Investigating Resistive and Gas Sensing Properties of TiO_2, CuO and TiO_2-CuO Thick Films

Kunal H. Patil[1], Neha N. Malpure[2], Rajendra S. Khadayate[3*]

[1,2]Research Student, Research Lab, Department of Physics, G.D.M. Arts, K. R. N. Commerce and M. D. Science College, Jamner, Dist. Jalgaon, Maharashtra, INDIA
[3]Research Guide and Professor, Research Lab, Department of Physics, G.D.M. Arts, K. R. N. Commerce and M. D. Science College, Jamner, Dist. Jalgaon, Maharashtra, INDIA
*Corresponding author: rskhadayate@gmail.com

Abstract:
New inventions in modern research work related to material science always based on the preparation of a well adhered film (thin or thick) of suitable base material on a suitable substrate and investigating their functional characteristics.
In our work we used TiO_2 and CuO as base materials. In our work, we prepared thick films of TiO_2, CuO and TiO_2-CuO films of variable percentage. All the films were prepared on a suitably small electrode pattern Printed Circuit Board. Then the I-V characteristic of all prepared thick film was investigated by simple lab prepared two probe method. Variation in resistive properties of each film was investigated. Also, gas sensing performance of each film was investigated.

Keywords: TiO_2, CuO, TiO_2-CuO, thick films, I-V Characteristics, gas sensing

1. Introduction:

Commercially available AR grade nano oxide powder or synthesized nano oxide powder by different methods [1-2] founds very useful in different applications such as gas sensors, humidity sensors, photo sensors and various types of sensors [3-16]. Before using for various applications, investigation of various parameters of oxide materials are to be investigated. To investigate the various parameters, thick films of oxide materials should be formed on suitable substrates. Also, variation in resistivity is important parameter in various types of research to achieve certain specific useful applications. Variation in conductivity can be achieved by adding different oxide material in different proportion with that of base material.
Thick film resistors are produced by applying paste of resistive material, a mixture of glass and conductive materials, to a substrate [17-19]. Thick film technology allows high resistance values to be printed on a cylindrical or flat substrate either covered entirely or in various patterns. Many researchers are working in different fields [3-16,19] are in the need of well adhered film of suitable oxide materials on glass plate or alumina substrate.
In recent years many researchers are working in field of quick detection of hazardous gases [3-14]. Hence a sensor element with low operating temperature and fast response to gases is desired. Most of the

researchers working in the field oxide gas sensor prepared a well adhered film of suitable oxide material on glass plate or alumina substrate.

In this work, the most popular oxide materials i.e. TiO_2 (titanium oxide) and CuO (Copper oxide) were used. The new thing in our work was that, all the thick films were prepared on a small size electrode pattern PCB. TiO_2 (100%), CuO (100%), TiO_2 (75%) + CuO (25%), TiO_2 (50%)+ CuO (50%) and TiO_2 (25%)+ CuO (75%) , these five types of thick films were prepared. Then the I-V characteristic of each prepared thick film was investigated by simple lab prepared two probe method. Resistance of each film was calculated and compared. Also all the prepared thick films was individually exposed to fumes of acetone, ethanol and ammonia and their fume (gas) sensing properties will be investigated.

2. Experimental Work:

a) **Crushing of TiO_2 and CuO powder**

Commercially available AR grade TiO_2 and CuO powder (1gm) will be crushed separately in agate type mortor –pestel for ½ hour.

b) **Preparation of electrode pattern PCB**

A Comb type structure is drawn and painted on a suitable size copper clad and etched with concentrated $FeCl_3$ solution to obtain a microelectrode pattern.

c) **Preparation steps of thick films**

AR grade powder of each base material was grinded for 1/2 hours. 0.5 gm of grinded powder was taken in petry dish. Few drops of distilled water were well mixed with grinded powder so as to form a paste. The paste so obtained was applied on comb type micro electrode on printed circuit board in 4 x 2 cm dimension by using a suitable brush to form a thick film. The thick films of various percentage of base materials TiO_2 and CuO were prepared as tabulated below.

No.	Thick films
1	**CuO (100%)**
2	**TiO_2 (75%)+ CuO (25%)**
3	**TiO_2 (50%)+ CuO (50%)**
4	**TiO_2 (25%)+ CuO (75%)**
5	**TiO_2 (100%)**

d) **characteristics of all prepared thick films**

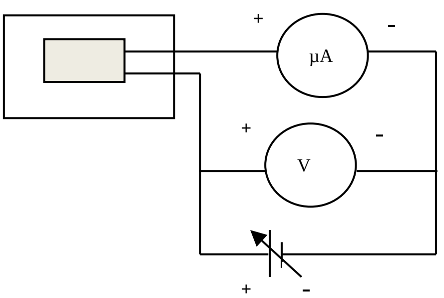

Fig. 1: I-V characteristics circuit diagram (two probe method)

The I-V characteristic of the prepared CuO (100%) thick films was investigated with the help of simple lab prepared two probe method. Fig. 1 shows circuit diagram of I-V characteristics set up (two probe method).

e) Acetone, Ethanol, Methanol and CO + CO_2 sensing properties of all prepared thick films

The fumes (gas) sensitivity experiment was performed in lab prepared static gas sensing unit (fig. (2)) at room temperature. Each film was kept in the closed environment of 500 ml beaker and exposed to 20 ml fumes of acetone, ethanol, methanol and CO + CO_2 respectively and sensitivity is recorded.

Fig. 2: Lab prepared static gas sensing unit

3 Characterizations, Results and Discussions:

I-V characteristics of all the prepared thick films:

The I-V characteristics of all prepared thick films were investigated with the help of simple lab prepared two probe method as mentioned above. The I-V characteristics of prepared thick films of CuO (100%), TiO_2(100%), TiO_2 (50%) + CuO (50%), TiO_2 (75%)+ CuO (25%) and TiO_2 (25%) + CuO(75%) are shown in fig. 3, 4, 5, 6 and 7 respectively. Resistance per square cm of all the films are calculated from the slopes of the respective graphs of the films and tabulated as follows –

No.	Thick films	Resistance
1	**CuO (100%)**	**39.40 Ω/cm^2**
2	**TiO_2 (75%)+ CuO (25%)**	**190476 Ω/cm^2**
3	**TiO_2 (50%)+ CuO (50%)**	**1264.05 Ω/cm^2**
4	**TiO_2 (25%)+ CuO (75%)**	**537414 Ω/cm^2**
5	**TiO_2 (100%)**	**588.74 Ω/cm^2**

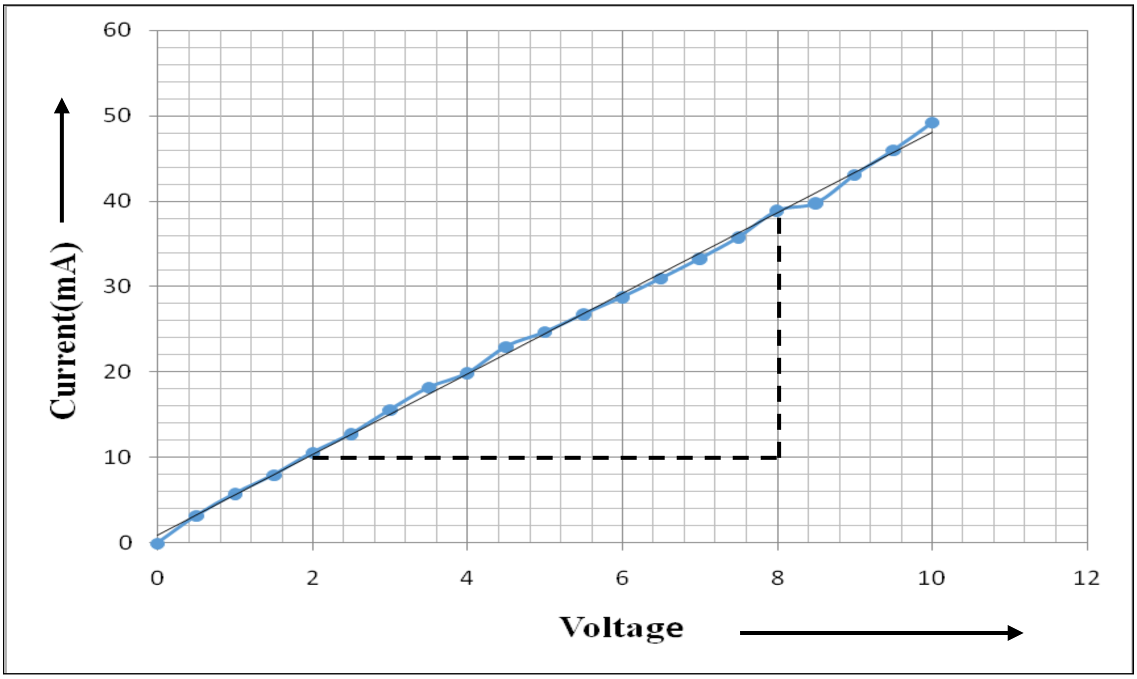

Fig. 3: I-V Characteristics of CuO (100%) thick film

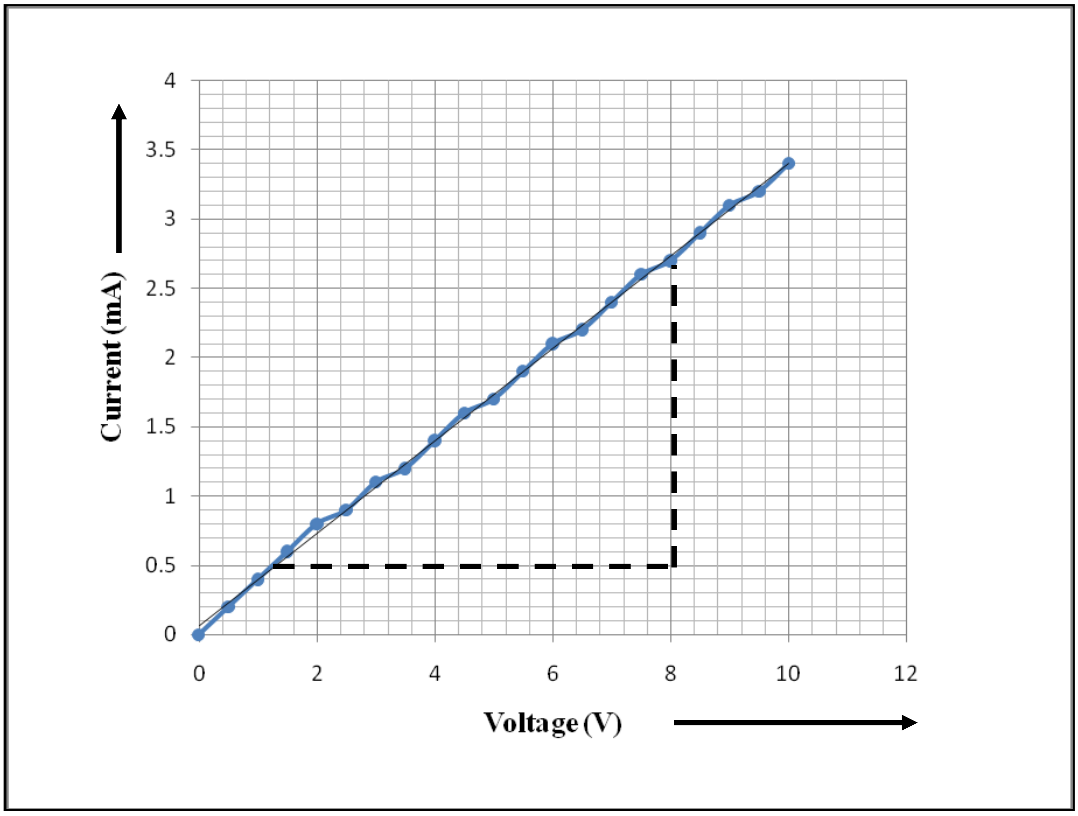

Fig. 4: I-V Characteristics of TiO_2 (100%) thick film

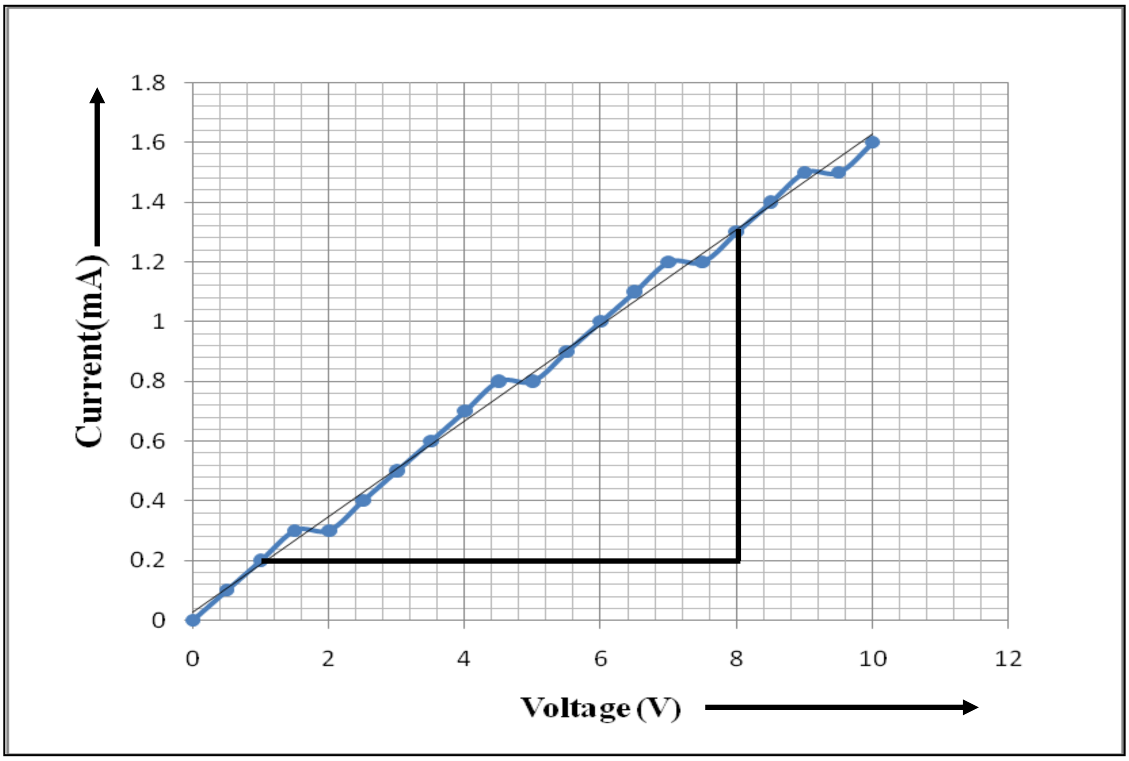

Fig.5: I-V Characteristics of TiO_2 (50%) + CuO (50%) thick film

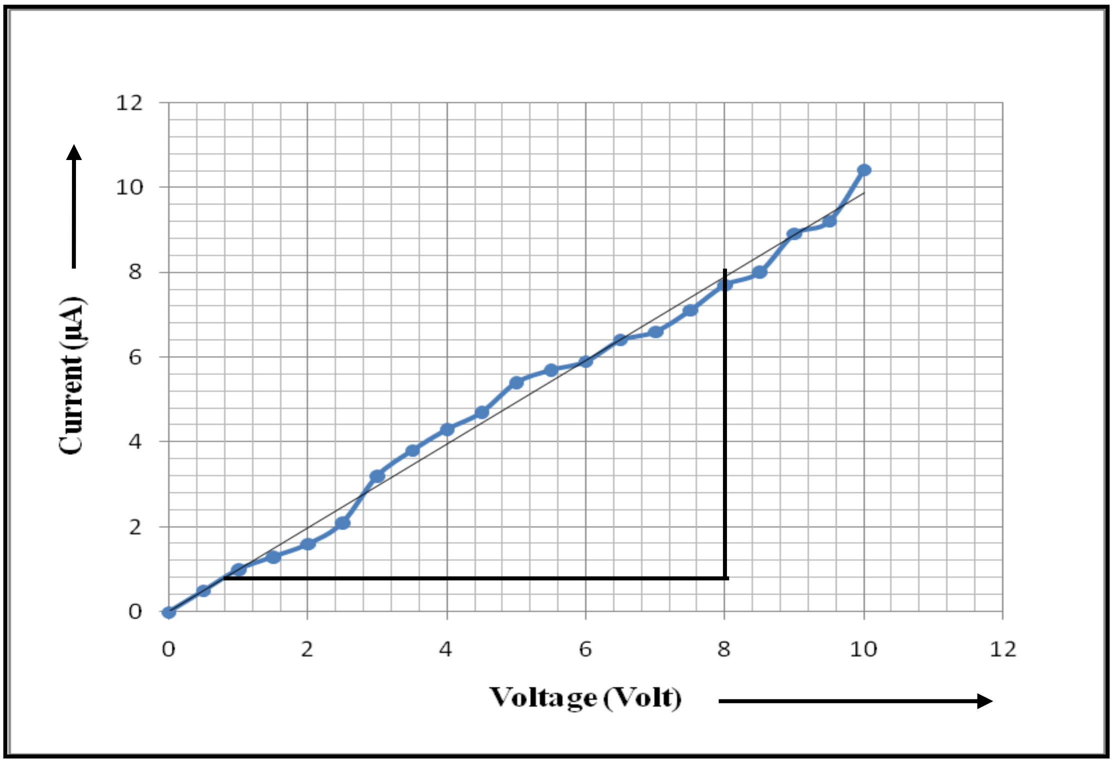

Fig. 6: I-V Characteristics of TiO_2 (75%) + CuO (25%) thick film

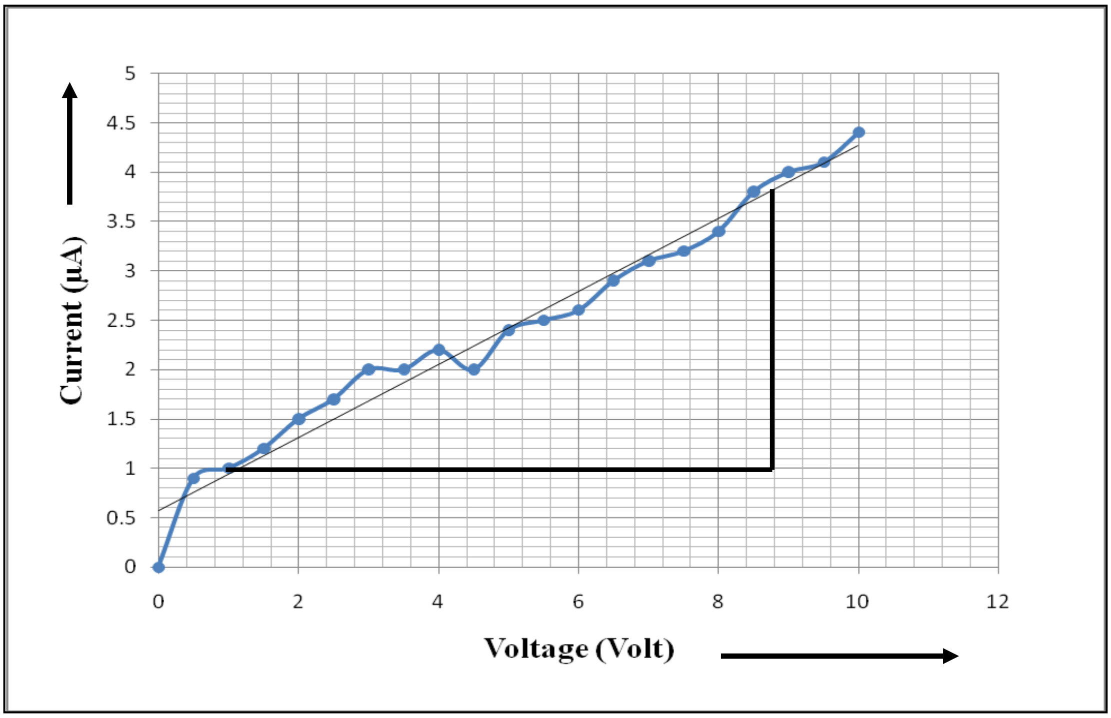

Fig. 7: I-V Characteristics of TiO_2 (25%) + CuO (75%) thick

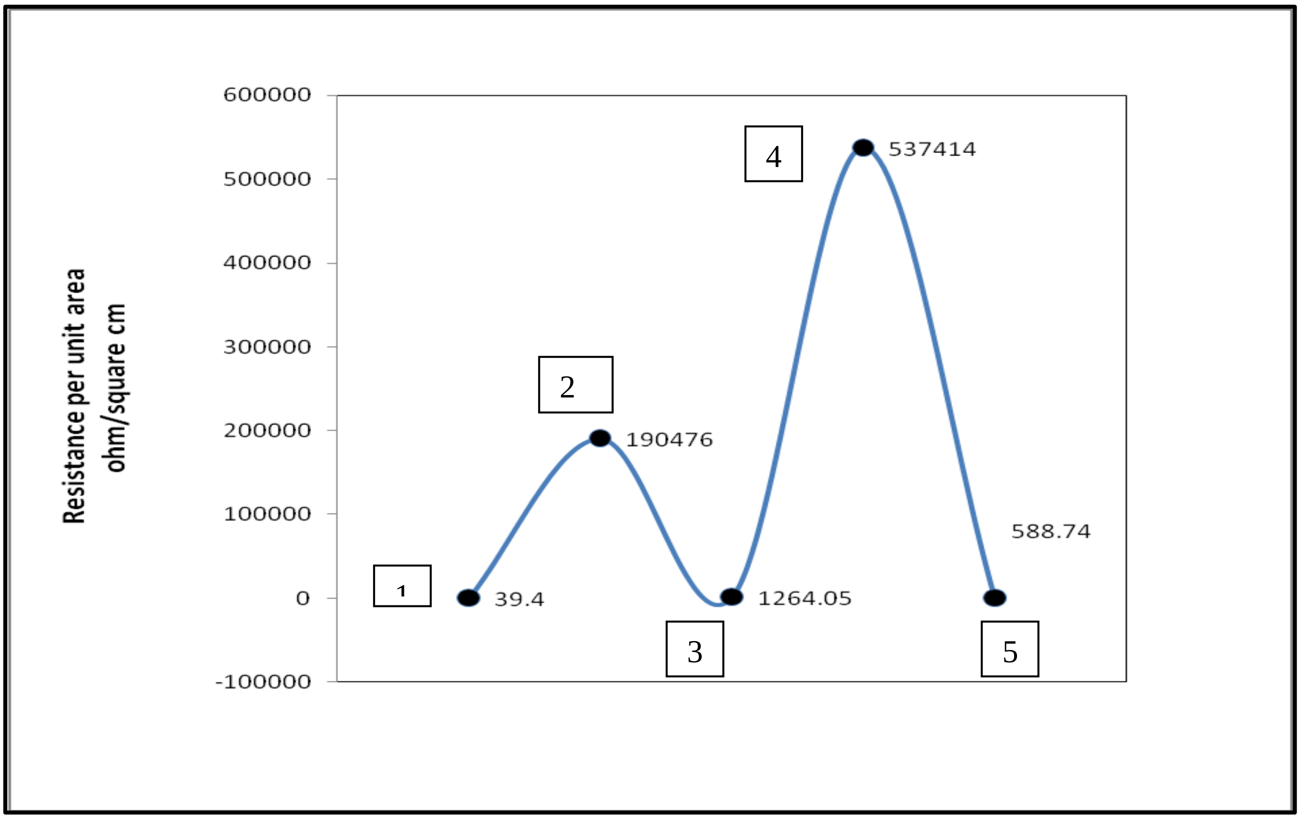

Fig.8: Variation in the resistance value per unit area of the film with different percentage of TiO_2 and CuO

Fig. 8 shows variation in resistance value per unit area of the film as per various percentages.

- It is found that prepared film of CuO (100%) has resistance 39.40 Ω/cm^2 whereas prepared film of TiO_2 (100%) has resistance 588.74 Ω/cm^2.
- The resistance of the prepared film of combination TiO_2 (75%) + CuO (25%) and TiO_2 (25%) + CuO (75%) is found to be 190476 Ω/cm^2 and 537414 Ω/cm^2 , which is very high as compared pure CuO and TiO_2 films.
- The resistance of the prepared film of combination TiO_2 (50%) + CuO (50%) is found again to decrease to moderate value and is equal to 1264.05 Ω/cm^2.

Gas sensing characteristics of all the prepared thick films

Preparing gas sensor element working at room temperature is very important as using all the sensor elements at room temperature is convenient and leads to power saving and cost saving [20-21]. In our work, gas sensing properties of all the prepared thick films were investigated at room temperature. Each film was exposed to 20 ml fumes of acetone, ethanol, methanol and CO + CO_2 respectively. After exposure, resistance change was noted to calculate sensitivity of the film to the particular fumes. The formula used to calculate sensitivity is,

$$S\ (\%) = \frac{\text{Resistance before expouser} - \text{Resistance after expouser}}{\text{Resistance before expouser}} \text{x100}$$

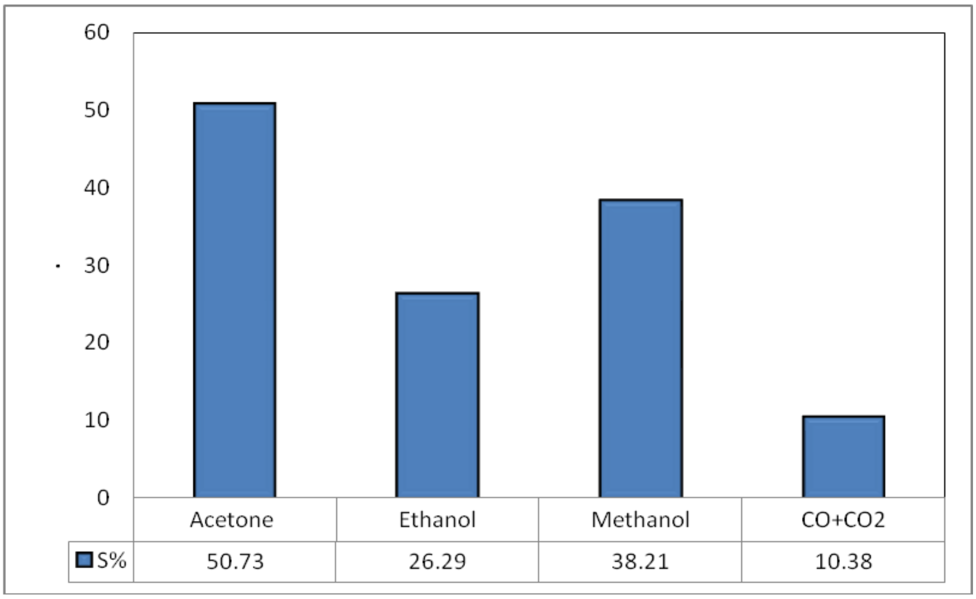

Fig.9: Percentage Sensitivity shown by CuO (100%) thick film when exposed to (20ml) fumes of different gases

Fig. 9 shows percentage sensitivity of CuO (100%) thick film when exposed to (20ml) fumes of different gases. The CuO (100%) thick film shows highest sensitivity to Acetone fumes (50.73%) as compared to fumes of ethanol, methanol and CO + CO_2.

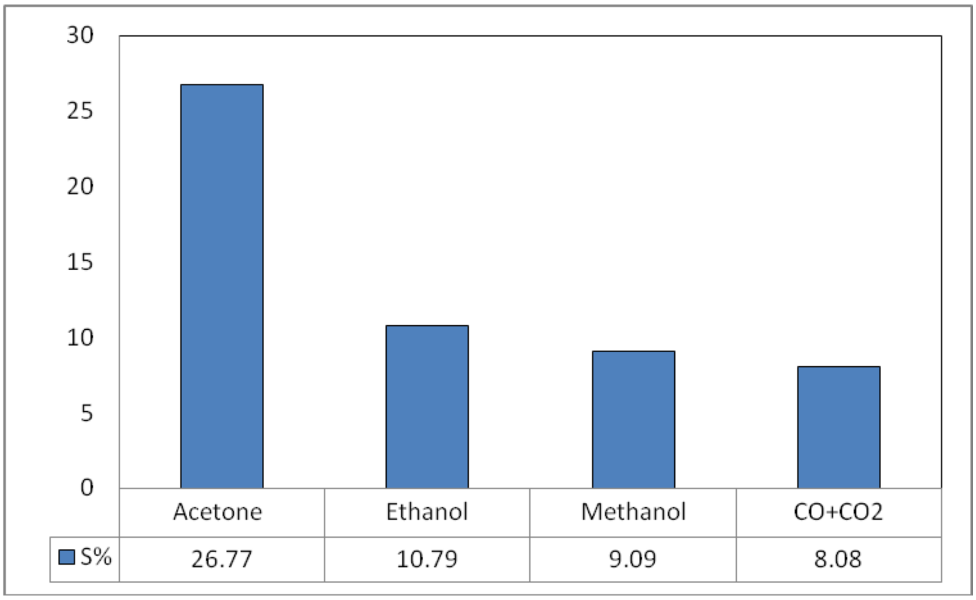

Fig. 10: Percentage Sensitivity shown by TiO_2 (100%) thick film when exposed to (20ml) fumes of different gases

Fig. 10 shows percentage sensitivity of TiO_2 (100%) thick film when exposed to (20ml) fumes of different gases. The TiO_2 (100%) thick film shows highest sensitivity to Acetone fumes (26.77%) as compared to fumes of ethanol, methanol and CO + CO_2.

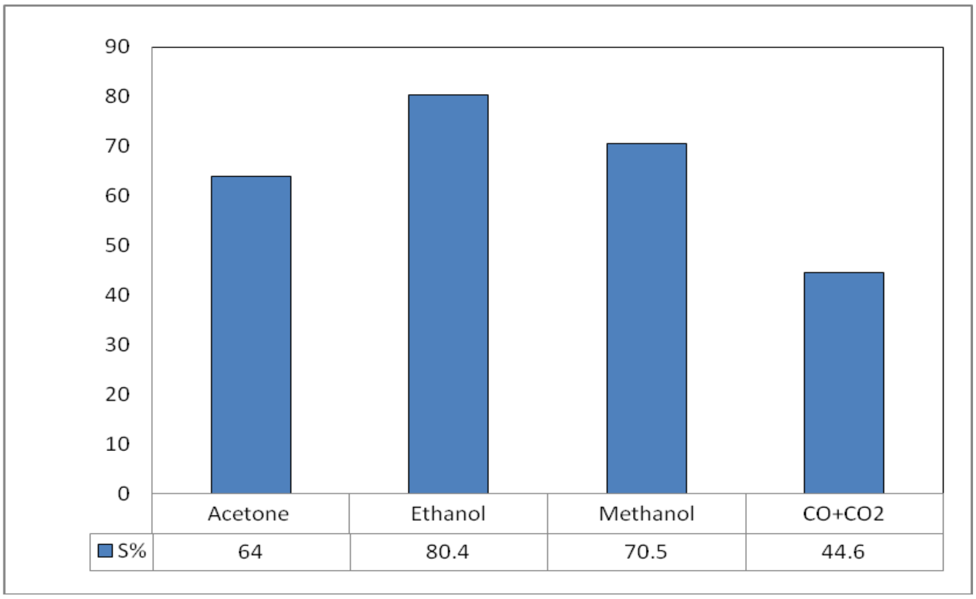

Fig. 11: Percentage Sensitivity shown by TiO_2 (75%) + CuO (25%) thick film when exposed to (20ml) fumes of different gases

Fig. 11 shows percentage sensitivity of TiO_2 (75%) + CuO (25%) thick film when exposed to (20ml) fumes of different gases. The TiO_2 (75%) + CuO (25%) thick film shows highest sensitivity to Ethanol fumes (80.4%) as compared to fumes of acetone, methanol and CO + CO_2.

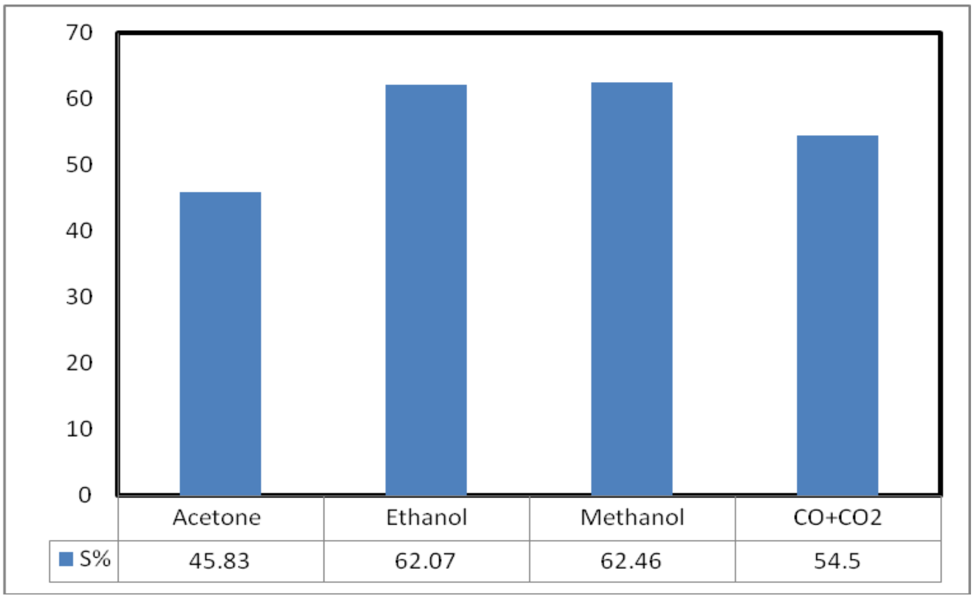

Fig. 12: Percentage Sensitivity shown by TiO_2 (25%) + CuO (75%) thick film when exposed to (20ml) fumes of different gases

Fig. 12 shows percentage sensitivity of TiO_2 (25%) + CuO (75%) thick film when exposed to (20ml) fumes of different gases. The TiO_2 (25%) + CuO (75%) thick film shows almost same sensitivity to methanol as well as ethanol fumes (~ 62 %) and higher as compared to fumes of acetone and CO + CO_2.

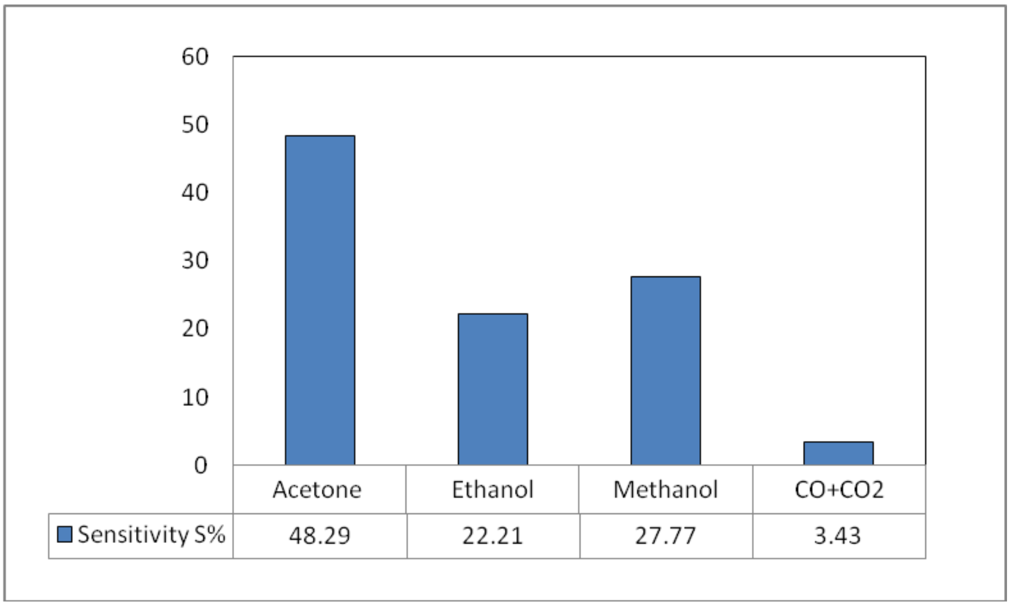

Fig. 13: Percentage Sensitivity shown by TiO_2 (50%) + CuO (50%) thick film when exposed to (20ml) fumes of different gases

Fig. 13 shows percentage sensitivity of TiO_2 (50%) + CuO (50%) thick film when exposed to (20ml) fumes of different gases. The TiO_2 (50%) + CuO (50%) thick film shows highest sensitivity to acetone fumes (48.29 %) and higher as compared to fumes of ethanol, methanol and CO + CO_2.

Conclusions:

1. The thick films of CuO (100%), TiO_2 (100%), TiO_2 (75%) + CuO (25%), TiO_2 (25%) + CuO (75%) and TiO_2 (50%) + CuO (50%) can be prepared on electrode pattern PCB.
2. I-V characteristics of all the prepared thick films can be investigated.
3. Resistance of each film can be calculated from IV characteristics of each film.
4. It is found that prepared film of CuO (100%) has resistance 39.40 Ω/cm^2 whereas prepared film of TiO_2 (100%) has resistance 588.74 Ω/cm^2.
5. The resistance of the prepared film of combination TiO_2 (75%) + CuO (25%) and TiO_2 (25%) + CuO (75%) is found to be 190476 Ω/cm^2 and 537414 Ω/cm^2 , which is very high as compared pure CuO and TiO_2 films.
6. The resistance of the prepared film of combination TiO_2 (50%) + CuO (50%) is found again to decrease to moderate value and is equal to 1264.05 Ω/cm^2.
7. Gas sensing properties of all the prepared thick films can be investigated.

Acknowledgment:

The authors gratefully acknowledge the support provided by the Research lab, Department of Physics, G. D. M. Arts, K.R.N. Commerce, and M. D. Science College, Jamner Dist. Jalgaon

References:

1. Synthesis and Characterization of CuO, TiO2, and CuO-TiO2 Mixed Oxide by a Modified Oxalate Route, E. P. Etape et. All., Jour. of Applied Chemistry 2017, pp 1-10
2. Green Synthesis of CuO-TiO2 Nanoparticles for the Degradation of Organic Pollutants: Physical, Optical and Electrochemical Properties, D. A. Bopape and et. all, Catalysts 2023, 13, 163 pp 1-20
3. Electrical and Optical Properties of Germanium-Doped Zinc Oxide Thin Films, Makoto Arita, Mayu Yamaguchi and Masataka Masuda, Materials Transactions, Vol. 45, No. 11 (2004) pp. 3180 to 3183.
4. Synthesis and characterization of nano-CuO and CuO/TiO2 photocatalysts, T H Nguyen et al, Advances in Natural Sciences: Nanoscience and Nanotechnology, 4 (2013), 025002, 1-6.
5. Nickel-Oxide Based Thick-Film Gas Sensors for Volatile Organic Compound Detection, S. K. Ayyala and J. A. Covington, Chemosensors, 2021, 9, 247-257
6. Acetone vapour sensing properties of screen printed WO3 thick films, R. S. Khadayate, J. V. Sali and P. P. Patl, Talanta 72 (2007) 1077–1081
7. Effect of Firing Temperature on Humidity Sensing Properties of SnO_2 Thick Film Resistor R. Y. Borse, Sensors and Transducers, Vol. 111, Issue 12, December 2009, pp. 155-165
8. Applications of V_2O_5-ZnO Nanocomposite for Humidity sensing studies, Narendra Kumar Pandey, International Journal of material science and applications,2017:6(3):119-125
9. Synthesis Characterization and Sensing properties of AZO and IZO nanomaterials, Moktar Hgiri, Chemosensors,2014,2, pp 121-130
10. ZnO and TiO_2 Nanocomposite characterization and moisture sensing studies, N. K. Pandey, et. all, Bull. mater Science, Vol. 3 june 2012, pp 347-352
11. Humidity Sensors Based On Nanostructured Ferric Oxide Thick Flims, Richa Shrivastav. etc all, International Journal of Green Nanotechnology,4:215-218,2012.
12. Study of CuO-TiO_2 composite thick film as gas sensor for ammonia gas (NH_3), Vidyabharati International Interdisciplinary Research Journal March 2021, 12(1) 150-156.

13. TiO_2 thick films: Preparation and Characterization, Rohit Janjal and R. S. Khadayate, Journal of Engineering Sciences, Vol 11, Issue 5, May 2020, p 490-492.
14. SnO_2 and SnO_2-AgO thick films: Preparation and Characterization, R. S. Khadayate et all., Journal of Engineering Sciences, Vol 11, Issue 5, May 2020, pp 499-502.
15. Resistance based Humidity sensing properties of TiO_2, B. C. Yadav etc all, Sensors & Transducers Journal, Vol.81, Issue 7, July 2007, pp. 1348-1353.
16. Nanostructured Metal Oxide Based Thick Film Sensors, Sharada N. Ohatkar, Sunit B. Rane and et. all., International Journal of Latest Technology in Engineering, Management & Applied Science, May 2016, Volume V, Issue V, pp 93-97.
17. Recent Advances in thick film resistors and target applications, Tetsuya Sumida, IEEE Power Electronic Magazine, March 2022, pp 70-72.
18. Studies on electrical properties of polymer thick film resistors, Y. Srinivasa Rao, Microelectronics International 24, 1 (2007) 8–14.
19. Electrical and Structural Properties of WO_3-SnO_2 Thick-Film resistors Prepared by Screen Printing Technique, Garde A. S., Research Journal of Recent Sciences January **(2015),** Vol. **4(1),** 55-61.
20. Synthesis of Tin Oxide Thick Film and Its Investigation as a LPG Sensor at Room Temperature, T. Shukla, Journal of Sensor Technology, 2012, 2, pp 102-108.
21. Room Temperature Chemiresistive Gas Sensors Based on 2D MXenes, Ali Mirzaei, Myoung Hoon Lee, Haniyeh Safaeian and et. all, Sensors 2023, 23, 8829, pp 1-33.