide nanostructures are an exceedingly exciting type of nanomaterial [2, 3]. The synthesis of these materials holds promise. After the adsorption and photocatalysis processes are complete, the latter will reduce the losses of metal oxide nanoparticles by stabilizing the nanomaterials in the concrete mixture, which will also improve the filtration. Due to their structure, nanostructures also have unique, frequently unique, physical and chemical properties that can be exploited in a variety of fields, such as the development of new materials for use in the ecology, medicine, and energy [4-6].

Thick films made of ZnO and CuO are frequently used in applications where variations in the electrical conductivity of the film can be linked to oxygen atom physisorption and chemisorption. Many monometallic transition base metal oxides, like ZnO and CuO, offer exceptional physical qualities, including a high dielectric constant, solid chemical and mechanical stability, and excellent insulation characteristics [7, 8].

CuO is a p-type metal oxide semiconductor with a straight band gap of 2.0–2.2 eV. Due to its promising use in MEMS materials, solar cells, and gas sensors, it has drawn growing interest. The superior characteristics of CuO nanostructures have been proven as compared to bulk material. Because of their

intriguing characteristics and potential in a variety of applications, cupric oxide nanostructures are of great interest [9]. A black solid with a density of 6.4 g/cm^3, pure cupric oxide is opaque. It is also insoluble in water and has a high melting point of 1330 ^{o}C. Cuprous oxide (Cu$_2$O) and cupric oxide are the two types of polymorphism that appear in CuO. The two most significant stoichiometric elements in the CuO system are these oxides [8, 9].

ZnO is an n-type semiconductor, has a band gap of about 3.3 eV at ambient temperature, which is significantly larger. Higher breakdown voltages, the capacity to withstand huge electric fields, reduced electronic noise, and high-temperature and high-power operation are benefits connected with a large band gap [7, 10]. The electrical conductivity of ZnO is caused by an overabundance of zinc, likely interstitial and in oxygen vacancies in the lattice [10]. Hydrogen faults that are extrinsic have a higher likelihood of being assimilated as shallow donors. The goal of the existing research is to fabricate thick films of CuO-ZnO employing a screen printing technique and examining the electrical properties of CuO-ZnO thick films.

2. Experimental work

2.1 Preparation of thick films using screen-printing technique

Fig. 1 depicts the setup process for the screen-printing technique and the preparation of thick films. As depicted in fig. 1, the screen-printing of the active powder paste was performed in three steps.
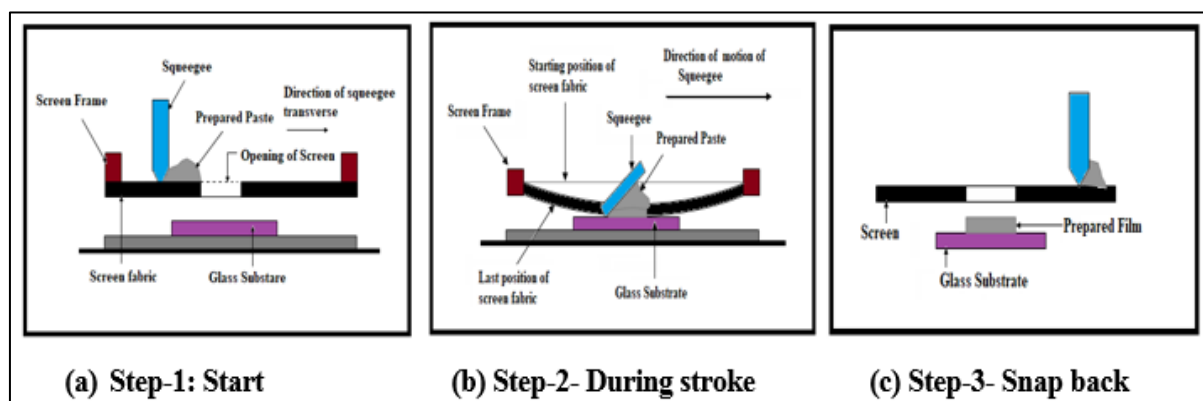

Figure 1: Steps for preparation of thick film sample using screen printing technique

CuO is used as an additive and ZnO is the base material in this work. In 70% inorganic material, the base material nanopowder was utilized with X wt. % additive (X = 1 wt. %, 3 wt. %, and 5 wt. %). Ethyl Cellulose was employed in 30 wt% of the organic material, whereas Butyl Carbitol Acetate (BCA) was used in 92 wt%. On a glass substrate, thick films of CuO-ZnO nanostructures were developed. The temporary binder was removed from the films by drying them under an infrared (IR) lamp for 30 minutes and then annealed at 250°C in a muffle furnace for two hours [11]. Fig. 2 shows the schematic of details experimental work.
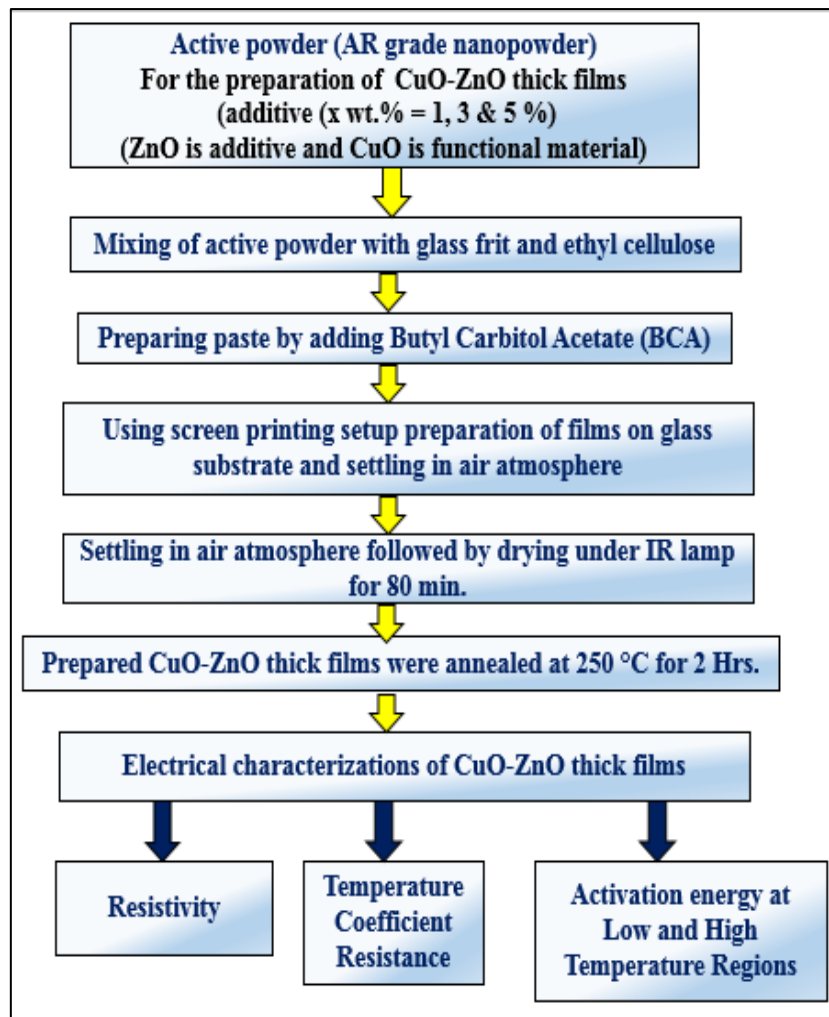
Figure 2: Schematic of experimental work

2.2 Electrical Characterizations of CuO-ZnO thick films
2.2.1 Electrical Characterizations

The electrical characterizations of CuO-ZnO thick films were studied using standard parameters like resistivity, TCR and activation energy at high and low temperature regions. Because this parameters shows the electric behaviours of the films for gas sensing and other applications. The system's components include a glass chamber or dome, a 2000 W nichrome heating coil, and a digital temperature indicator. A heater coil made of nichrome wire and a glass chamber make up the characterization system. By adjusting its voltage with a dimmer stat, the electric coil was utilized to raise the temperature from room temperature to 300°C. The prepared CuO-ZnO thick films electrical parameters were study using static electric circuit and electronic circuit which is called as half bridge method [11, 12]. Fig. 3 shows the schematic diagram of static electrical characterization system.
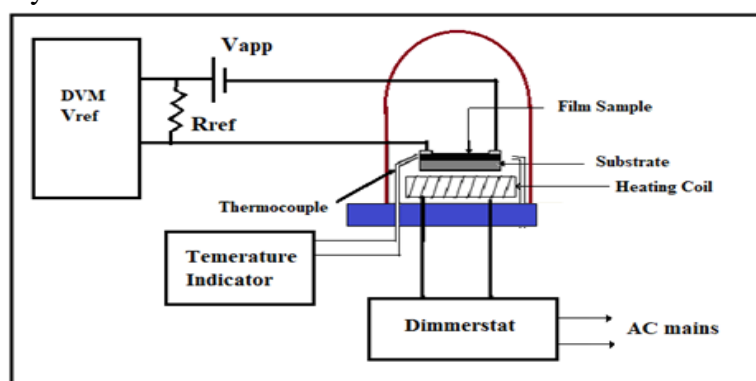

Figure 3: Schematic diagram of static electrical characterization system

---

The D.C. resistance of thick films was measured as a function of temperature in the range of 30 to 300° C using half bridge method [12]. The resistance of the sample under study was calculated by using equation 1.

$$R\,sample = R\,ref\left[\left(\frac{V\,supply}{V\,ref}\right) - 1\right] \quad \text{............ (1)}$$

The electrical properties of CuO-ZnO thick films were calculated using eequations 2, 3 and 4 for resistivity, TCR and activation energy respectively [12, 13].

$$\rho = \left(\frac{R \times b \times t}{l}\right)\Omega - m \quad \text{............ (2)}$$

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.

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right)/^o C \text{............ (3)}$$

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

$$\Delta E = \frac{\log R}{\log\,Ro} \times KT \text{............ (4)}$$

Where, ΔE = Activation energy, R = Resistance at elevated temperature, R_0 = Resistance at room temperature.

2.2.2 Thickness measurement:

The thickness of the films also one of the important parameter of any films sensor. The thickness determine the prepared film is thick or thin. Also the electrical and other properties of the films is depends upon the thickness of the film. Many thickness measurement techniques are available among them weight difference technique is less time consuming and less expensive technique. Hence the thickness of CuO-ZnO thick films was calculated by weight difference technique. Eq. 5 is implemented for measurement of CuO-ZnO thick films [12].

$$t = \Delta m/\rho A \text{............ (5)}$$

Where, Δm is the difference in mass before and after deposition, ρ = Composite density of materials and A= Area of the film.

3. RESULT AND DISCUSSION:
3.1 Electrical Properties:
3.1.1 Resistivity:

The resultant plot, which is depicted in Figure 4, shows semiconducting behavior of CuO-ZnO thick films.
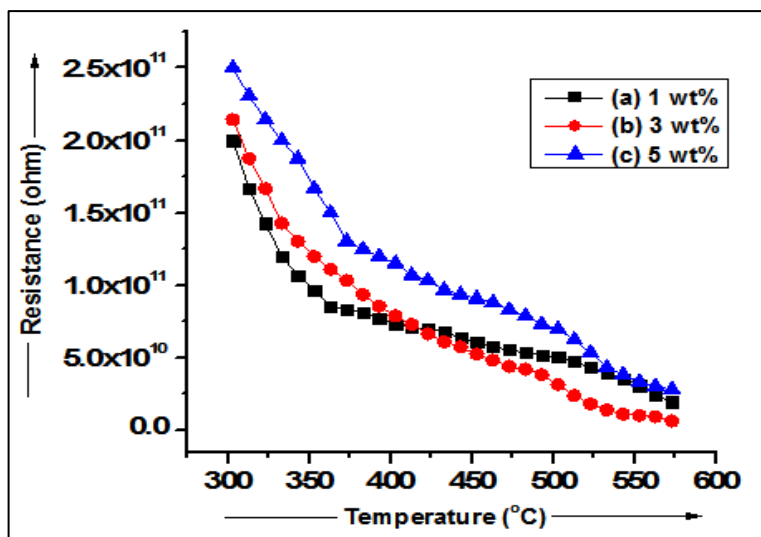

Figure 4: Resistance verses temperature plot of (a) 1 wt. %, (b) 3 wt. %, and (c) 5 wt. %, CuO-ZnO thick film

---

The film resistivity in MOS-based sensors is correlated with the densities of electrons and holes as well as the velocity of charge carriers. ZnO additives changes the resistivity of CuO material as shown in fig. 5. Thick films of CuO-ZnO were tested for resistance as a response to temperature. The resistance of the CuO-ZnO thick films in the electrical characterization system decreases with rising ambient temperature [12, 13].

Resistivity also provides information on the charge carriers' mean free route and charge mobility. The resistivity verses wt % CuO-ZnO thick film as shown in Fig. 5.
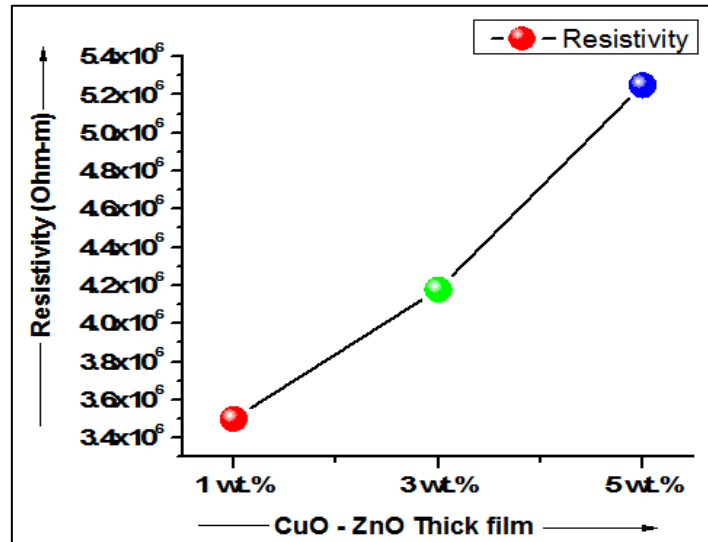

Figure 5: Resistivity verses wt % CuO-ZnO thick film

3.1.2 Temperature coefficient of resistance (TCR):

The TCR of thick films is key parameter in the electrical characterization of thick or thin films. TCR for metal is positive whereas for semiconductors [11, 14] TCR is negative as shown in Fig. 6. The TCR verses wt % CuO-ZnO thick film as shown in Fig. 6.
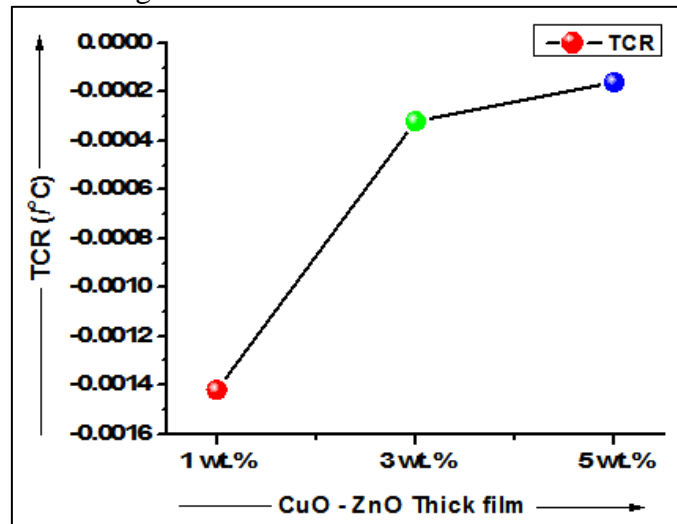

Figure 6: TCR verses wt % CuO-ZnO thick film

3.3.3 Activation energy:

The amount of energy needed for an electron to migrate from the valence to the conduction band is known as the activation energy. It significantly alters the electrical properties of the transport band by changing the carrier concentration [14, 15]. Figure 7 reveals the Arrhenius plot of log Rc vs. 1/T of CuO-ZnO thick films. The activation energy at higher temperature and at lower temperature region are tabulated in table 1.
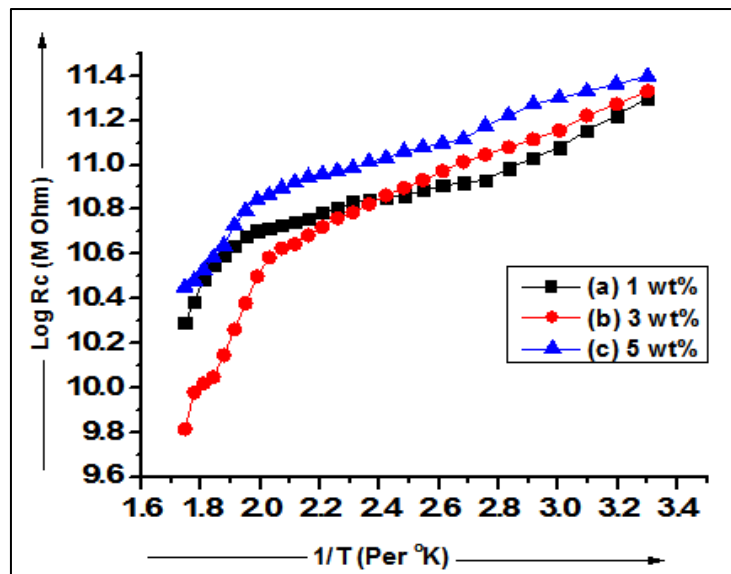
Figure 7: Arrhenius plot of log Rc vs. 1/T of (a) 1 wt. %, (b) 3 wt. %, and (c) 5 wt. %, CuO-ZnO thick film

The thickness of CuO-ZnO thick films was found to be 35, 39 and 42 µm for 1 wt. %, 3 wt. %, and 5 wt. % respectively. It is observed that the thickness of all films were found in micro range and as wt. % ZnO additive increased Thickness of film also decreased. The Fig. 8 illustrate thickness verses wt % CuO-ZnO thick film.
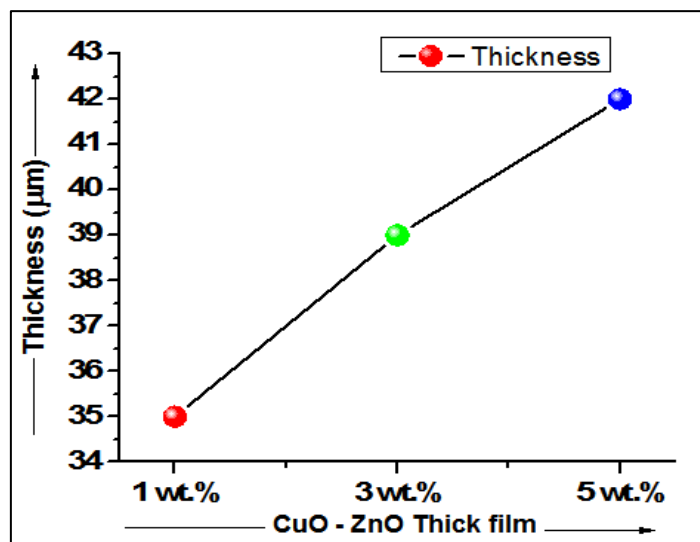

Figure 8: Thickness verses wt % CuO-ZnO thick film

All investigated electrical outcomes of CuO-ZnO thick films are tabulated in Table 1.

Table-1: Electrical outcomes of CuO-ZnO thick films.

Thick film (ZnO additive)	Thickness (µm)	Resistivity (Ω-m)	TCR (/°C)	Activation Energy (eV)	
				HTR	LTR
1 wt.%	35	3499825	-0.00142	0.083979	0.137553
3 wt.%	39	4178376	-0.00032	0.403342	0.117202
5 wt.%	42	5249790	-0.00016	0.166557	0.063845

Conclusions:
1. The CuO-ZnO thick films were successfully prepared by using screen-printing technique.
2. Temperature coefficient of resistance is found to be negative to all wt. % films.
3. The wt. % ZnO additive increased the thickness, resistivity and TCR of the films are also increased.
4. The impact of wt. % ZnO additive on the electrical properties of CuO was investigated.

References
1. Zhang, D., Yang, Z., Yu, S., Mi, Q. and Pan, Q., 2020. Diversiform metal oxide-based hybrid nanostructures for gas sensing with versatile prospects. *Coordination Chemistry Reviews*, *413*, p.213272.
2. Zhou, Y., Yang, P., Zu, H., Gao, F. and Zu, X., 2013. Electronic structures and magnetic properties of MoS 2 nanostructures: atomic defects, nanoholes, nanodots and antidots. *Physical Chemistry Chemical Physics*, *15*(25), pp.10385-10394.
3. Garoli, D., Mosconi, D., Miele, E., Maccaferri, N., Ardini, M., Giovannini, G., Dipalo, M., Agnoli, S. and De Angelis, F., 2018. Hybrid plasmonic nanostructures based on controlled integration of MoS 2 flakes on metallic nanoholes. *Nanoscale*, *10*(36), pp.17105-17111.
4. Wang, C., Yin, L., Zhang, L., Xiang, D. and Gao, R., 2010. Metal oxide gas sensors: sensitivity and influencing factors. *sensors*, *10*(3), pp.2088-2106.
5. Kalidoss, R., Surya, V.J. and Sivalingam, Y., 2022. Recent progress in graphene derivatives/metal oxides binary nanocomposites based chemi-resistive sensors for disease diagnosis by breath analysis. *Current Analytical Chemistry*, *18*(5), pp.563-576.
6. Gerasimov, G.N., Gromov, V.F., Ilegbusi, O.J. and Trakhtenberg, L.I., 2017. The mechanisms of sensory phenomena in binary metal-oxide nanocomposites. *Sensors and Actuators B: Chemical*, *240*, pp.613-624.
7. Chabane, L., Zebbar, N., Zeggar, M.L., Aida, M.S., Kechouane, M. and Trari, M., 2015. Effects of CuO film thickness on electrical properties of CuO/ZnO and CuO/ZnS hetero-junctions. *Materials Science in Semiconductor Processing*, *40*, pp.840-847.
8. Yatskiv, R., Tiagulskyi, S., Grym, J., Vaniš, J., Bašinová, N., Horak, P., Torrisi, A., Ceccio, G., Vacik, J. and Vrňata, M., 2020. Optical and electrical characterization of CuO/ZnO heterojunctions. *Thin Solid Films*, *693*, p.137656.
9. Hou, L., Zhang, C., Li, L., Du, C., Li, X., Kang, X.F. and Chen, W., 2018. CO gas sensors based on p-type CuO nanotubes and CuO nanocubes: Morphology and surface structure effects on the sensing performance. *Talanta*, *188*, pp.41-49.
10. Zhang, Z., Shao, C., Li, X., Wang, C., Zhang, M. and Liu, Y., 2010. Electrospun nanofibers of p-type NiO/n-type ZnO heterojunctions with enhanced photocatalytic activity. *ACS applied materials & interfaces*, *2*(10), pp.2915-2923.
11. 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.
12. Deore, M.K., Gaikwad, V.B. and Jain, G.H., 2016. Role of CuO-ZnO Heterojunctions in Gas Sensing Response of CuO-ZnO Thick Films. *Journal of Physical Science and Application*, *6*(2), pp.51-60.
13. Wagh, S., Tupe, U., Patil, A. and Patil, A., 2022. Influence of Annealing Temperature on Structural and Electrical Properties of Screen Printed Lanthanum Oxide Thick Films. *Iranian Journal of Materials Science and Engineering*, *19*(4), pp.1-9.
14. Salunke, V.T., Buchade, P.B., Shaligram, A.D. and Borse, R.Y., 2022, October. Screen printed ZnO thick films for NH3 gas sensing. In *IOP Conference Series: Materials Science and Engineering* (Vol. 1263, No. 1, p. 012027). IOP Publishing.
15. Krishnan, B. and Nampoori, V.P.N., 2005. Screen printed nanosized ZnO thick film. *Bulletin of Materials Science*, *28*, pp.239-242.