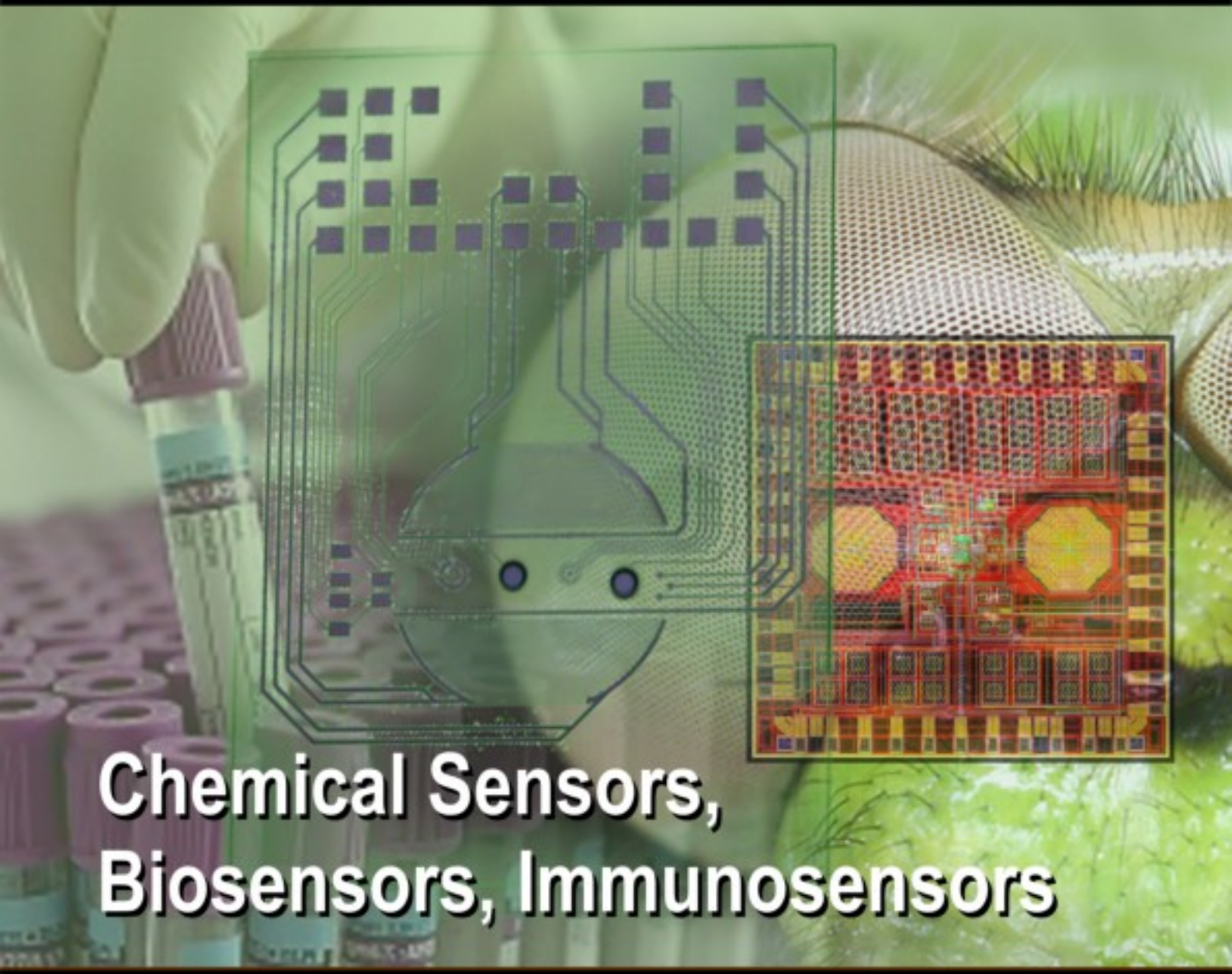
ISSN 1726-5479

SENSORS & TRANSDUCERS

vol. 113
2/10



Chemical Sensors, Biosensors, Immunosensors

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 113, Issue 2, February 2010 | **www.sensorsportal.com** | **ISSN 1726-5479**

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and on CD.

Sensors & Transducers Journal

Contents

Volume 113
Issue 2
February 2010

www.sensorsportal.com

ISSN 1726-5479

Research Articles

Authors are encouraged to submit article in MS Word (doc) and Acrobat (pdf) formats by e-mail: editor@sensorsportal.com
Please visit journal's webpage with preparation instructions: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm

International Frequency Sensor Association (IFSA).

Sensors & Transducers Journal, Vol. 113, Issue 2, February 2010, pp. 48-55

www.sensorsportal.com

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

Humidity Sensing Properties of CuO, ZnO and NiO Composites

Vedhakkani JESEENTHARANI, Boniface JEYARAJ, John PRAGASAM, Arunachalam DAYALAN, *Karachalacheruvu Seetharamaiah NAGARAJA

Department of Chemistry, Loyola Institute of Frontier Energy (LIFE),
Loyola College, Chennai 600 034, India
*Tel.:+91- 44 28178200, fax:+91 44 28175566
E-mail: jeseentha@gmail.com, dr.ksnagaraja@gmail.com

Received: 15 December 2009 /Accepted: 19 February 2010 /Published: 26 February 2010

Abstract: The mixed metal oxides were investigated for humidity sensing properties. The composites were prepared by mixing 1:1 mole ratio of CuO-ZnO, CuO-NiO, and NiO-ZnO compound. The samples sintered at 800 ^{o}C for 5h, were subjected to do resistance measurements as a function of relative humidity (RH) in the range of 5-98 % and the sensitivity factor was calculated. Among the three composites, CuO-NiO compound possessed the highest humidity sensitivity of 2834.8 while the other two possessed a very low sensitivity factor. The response and recovery of the CuO-NiO composites were 650 and 80 s. X-ray diffraction, and scanning electron microscopy (SEM) was employed to identify the structural phases, and surface morphology of the metal oxide compounds. *Copyright © 2010 IFSA.*

Keywords: humidity sensor; solid state electrical conductivity, mixture oxides of Cu, Zn and Ni

1. Introduction

The measurement of humidity has received great attention during the last two decades due to the recognized importance of vapour concentration in many areas such as meteorology, medicine, industry and agriculture. The desirable characteristics of humidity sensors are high sensitivity, good chemical and thermal stability and short response time [1]. A disc-type porous ceramic sensor would offer higher sensitivity towards humidity than a film-type one, probably due to larger capacity towards water adsorption [2, 3]. Bulk ceramic humidity sensors based on porous and sintered oxides have received much attention due to their chemical and physical stability. The relative humidity (RH),

which is the ratio of actual vapour pressure to the saturated vapour pressure at a given temperature, is the most frequently used parameter to specify humidity.

The sensors made from inorganic oxides like iron oxide [4, 6], titanium oxide [5], aluminum oxide and tin oxide [7] have emerged as economic humidity sensors in recent years [4-7]. Materials based on ZnO, CuO, NiO are well studied individually for sensing application. The present study was undertaken for the combination of the oxide materials for sensing applications.

2. Experimental

The composites of CuO-ZnO, CuO-NiO and NiO-ZnO were prepared by mixing the 1:1 mole ratio (Table 1) of the corresponding oxide, grinding under acetone with 2% PVA for about 3 h, and then calcined at 700 ^{o}C for 5 h. The calcined sample was made in the form of cylindrical pellets of dimension 13 mm diameter and 2-3 mm thickness using a hydraulic press at a pressure of 400 MPa. The pellets were then sintered at 800^{o}C for 5 h in ambient air atmosphere. The samples were cooled down to room temperature at the natural cooling rate of the furnace.

Table 1. Sample code, activation energy and sensitivity factor for binary composites.

S. No	Compound	Sample code	Resistance		$S_f = R_{5\%}/R_{98\%}$	Activation Energy, Ea (meV)
			$R_{5\%}$ (Ω)	$R_{98\%}$ (Ω)		
1.	CuO-ZnO	COZO	6.6033×10^{5}	1.8064×10^{5}	3.65±2	25
2.	CuO-NiO	CONO	1.4325×10^{10}	5.0533×10^{6}	2834.8±500	95
3.	NiO-ZnO	NOZO	1.9661×10^{8}	1.991×10^{7}	9.83±4	77

The structural studies were carried out using a Philips X'pert diffractometer for 2θ values ranging from 10 to 80^{o} using Cu Kα radiation at λ = 0.154 nm. The surface morphology of the sintered porous compacts was determined by a Leo-Jeol scanning electron microscope at the desired magnification.

The DC electrical resistance in different humidity levels for the samples in the form of pellets was determined by a two-probe method to measure the changes in surface conductivity as a function of applied field. Conducting silver paste was employed to ensure the ohmic contacts. The samples were electrically connected to a dc power supply and a Keithley 6485 picoammeter in series. Given the high resistivity of the materials under investigation, the potential inaccuracy due to contact resistance is assumed negligible. The controlled humidity environments were achieved using anhydrous P_2O_5 and saturated aqueous solution of $CaCl_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, NH_4Cl, and $CuSO_4 \cdot 5H_2O$ in a closed glass vessel at 298 K, yielded approximately 5, 31, 51, 79, and 98 % as relative humidity (RH) respectively, and was exactly measured with a Barigo hygrometer. Heat cleaning of the samples was found to be a must for better sensitivity. Hence the sample was heated to 373 K, followed by cooling in a humidity-free atmosphere before and after the sensitivity measurements, especially when the sensors were operated at higher RH. The samples were exposed to the respective % of RH until the saturation is reached around 2 h. The sensitivity factor S_f was calculated by the ratio of resistances, $R_{5\%}/R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ were the dc resistances at 5 and 98% RH, respectively. A degassed glass chamber (200 cm^3) was used for the evaluation of response and recovery characteristics. This chamber has a provision for a two-way inlet, one for transpiring dry air from 5% RH and the other for transpiring moist air from a wet candle containing 98% RH. The response and recovery characteristics were studied between 5 and 98% RH conditions. The resistance measurements in dry air as well as in moist air alternatively helped to establish the recovery and response characteristics for moisture sensing.

The temperature dependent resistance experiments were carried out to determine the activation energy of the samples using the linearised form of the expression $I = I_0 \exp^{-Ea/kT}$, where I is the current, E_a the activation energy, k the Boltzmann constant and T the temperature (K). For this purpose the samples were kept inside a cylindrical furnace, which was connected to a microprocessor controlled temperature programmer. The activation energy of the composites was determined from the temperature dependence conductance experiments in the temperature range 120–300 ^{o}C under ambient conditions.

3. Results and Discussion

3.1. X-ray Diffraction Studies

X-ray diffraction patterns of the mixed binary oxides (Fig. 1a-c) showed the peaks corresponding to CuO-NiO, CuO-ZnO and NiO-ZnO respectively. In the XRD patterns, no third phase is formed and the peaks correspond to the metal oxides. The phases CuO (JCPDS: 74-1021, monoclinic), NiO (JCPDS: 75-0197, Cubic) and ZnO (JCPDS: 79-0205, Hexagonal) are identified.

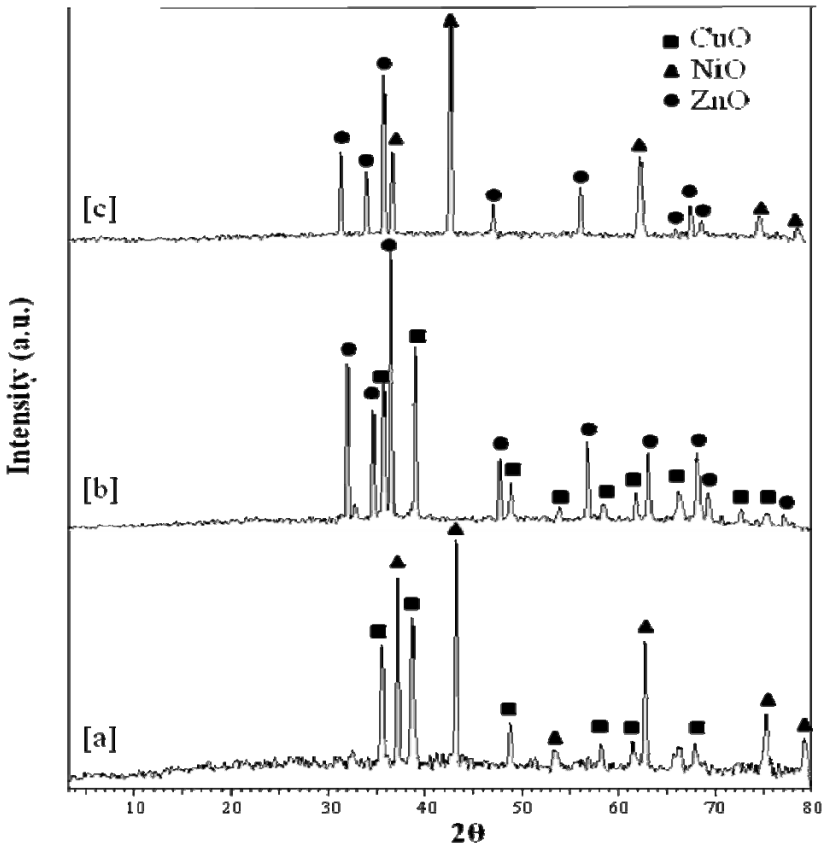


Fig. 1. X-ray diffraction patterns of (a) CuO-NiO (CONO), (b) CuO-ZnO (COZO) and (c) NiO-ZnO (NOZO).

3.2. Scanning Electron Microscopy (SEM)

Fig 2 a-f depicts the intergranular porous structure of the composite materials qualitatively. In the micrograph of CuO-NiO (CONO) the size of the grains are distributed equally when compared to the other two composites (COZO and NOZO). In COZO, the CuO particles were found to be larger grains where as pure ZnO had smaller grains. A similar morphology was present in the NOZO composites

and NiO present as larger grains distinctly in a single phase. In the CONO, the pores are bigger when compared to the COZO and NOZO. The grains sizes were compared qualitatively from the SEM pictures of pure ZnO, NiO and CuO heated grinding same conditions and cooled.

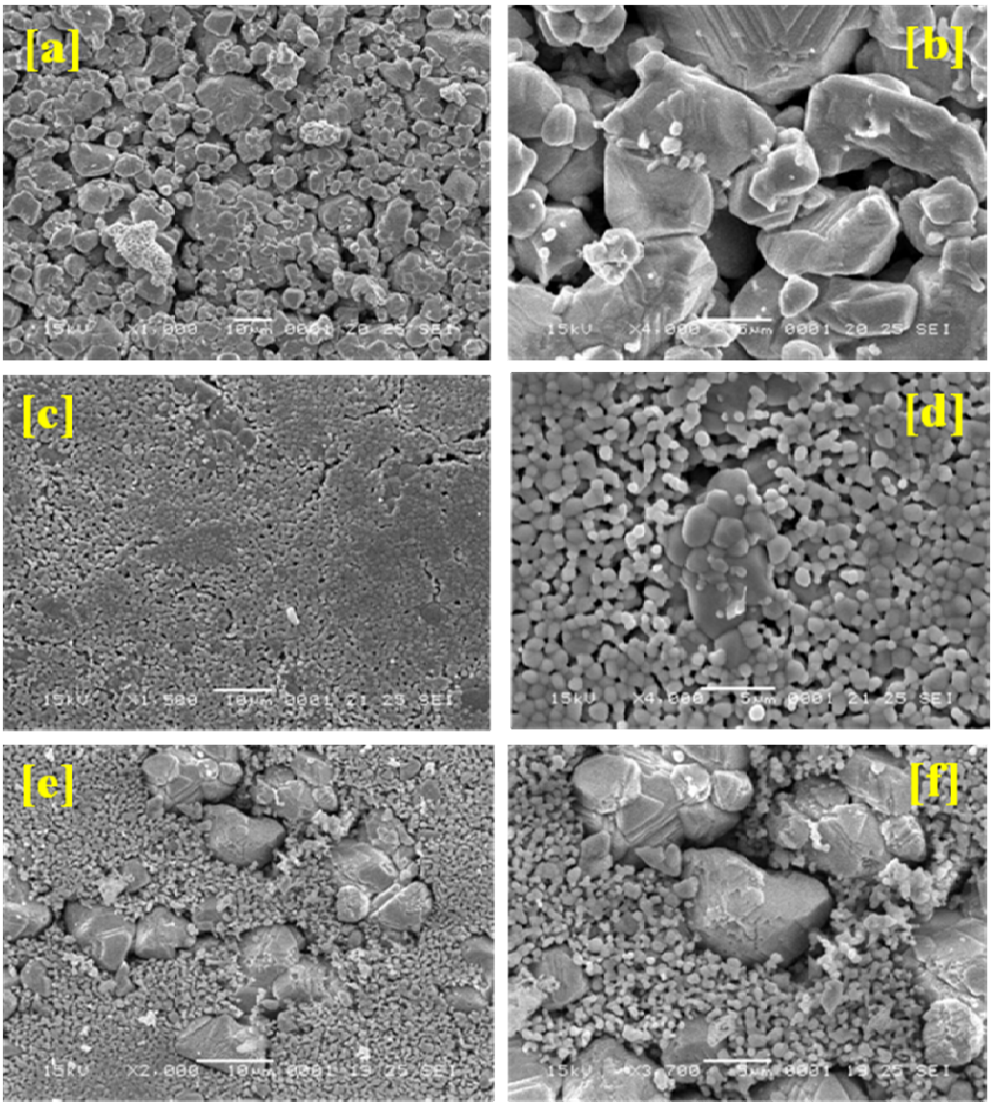


Fig. 2. SEM image with magnification 10 and 5 μm of (a, b) CuO-NiO (CONO), (c, d) CuO-ZnO (COZO) and (e, f) NiO-ZnO (NOZO).

3.3. Electrical Conductance Studies

The room temperature electrical conductance measurement of the composites prior to relative humidity measurements signified that the current increased linearly with the applied voltage, indicating the ohmic contact of the electrodes. The temperature dependence of electrical conductance carried out in the temperature rang 100-300 ^{o}C suggested that the current (I) increased with an increase in temperature (T). The activation energies calculated from the temperature dependence of conductance data are shown in table 1. The activation energy for electrical conduction in polycrystalline materials involves the combination of the energy required to raise the carriers from the dominant levels to their corresponding transport bands and the energy required to create the carriers in the dominant levels. The low activation energy predicts that the small polaron conduction dominates in the studied temperature range.

3.4. Humidity Measurements

The resistance measurement as a function of relative humidity (RH) at a fixed ambient temperature of 25°C (Fig. 3) correspond to the average of measurements made on three samples to check the reproducibility of the results. All the sensor samples studied showed a decrease in resistance values with increase in relative humidity, showing that the conduction occurred mainly at the grain surface, which was governed by the adsorbed water molecules [8]. The resistance of CuO-NiO changed by almost three orders of magnitude between 5 and 98 % RH. The resistance changes in porous oxides with increasing the humidity levels occur because of adsorption and capillary condensation of water. At low humidity levels, chemisorptions takes place leading to the formation of two surface hydroxyls with the charge transport occurring by the hopping mechanism [9]. While at high humidity levels, water is physisorbed on the top of the chemisorbed layer. When water molecules are available at low humidity, they chemisorbs on grain surfaces of the ceramic to form hydroxyl groups as surface charge carriers. When initial water molecules are adsorbed, each water molecules is hydrogen-bonded to two hydroxyls, and the dominant surface charge carriers will be H_3O^+. When still more water is adsorbed, clustering of the water molecules takes place, forming a liquid-like multilayer film of hydrogen-bonded water molecules, where each water molecule is only singly bonded to a hydroxyl group. Since dissociation of H_3O^+ into H_2O and H^+ is energetically favourable in liquid water, the dominant charge carrier in high moisture environment is H^+ [10].

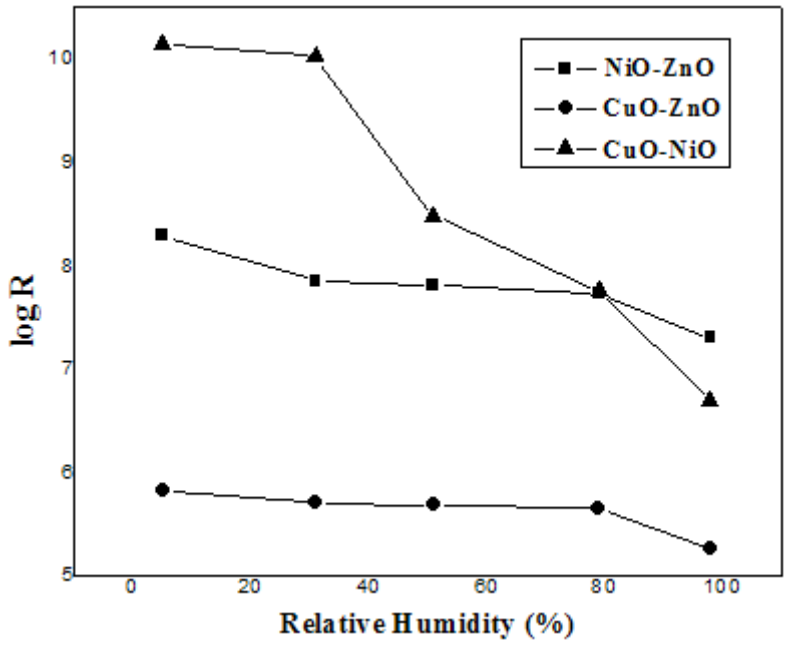


Fig. 3. Relative humidity vs. log R plots at ambient temperature.

The increase in porosity as evidenced from SEM images confirmed the presence of more junctions hetero and therefore sites for water adsorption, which produces more charge carriers for electrical conduction. The observed increase in conductance and thereby sensitivity (Table 1) of the composites is due to the combination of chemisorption, physisorption and/or capillary condensation of water within the pore structure of the composites.

The addition of ZnO to the matrix increased the conductance and decreased the resistance and hence sensitivity factor decreased. The sensitivity factor was found to be 2.3 -3.0 [11, 12] for pure ZnO. When ZnO is added to the matrix it will not enhance the conductance. In addition the SEM

photographs also reveal that the CuO-NiO produces fine particles with smaller grains compared with the other, indicating that the smaller the grain size, the higher will be the surface energy and the adsorption capacity. Thus the composite CONO possessed comparatively high sensitivity factor of 2834.8 while that of COZO and NOZO had only 3.6 and 9.8 respectively.

The distinct phases of ZnO and NiO with less number of pores confirmed the lower sensitivity of the sample NOZO, there is also no mixing of phases. In the sample COZO, although more pores are observed, the pore size of the composites may be larger than the size of the water molecule. Also the phases CuO and ZnO are significantly distinct and can be observed. The CONO shows higher sensitivity factor towards the humidity due to increased grain boundaries and high porosity. The adsorption process would have proceeded through a sequence of diffusion steps from the bulk phase into the mesopores ($2<d<50$ nm) and then to the micropores ($d < 2$ nm). As the molecular size of water is about 0.278 nm pores less than 2nm would be a suitable site for the adsorption of water vapor in the composites [13].

The higher sensitivity of CONO, can be attributed to the random distribution in the particle size, high heterogeneity and high surface area available for adsorption of water vapor. It is due to the reduction in barrier height making the charge carrier transfer feasible. The fall in resistance is mainly due to the increased amount of conduction electrons or charge carriers upon adsorption of vapor over the surface layer. Basically adsorption of water molecules occurs at various stages. Initially the adsorbed water molecules get ionized on the surface and hydronium ions are produced by the assistance of high electric charge density in the neighborhood of the hydroxyl (OH^-) sites, resulting in protonic conduction to the adjacent sites. At higher humidity, the condensation of water in the capillary like pores leads to a liquid like layer leading to electrolytic conduction [14]. 0.25CuO/NiO acted as an active catalyst for CO oxidation by O_2 under static and flow conditions [15]. CO and H_2O act a Lewis bases. For CuO-NiO, both are p-type material with positive hole in the structure that is why it acted as a good catalyst for CO oxidation. Since CuO and NiO are p-type semiconductors the adsorption of water molecule will occur in positive holes by donating lone pair electrons. CONO composite may result in formation of a strong electrostatic matrix, representing easily accessible sites for chemisorption of water molecules.

The stability of CONO was continuously measured by change in resistance at 98 % RH for 30 days at room temperature. It was found that its resistance was stale except a small variation from 1×10^7 to 2×10^7 Ohm within the studied duration (Fig. 4). This indicated the good stability and durability of the CONO compound.

3.5. Response and Recovery Characteristics

The response and recovery characteristics were studied for CuO-NiO composite between 5 and 98% RH. The response and recovery time of CONO was 650 and 80 s, which is due to good linearity in the resistance versus RH plot (Fig. 3). The results suggest that more linear the plot, the better is the response, recovery and sensitivity of the material. The response and recovery transient of the CONO was shown in Fig. 5.

4. Conclusion

The composites CONO, COZO, NOZO were prepared by mixing 1:1 mole ratio of the particular oxides and heated to 800^{o}C for 5hr and studied for humidity sensing applications. To understand the mechanism of humidity sensing, the surface morphology was studied by scanning electron micrograph analysis. The studies revealed that the CONO has more microscopic pores hence is a good candidate materials for humidity sensor, which was further evidenced by the surface studies and high sensitivity

factor 2834.8. The good response and recovery characteristic at ambient temperature is an added advantage for a good humidity sensor. It is noteworthy that both CuO and NiO are p-type semiconductors which showed the highest sensitivity.

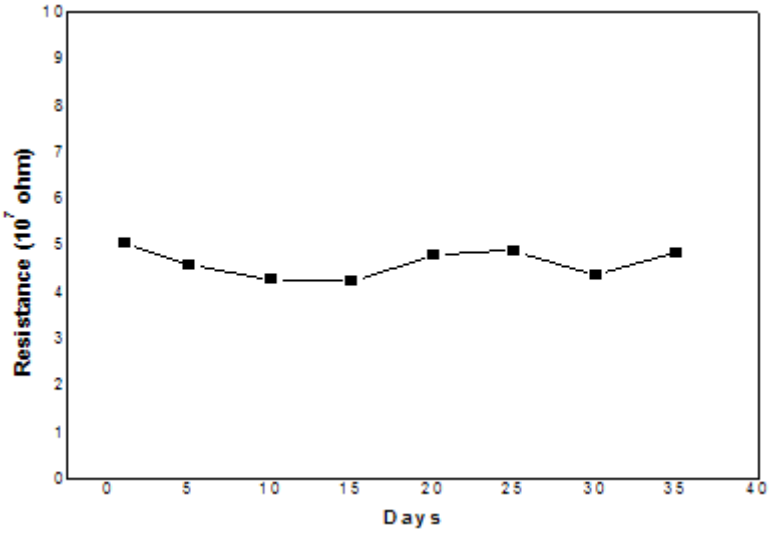


Fig. 4. Resistance stability of CONO compound at 98% RH.

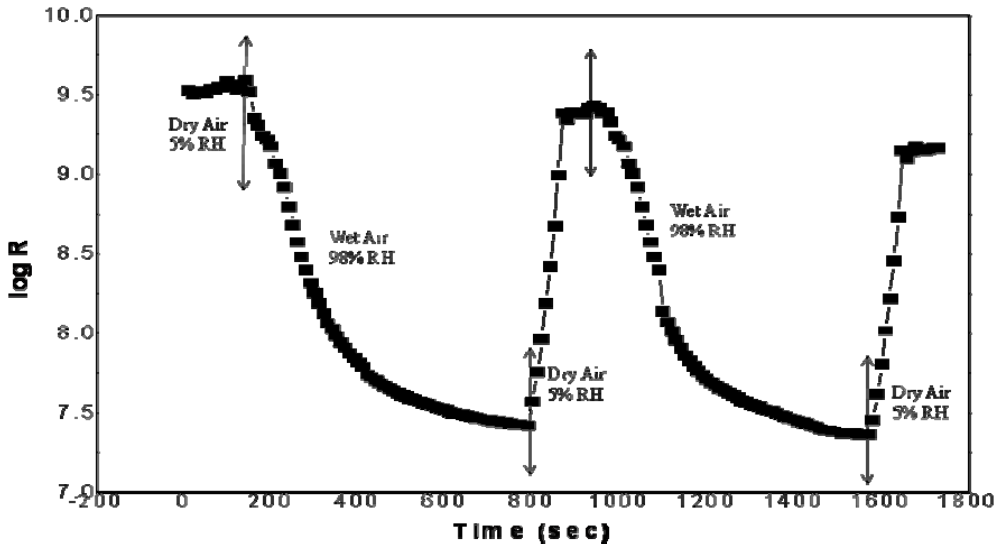


Fig. 5. Response and recovery transients of CONO compound between 5 and 98% RH.

Acknowledgement

The authors acknowledge the funding from UGC - Major Research Project 32-249/2006 (SR). We thank Rev. Fr. Albert Muthumalai S.J, Principal and Rev.Fr. Xavier Alphonse S.J. for their constant encouragement and support.

References

[1]. Shun Hua Xiao, Hai Jun Xu, Jin Hu, Wei Fen Jiang, Xin Jian Li, Structure and humidity sensing properties of barium strontium titanate/silicon nanoporous pillar array composite films, *Thin Solid Films,* Vol. 517, Issue 2, 2008, pp. 929-932.

[2]. G. Gusmano, G. Montesperelli, E. Traversa, G. Mattogno, Microstructure and electrical properties of $MgAl_2O_4$ thin films for humidity sensing, *J. Am. Ceram. Soc.,* Vol. 76, Issue 3, 1993, pp. 743-750.

[3]. J. Judith Vijaya, L. John Kennedy, A. Meenakshisundaram, G. Sekaran, K. S. Nagaraja, Humidity sensing characteristics of sol-gel derived Sr(II)-added $ZnAl_2O_4$ composites, *Sens. Actuators B,* Vol. 127, Issue 2, 2007, pp. 619-624C.

[4]. Cantalinic, M. Pelino, Microstructure and humidity sensitive characteristics of α-Fe_2O_3 ceramic sensors, *J. Am. Ceram. Soc.,* Vol. 75, Issue 3, 1992, pp. 546–551.

[5]. M. Li, Y. Chen, An investigation of response time of TiO_2 thin film oxygen sensors, *Sens. Actuators B,* Vol. 32, Issue 1, 1996, pp. 83-85.

[6]. H. Yagi, M. Nakata, Humidity sensor using Al_2O_3, TiO_2 and SnO_2 prepared by sol–gel method, *J. Ceram. Soc. Jpn.,* Vol. 100, Issue 2, 1992, pp. 152–156.

[7]. P. Chauhan, S. Annapoorni, S. K. Trikha, Humidity sensing properties of nanocrystalline haematile thin film prepared by sol–gel processing, *Thin Solid Film,* Vol. 346, Issues 1-2, 1999, pp 266-268.

[8]. R. Sundaram, E. S. Raj, K. S. Nagaraja, Microwave assisted synthesis, characterization and humidity dependent electrical conductivity studies of perovksite oxides, $Sm_{1-x}Sr_xCrO_3$, *Sens. Actuators B,* Vol. 99, Issues 2-3, 2004, pp 350-354.

[9]. R. Sundaram, K. S. Nagaraja, Solid-state electrical conductivity and humidity sensing studies on metal molybdate-molybdenum trioxide composites ($M=Ni^{2+}$, Cu^{2+} and Pb^{2+}), *Sens. Actuators B,* Vol. 101, Issue 3, 2004, pp. 353-360.

[10]. Jaeho Yuk, Tom Troczynski, Sol-gel $BaTiO_3$ thin film for humidity sensors, *Sens. Actuators B,* Vol. 94, Issue 3, 2003, pp 290-293.

[11]. R. Sundaram, K. S. Nagaraja, Humidity sensing properties of $ZnWO_4$-ZnO composite, *Sensors and Transducers,* Vol. 37, Issue 11, 2003, pp. 30-37.

[12]. A. M. Edwin Suresh Raj, C. Mallika, K. Swaminathan, O. M. Sreedharan, K. S. Nagaraja, Zinc(II) oxide-Zinc(II) Molybdate composite humidity sensor, *Sens. Actuators B,* Vol. 81, Issues 2-3, 2002, pp. 229-236.

[13]. R. Tahery, J. Satherly, H. Modarress, Scaled particle theory: relationships between Compressibility, surface tension, and molecular diameter, *Cell. Mol. Bio. Lett.,* Vol. 9 Supplement 2, 2004, pp. 129-132.

[14]. Z. A. Ansari, T. G. Ko, J. H. Oh, Humidity sensing behavior of thick films of strontium-doped lead–zirconium–titanate, *Surf. Coat. Technol.,* Vol. 179, Issues 2-3, 2004, pp. 182-187.

[15]. G. A. El-Shobaky, N. R. E. Radwan, M. S. El-Shall, A. M. Turky, H. M. A. Hassan, The role of method of preparation of CuO–NiO system on its physicochemical surface and catalytic properties, *Colloids and Surfaces A: Physicochem. Eng. Aspects,* Vol. 311, Issues 1-3, 2007, pp. 161-169.

Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail editor@sensorsportal.com 8-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal's webpage: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm Authors must follow the instructions strictly when submitting their manuscripts.

Advertising Information

Advertising orders and enquires may be sent to sales@sensorsportal.com Please download also our media kit: http://www.sensorsportal.com/DOWNLOADS/Media_Kit_2009.pdf

Subscription 2010 is open!
SUBSCRIBE TODAY!

Sensors & Transducers Journal provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes reviews, regular research and application specific papers and short notes. This peer reviewed international journal is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List (ICV=6.31 at the end of 2008), Open J-Gate, Google Scholar, Scirus, etc.

Topics of Interest

Include, but are not restricted to:
Physical, chemical and biosensors
Digital, frequency, period, duty-cycle, pulse number output sensors and transducers
Theory, principles, effects, design, standardization and modelling
Smart sensors and systems
Sensor instrumentation
Virtual instruments
Sensors interfaces, buses and networks
Signal processing
Technologies and materials
Nanosensors
Microsystems
Applications

2008
e-Impact Factor
205.767

IFSA
www.sensorsportal.com

editor@sensorsportal.com
http://www.sensorsportal.com/HTML/DIGEST/Journal_Subscription_2010.htm

www.sensorsportal.com