

Synthesis, Characterization and Development of Opto-Electronic Humidity Sensor using Copper Oxide Thin Film

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Abstract: The present paper reports the study of modulation in light transmitted through nanostructured cupric oxide thin films with the exposure of moisture at room temperature. For this purpose the precursor of CuO was prepared and was then investigated using SEM and UV-visible absorption techniques. SEM showed the porous nature of the material and energy band-gaps were estimated as 2.8-3.2 eV for different concentrations by UV-Vis spectrophotometer. The precursor of CuO in the form of gel was prepared and later used for the deposition of thin film on borosilicate substrates with dimensions 1.5×1.5 cm² using sol-gel spin coating technique. The film was employed as transmission based opto-electronic humidity sensor. Maximum sensitivity was found 0.85 μW/%RH. As the investigated opto-electronic sensor has remote access capability, therefore, may be used to replace an electrical humidity sensor.

Keywords: Nanostructure, opto-electronic humidity sensor, sol-gel spin coating, cupric oxide.

I. INTRODUCTION

In recent years advancements in sensor manufacturing technologies have driven by post-process high-speed, low-power and low-cost microelectronic hybrid circuits [1-3], modern signal conditioning methods and progress in miniaturization technologies [4-5] product reliability. Furthermore, it is vital to know the degree of efficiency of each sensor related to its calibration circumstances and sensing mechanism [6-7]. Today, simulation techniques and design aids are adequately used to predict and improve output data prior to implementation of mass production processes to save time and enhance quality [10-11]. Miniaturization of sensor devices offers numerous advantages such as low hysteresis [5], batch fabrication [12], and ease of packaging/integration along with the corresponding cost reductions [13-16].

It is well documented that humidity plays a significant role in every part of the Earth including biology and automated industrial processes. To have a desirable surrounding atmosphere, it is essential to monitor, detect and control the ambient humidity under different conditions ranging from low temperature to high or in mixtures with other gases by precise and provident sensors [17-18]. Utilization in intelligent systems and networks as monitoring sensors to determine the soil moisture during irrigation in agriculture, or for diagnosis of corrosion and erosion in infrastructures and civil engineering are among the major applications of humidity sensors [19]. In fact, the need for protection of environmental conditions has been leading to extensions in various humidity sensor developments based on the use of physical and chemical methods in presence of organic, inorganic or hybrid materials since long back [20-21]. Advancement of humidity sensor systems encompasses enhanced efforts in betterment of transducer performance such as sensing elements [22], structure design [23-24], principle of mechanism [25-26], and

fabrication technologies [27]. In this milieu, the transducer materials are the key features, followed by the availability of suitable manufacturing technologies, free choice of device geometrical properties to attain the required dimensional efficiencies, optimization of surface for the occurrence of conductance, ease of production flow and investment expenses.

Copper (II) oxide or cupric oxide (CuO) is the higher oxide of copper. As a mineral, it is known as tenorite. It is a black solid with an ionic structure which melts above 1200°C with some loss of oxygen. Copper (II) oxide belongs to the monoclinic crystal system, with a crystallographic point group of 2/m or C2h. The space group of its unit cell is C2/c, and its lattice parameters are a = 4.6837(5), b = 3.4226(5), c = 5.1288(6), α = 90°, β = 99.54(1)°, γ = 90°. The copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration [28].

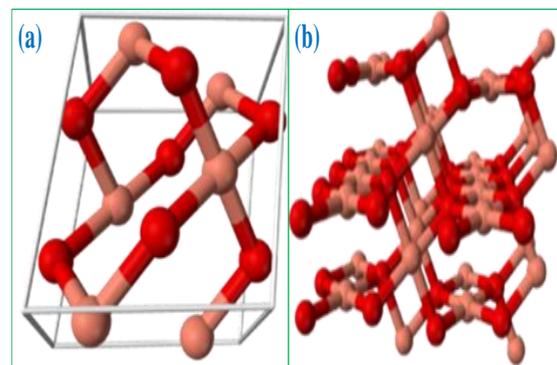


Fig. 1 CuO (a) Unit cell (b) Crystal structure

CuO has molar mass 79.545 g/mol and density 6.315 g/cm³. Its melting point and boiling points are 1326 °C and

200 nm-1100 nm. The UV-Vis photospectra of solution of CuO nanopowder in ethanol was recorded with respect to ethanol placed in the reference beam using single beam spectrophotometer. The spectra were analyzed [34] by plotting $(\alpha hv)^2$ vs hv , based on eq.

$$\alpha hv = A (hv - E_g)^{n/2}$$

Where, α is absorption coefficient, A is a constant and n is the exponent that depends upon the quantum selection rules for the particular material. Here the value of n is taken as $\frac{1}{2}$ showing the direct allowed type transition. A straight line is obtained when $(\alpha hv)^2$ is plotted against photon energy (hv), which indicates that the absorption edge is due to a direct allowed transition. The intercept of the straight line on hv axis corresponds to the optical band gap (E_g). The absorption spectra and optical band gap for different concentrations are shown in Fig. 3 and 4 respectively.

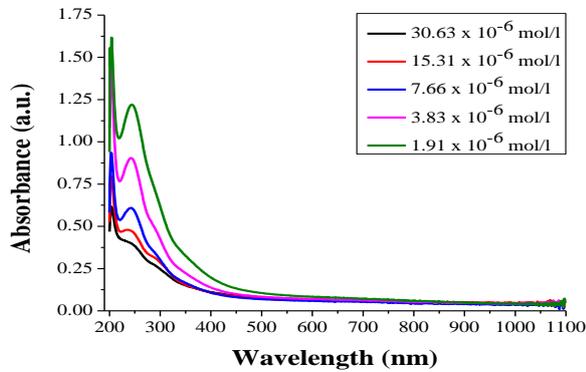


Fig. 3 Plot of absorption vs. wavelength for CuO-ethanol solution at different concentrations.

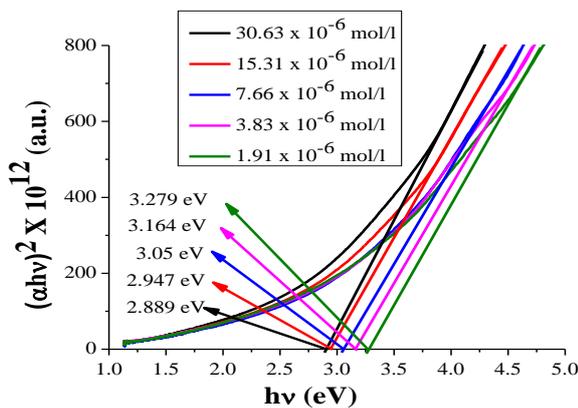


Fig. 4 Plot of $(\alpha hv)^2$ vs. hv for CuO - ethanol solution at different concentrations

Concentration (mol/l)	Optical Band gap (eV)
30.63×10^{-6}	2.89
15.31×10^{-6}	2.947
7.66×10^{-6}	3.05
3.83×10^{-6}	3.164
1.91×10^{-6}	3.279

Table I: Variation of optical band gap for different concentrations.

Variations of optical band gap for different concentrations are depicted in Table1 and it can be observed that as the concentration decreases the optical band gap increases.

IV. DEVICE ASSEMBLY

Fig.5 represents the schematic layout of the device [35] used. Humidity controlled chamber was designed in our laboratory using transparent glass, inside which hygrometer and humidifier/dehumidifier dish were placed and the film was fixed on the opposite wall of the chamber. A 2 mW He-Ne laser was used as input light source, the beam of which was expanded using beam expander having power 10X and allowed to fall on the whole surface of the sensing film. The light beam coming out from the humidity chamber was converged through a lens combination to an optical power meter. The change in light intensity with respect to change in relative humidity inside the chamber was then measured for an interval of 5 %RH. Saturated aqueous solution of K_2SO_4 was used as humidifier for increasing the %RH from 10 to 90 whereas saturated aqueous solution of KOH was used as dehumidifier to decrease the humidity inside the chamber from 90 to 10 %RH.

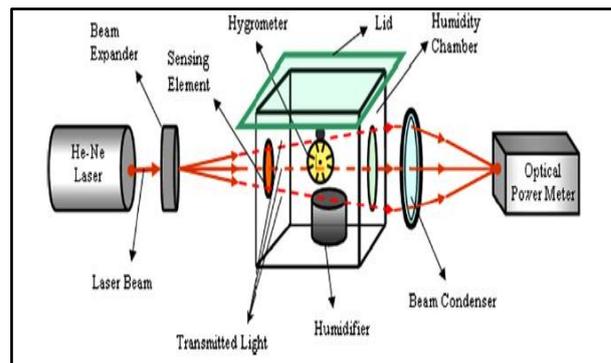


Fig.5 Device assembly for the study of opto-electronic humidity sensing

V. OBSERVATION

Fig. 6 shows the response of the humidity sensing film with the change in %RH inside the humidity chamber. Curve 'a' shows the linear decrease in transmitted power with increase in %RH; however, the Curve 'b' shows the increase in transmitted power with the decrease in %RH. While performing the decreasing mode of %RH, the ending values of optical powers were found to be reduced. Sensitivity of sensor was calculated using the following formula[36]:

$$\text{Sensitivity} = \frac{\text{Change in Output power}}{\text{Corresponding change in \%RH}}$$

$$S = \frac{\Delta I_t}{\Delta \%RH} \mu W / \%RH$$

The sensitivity obtained here for increasing mode of %RH is $0.85 \mu W / \%RH$ and the hysteresis obtained is 15%.

VI. RESULT & DISCUSSION

The humidity sensing characteristics of CuO based sensing film deposited on a plane transparent borosilicate glass

substrate were studied and variations in optical transmitted power with the variation of %RH were recorded. The corresponding data were plotted in Fig. 6. The modulation in the light intensity transmitted out from the sensing film was mainly due to the variation in refractive index and thickness of the film with the variation in %RH. Depending upon the surface morphology, the sensing mechanism is based on adsorption of water vapor and capillary condensation as shown in Fig.7 [37]. The range of %RH can be divided into three regions viz. dry (below 40%RH), medium (40-70%RH) and very humid (above 70%RH). Initially the cupric oxide film was free from water molecules, having only dry air in its pores. When exposed to low humidity, adsorption of water vapor takes place rapidly on the surface of film. Due to highly electropositive nature of metal ion at metal oxide surface of the sensing element, it has tendency to break one of the O-H bonds of H₂O to form a strong chemical bond between M⁺ and OH⁻. Thus initial layer is chemisorbed and in this layer output power starts decreasing due to the bending of light. As the %RH increases, adsorption on the surface increases. However, in mid humid region of 40-70 %RH, adsorption takes place on the surface as well as on the walls of capillaries, leading to a further decrease in the output power at detector. In very humid region the condensation of water vapor takes place through the capillaries and forms a meniscus in the capillaries of the film. Therefore in this region, the output power decreases stridently. Moisture detection would depend significantly on the porosity and thickness of the deposited film, as the extent of adsorption of water vapor causes the increase in refractive index of the film.

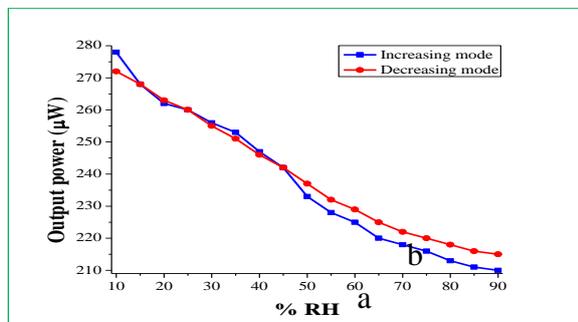


Fig. 6 Variation of the output power with increasing and decreasing %RH

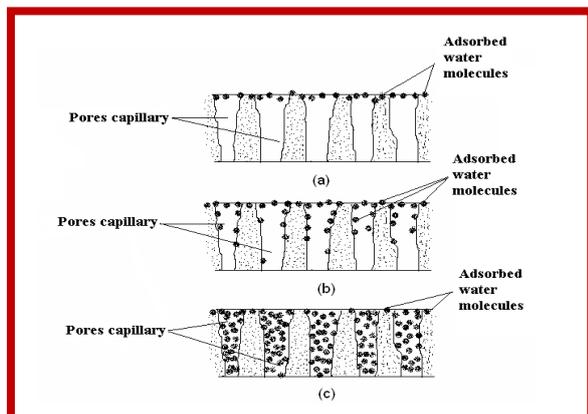


Fig. 7 Water adsorption mechanism on the film surface

VII. CONCLUSION

The present study, thus, leads to the conclusion that CuO thin films prepared by sol-gel spin coating technique can be employed as an optoelectronic humidity sensor based on the modulation in output power of light transmitted through the sensing element. SEM exhibited that the material being porous had sufficient adsorption sites to attract the moisture. Optical band gap of the material measured by UV-Vis spectrophotometer was in the range of 2.8-3.2 eV. The sensitivity of sensor was found as 0.85 µW/%RH. The remote access capability of such type of sensor based on CuO nanoparticles would be very useful for futuristic development of humidity sensor. Work is under investigation.

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REFERENCES

- [1] H. L. Penman, Humidity, The Institute of Physics, London, 1955.
- [2] F. W. Gole, Introduction to Meteorology, John Wiley & Sons Inc., New York, 1970.
- [3] G. J. Visscher, "Standard Psychrometers: a matter of preferences," Meas. Sci. Technology, vol. 6, pp. 1451-1461, 1995.
- [4] Z. M. Rittersma, "Recent Achievements in Miniaturized Humidity Sensors-A Review of Transduction Techniques," Sens. Actuators A: Phys., vol. 96, pp. 196-210, 2002.
- [5] H. Farahani, R. Wagiran and Mohd N. Hamidon, "Humidity Sensors Principle, Mechanism, and Fabrication Technologies: A Comprehensive Review", Sens. Actuators, vol.14, pp.7881-7939, 2014.
- [6] L. J. Golonka, B. W. Licznarski, K. Nitsch, H. Terycz, "Thick Film Humidity Sensors," Meas. Sci. Technology, vol. 8, pp. 92-98, 1997.
- [7] E. Traversa, "Ceramic Sensors for Humidity Detection: the State of the Art and Future Developments," Sens. Actuators B: Chem., vol. 23, pp. 1335-1356, 1995.
- [8] W. Qu, R. Green, M. Austin, "Development of Multi-Functional Sensors in Thick-Film and Thin-Film Technology," Meas. Sci. Technology, vol. 11, pp. 1111-1118, 2000.
- [9] Y. Shimizu, H. Arai, T. Seiyama, "Theoretical Studies on the Impedance-Humidity Characteristics of Ceramic Humidity Sensors", Sens. Actuators vol.7, pp.11-22, 1985.
- [10] R. Buchhold, A. Nakladal, G. Gerlach, P. Neumann, "Design Studies on Piezoresistive Humidity Sensors," Sens. Actuators B: Chem., vol. 53, pp. 1-7, 1998.
- [11] N. T. T. Ha, D. K. An, P. V. Phong, P. T. N. Hoa, L. H. Mai, "Study and Performance of Humidity Sensor Based on the Mechanical-Optoelectronic Principle for the Measurement and Control of Humidity in Storehouses," Sens. Actuators B: Chem., vol. 66, pp. 200-202, 2000.
- [12] F. Pascal-Delannoy, B. Sorli, A. Boyer, Quartz Crystal Microbalance (QCM) Used as Humidity Sensor," Sens. Actuators A: Phys., vol. 84, pp. 285-291, 2000.
- [13] J. Reibel, U. Stahl, T. Wessa, M. Rap, "Gas Analysis with SAW Sensor Systems," Sens. Actuators B: Chem., vol. 65, pp. 173-175, 2000.
- [14] E. T. Zellers, M. Morishita, Q. C. Cai, "Evaluating Porous Layer Open-Tubular Capillaries as Vapor Preconcentrators in a Microanalytical System," Sens. Actuators B: Chem., vol. 67, pp. 244-253, 2000.
- [15] C. Barriain, R. Matias, F. J. Arregui, M. Amo, "Optical Fiber Humidity Sensor Based on a Tapered Fiber Coated with Agarose Gel," Sens. Actuators B: Chem., vol. 69, pp. 127-131, 2000.
- [16] F. Arregui, Y. Liu, R. Matias, R. "Claus, Optical Fiber Humidity Sensor Using a Nano Fabry-Perrot Cavity Formed by the Ionic

Self-Assembled Method," *Sens. Actuators B: Chem.*, vol. 59, pp. 54-59, 1999.

- [17] B.C. Gupta, Ratnanjali, "A Novel Probe for a Fiber Optic Humidity Sensor," *Sens. Actuators B: Chem.*, vol. 80, pp. 132-135, 2001.
- [18] M. Kimura, "A New Method to Measure the Absolute Humidity Independently of the Ambient Temperature," *The 8th International Conference on Solid-State, Sensors and Actuators (TRANSDUCERS'95)*, vol. 119, pp. 843-846, 1995.
- [19] D. Lee, H. Hong, C. Park, G. Kim, Y. Jeon, J. Bu, "A Micromachined Robust Humidity Sensor for Harsh Environment Applications," *The 14th IEEE International Conference on Micro Electro Mechanical Systems (MEMS 2001)*, pp. 558-561, 2001.
- [20] D. Lee, H. Hong, C. Park, G. Kim, Y. Jeon, J. Bu, "A Micromachined Robust Humidity Sensor for Harsh Environment Applications," *The 14th IEEE International Conference on Micro Electro Mechanical Systems (MEMS 2001)*, pp. 558-561, Jan. 2001.
- [21] W. Qu, W. Wlodarski, "A Thin-film Sensing Element for Ozone, Humidity and Temperature," *Sens. Actuators B: Chem.*, vol. 64, pp. 42-48, 2000.
- [22] W. Qu, J. Meyer, "A Novel Thick Film Humidity Sensor," *Sens. Actuators B: Chem.*, vol. 40, pp. 175-182, 1997.
- [23] K. K. Dey, D. Bhatnagar, A. K. Srivastava, M. Wan, S. Singh, R. R. Yadav, B. C. Yadav and M. Deepa, "VO₂ nanorods for efficient performance in thermal fluids and sensors," *Nanoscale*, vol. 7, pp. 6159-6172, Feb. 2015.
- [24] N. Serin, T. Serin, B. Unal, "The Effect of Humidity on Electronic Conductivity of an Au/CuO/Cu₂O/Cu Sandwich Structure," *Semicond. Sci. Technology*, vol. 15, pp.112-116, 2000.
- [25] B. C. Yadav, "Sol-gel processed Titania films on prism substrates as an Optical Moisture Sensors," *Sensors & Transducers J.*, vol.79, pp. 1217-1224, Issue 5, 2007.
- [26] B. C. Yadav, R. Srivastava, C. D. Dwivedi and P. Pramanik, "Moisture sensor based ZnO nanomaterial synthesized through oxalate route," *Sens. Actuators B: Chem.*, vol.130, 2, pp. 216-222, vol.131, 2008.
- [27] A. K. Jaiswal, S. Singh, A. Singh, R. R. Yadav, P. Tandon and B. C. Yadav, "Fabrication of novel Cu/Pd bimetallic nanostructures with high gas sorption ability towards development of LPG sensor," *Materials Chemistry Physics*, vol.154, pp. 16-21, Jan. 2015.
- [28] [http://en.wikipedia.org/wiki/Copper\(II\)_oxide](http://en.wikipedia.org/wiki/Copper(II)_oxide).
- [29] S. Singh, N. Verma, A. Singh, B. C. Yadav, "Synthesis and characterization of CuO-SnO₂ nanocomposite and its application as liquefied petroleum gas sensor," *Mat. Sci. in Semicond. Processing*, vol.18C pp.88-96, 2014.
- [30] B. C. Yadav and A. K. Yadav, "Synthesis of nanostructured cuprous oxide and its performance as Humidity and Temperature Sensor," *Int. J. of Green Nanotechnology: Mater. Sci. & Engineering*, vol. 1(01), pp. 16-31, 2009.
- [31] M. Suleiman, M. Mousa, A. Hussein, B. Hammouti, T. B. Hadda, I. Warad, "Copper(II)-oxide Nanostructures: Synthesis, Characterizations and their Applications-Review" *J. Mater. Environ. Sci.*, Vol. 4, pp. 792-797, 2013.
- [32] A. Zainelabdin, G. Amin, S. Zaman, O. Nur, J. Lu, L. Hultman, M. Willander, "CuO/ZnO Nanocorals synthesis via hydrothermal technique: growth mechanism and their application as Humidity Sensor," *J. of Mat. Chemistry*, vol. 23, pp. 11583-11590, 2012.
- [33] N. Serin, T. Serin, B. Unal, "The Effect of Humidity on Electronic Conductivity of an Au/CuO/Cu₂O/Cu Sandwich Structure," *Semicond. Sci. Technology*, vol. 15, 112-116, 2000.
- [34] B. C. Yadav, R. C. Yadav, and P. K. Dwivedi, "Sol-gel processed (Mg-Zn-Ti) oxide nano-composite film deposited on Prism base as an Opto-Electronic Humidity Sensor," *Sens. Actuators B: Chem.*, vol.148, pp. 413-419, 2010.
- [35] B. C. Yadav, R. C. Yadav, S. Singh, P. K. Dwivedi, H. Ryu and S. Kang, "Nanostructured cobalt oxide and cobalt titanate thin films as optical humidity sensor: a new approach," *Opt. Laser Technology*, vol.49 pp. 68-74, 2013.
- [36] S. Sikarwar, B. C. Yadav, "Opto-electronic humidity sensor: A review," *Sens. Actuators A: Phys.*, vol. 233, pp. 54-70, 2015.
- [37] B. C. Yadav, N. Verma and S. Singh, "Nano crystalline SnO₂-TiO₂ thin film deposited on base of equilateral prism as an opto-electronic humidity sensor," *Opt. Laser Technology*, vol. 44 pp. 1681-1688, 2012.

BIOGRAPHIES



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