



Preparation and Gas Sensing Performance of Nanostructured Copper Doped Nickel Oxides

A.V.KADU¹, S.V.JAGTAP²& N.N.GEDAM³

 ¹ Department of Chemistry, Prof Ram Meghe College of Engineering & Management, Badnera,
 ² Department of Physics, Bar. R.D.I.K.N.K.D., Badnera, Amravati
 ³ Department of Chemistry, IBSS College of Engineering, Amravati Corresponding author: ashishkadu26@rediffmail.com

Abstract

Thick films of pure and Cu doped NiO were prepared by Sol- gel technique. The concentration of Cu in NiO was varied systematically from 1 to 5 wt.%. The structural characteristics of the material were studied by using X-ray diffraction and scanning electron microscopy. The XRD pattern shows a nanocrystalline solid solution of Cu doped NiO with an orthorhombic phase and the crystallite sizes is found to be in the range of 40-50 nm. The gas sensing properties were studied for different reducing gases such as, CO, NH₃, H₂S, ethanol and LPG. The 5 wt.% Cu doped NiO powder showed large response to CO gas at an operating temperature 250 $^{\circ}$ C. Further improvement in response was achieved by the addition of 0.1 wt% Pt to 5 wt.% Cu doped NiO. The sensor showed a good response to 200 ppm CO gas at an operating temperature 180 $^{\circ}$ C.

Keywords: CO gas sensor, Nanocrystalline, Response time, Recovery time.

Introduction

Semiconductor metal oxides as gas sensing materials have been extensively studied for a long time due to their advantageous features, such as good sensitivity to the ambient conditions and simplicity in fabrication [1, 2]. In the last few years, nanostructures of metal oxides have been found to be effective as gas-sensing materials [3–6]. Detection of nitrogen oxides [7], hydrocarbons [8], H₂ [9], C₂H₅OH [10], NH₃ and CO [11] has been demonstrated using metal oxide nanostructures. We were interested in developing sensors for CO using metal oxide nanostructures, since CO is a one of the most dangerous gases in air pollution and human life. CO is produced by incomplete combustion of fuels and commonly found in the emission of automobile exhausts, the burning of domestic fuels, etc. It is highly toxic and extremely dangerous because it is colorless and odorless.

Nickel oxide (NiO), which is a p-type semiconduction having band gap energy (3.5–4.0 eV) and room temperature resistivity in terms of several mega ohms may be used as a gas sensor. Hotovy et al. [12] proposed that NiO films deposited using dc reactive magnetron sputtering can be a promising material for gas sensing applications. Imawan et al. [13] proposed that modified TiOx/ NiO films shows highly sensitive to H₂ gas. Hotovy et al. [14] tested sputtered NiO films exhibits as a CO sensing property. Dirksen et al. [15] compared the performance of pure and Li-doped NiO thin film resistive gas sensors for



formaldehyde detection. Cantalini et.al [16], studied CO and H_2 gas sensing properties of nanocrystalline NiO and Co_3O_4 in porous silica sol–gel films. Miura et al. [17] fabricated the sensor device using an yttria stabilized zirconia (YSZ) tube and a NiO sensing electrode. Lee et. al [18] prepared NiO-based nanostructured films by pulsed-laser deposition (PLD) and a sol–gel method were used for CO sensing.

The grain size is of large importance for the sensitivity, since the surface-to-bulk ratio of the active layer is increased with decreasing grain size [19,20]. It is well known that, for example, the sensitivity of NiO-based sensors is increased with decreasing grain size [21], which puts nanocrystalline structures in the focus of interest. The sensor materials are often modified by dopants e.g. noble metals such as Pd or Pt in order to improve the performance [22-24].

To the best of our knowledge, no reports are available in the literature on Cu-doped NiO based material as a CO gas sensor. This communication deals with the preparation and characterization of Cu-doped NiO material for gas sensing applications. Further, the variation of sensitivity and selectivity of Cu-doped NiO samples with the systematic variation of Cu (metal powder, wt.%) as an dopant for LPG, CO ,NH₃ ,H₂S and Ethanol gases. The sensors are characterized by using XRD and SEM techniques to study the effect of the addition of Cu on sensor performance.

Experimental

Nanostructured undoped and doped NiO was synthesized by the modified Pechini citrate route using citric acid as the chelating agent as described by Niranjan et al. [25]. Briefly, an aqueous solution containing citric acid and ethylene glycol (mass ratio 60:40) was prepared. A known amount of nitrates of nickel and copper were added in this solution. This solution was then heated to evaporate water slowly; the residual viscous oily mass was then heated at a temperature 80°C, to polymerize citric acid and ethylene glycol by polycondensation resulting into a green colored solid resin. The solid resin is a cross-linking of the metal atoms with polyester through oxygen species. The resin formed was then heated to burn off the polymer matrix. The resulting resin was treated in a pressure vessel at an calcinations temperature 140 °C over 14 h to fully evaporate highly combustible species in the glassy mass and to burn down most of the organic constituents- charring. The ash-obtained powder is referred to as the "precursor" hereafter and was heat-treated 650°C for 6 h. Appropriate quantities of PtCl₂ and Cu doped NiO were dissolved in deionizer water. This mixture was vigorously stirred and slowly dried on a water bath. The dried compound was ground to a fine powder and calcined at 200°C for 1 h to decompose the chloride.

Structural & Gas Sensing Characterization

The synthesized samples were characterized for their structure by powder X-ray diffraction (XRD) using a Siemens D 5000 diffractometer. The XRD data were recorded by using Cu K_{α} radiation (1.5406 A°). The average crystallite size of the samples was estimated with the help of Scherrer equation using the





diffraction intensity of all prominent lines [26]. The fine powder was observed under a JEOL, JSM – 5600 N scanning electron microscope (SEM) by dispersion it on a carbon paste to determine the morphology.

The measuring principle of gas sensing properties is described elsewhere. The gas sensitivity (S) is defined as the ratio of the change of resistance in presence of gas (R_g) to that in air (R_a) ,

$$S = (R_a - R_g)/R_a = \Delta R/R_a$$
⁽¹⁾

Results and Discussion

X-ray Diffraction Study

In order to understand the phase symmetry of Cu doped NiO system i.e. modified with different concentrations of Cu (calcined at 650°C), the X-ray diffraction study was undertaken. Fig. 1 shows the XRD patterns of different wt.% Cu doped NiO system. The XRD pattern (a) of the pure nickel oxide confirm that the formed material is nickel oxide and matches with the standard values (orthorhombic system ICDD-JCPDS card no. 40-1179) [27]. They are consistently present in all the Cu modified samples also. In addition, the reflections corresponding to the monoclinic phase of CuO [ASTM card no. 5-0661] are also found to be present in the XRD patterns (c & d). The crystallite size for all the samples is calculated by using the Scherrer equation: D=0.9 λ / β cos θ where, β =FWHM in radians. The crystallite sizes of the samples wt.% Cu doped NiO and calcined at 650°C are found to be in the range of 40-50 nm.



Fig.1. XRD pattern of (a) NiO, (b) 1 wt.% Cu : NiO, (c) 3 wt.% Cu : NiO and (d) 5 wt.% Cu : NiO calcined at 650^{0} C

Morphology study

The SEM technique was employed for finding morphology of 5 wt.% Cu doped NiO as synthesized powder, calcined at 650° C. One can notice the presence of macro-agglomerations of very fine particles.





The particle shapes are not well defined. Many large and small pores are present in the whole material. We assumed that the pores are mainly inter-granular because intra-granular pores are not seen on the SEM photograph.



Fig.2. SEM image of 5 wt.% Cu : NiO calcined at 650°C

Gas sensing characteristics

Response magnitude test

To determine the optimum working temperature of the of pure and different wt.% Cu doped NiO sensors, the sensitivity are examined as a function of temperature towards reducing gas such as CO, as shown in Fig. 3. It is observed that when exposed to CO, the responses of all the samples increase with the operating temperature. When the operating temperature increases, the responses for pure and 1 wt.% Cu-doped NiO decrease at an operating temperature 230° C. But for 3 and 5 wt.% Cu-doped NiO, the optimum temperature is about 250° C, then the responses fall with the rising temperature. We selected the temperature of 250° C for comparison of the sensing properties of the four sensors. Thus 5 wt.% Cu doped NiO shows high CO response at an operating temperature 250° C.



Fig.3. Gas sensitivity of pure and Cu doped NiO for 1000 ppm CO gas.





Selectivity test

Fig. 4 shows the response of 5 wt.% Cu doped NiO to LPG, CO, NH_3 , H_2S and ethanol as a function of operating temperature. The sensor characteristics show that response towards CO and LPG are almost similar, although CO shows slightly higher response was observed at an operating temperature 250°C. Other gases such as H_2S and ethanol show negligible response.

Effect of Pt as an additive

Fig. 5 shows the sensor response versus operating temperature for the 0.1 wt.% Pt incorporated 5 wt.% Cu doped NiO nanoparticles towards CO and LPG. From the graph it is clearly evident that incorporation of Pt results in a drastic decrease in the operating temperature for maximum response by more than 50°C. The operating temperature for the maximum response is observed around 180°C. The Pt doped makes possible CO adsorption at lower operating temperatures, and thus the sensitivity of the Pt doped sensor to CO is quite large, whereas the response towards LPG is lower with respect to CO. Hence due to incorporation of noble metal Pt in synthesized samples, it not only increases the sensor response but also increases the selectivity of CO gas against LPG.



Fig.4. Selectivity of 5 wt.% Cu doped NiO for different reducing gases.



Fig.5. Gas sensitivity of 0.1 wt.% Pt : 5 wt.% Cu doped NiO for LPG & CO gas.





Effect of Gas Concentration

The variation of gas response of 0.1 wt.% Pt incorporated 5 wt.% Cu doped NiO sample with CO gas concentration is represented in Fig. 6. It is observed that the response increases with increasing the gas concentration from 200 ppm, but gets saturated at higher concentrations above 200 ppm. The monolayer of the gas molecules formed on the surface covers the whole surface of the film. The gas molecules from that layer would reach the surface active sites of the film. The excess gas molecules remain idle and would not reach the surface active sites of the sensor. Thus, the active region of the sensor would be up to 200 ppm.



Fig.6. Variation of Gas sensitivity with gas concentration.

Response and recovery time

Fig. 7 shows the response characteristics for the 0.1 wt. % Pt incorporated 5 wt.% Cu doped NiO nanoparticles to 200 ppm CO gas at 180° C. The response and recovery times for CO were found to be 50 s and 70 s.



Fig.7. Response and recovery time of 0.1 wt. % Pt incorporated 5 wt.% Cu doped NiO





Conclusions

Cu doped NiO thick films were prepared by a sol-gel technique which is a simple and in expensive method. The XRD patterns also show high degree of crystallinity and complete phase formation with grain size of about 40-50 nm. From the results obtained, pure NiO showed low response to CO gas. Cu doped NiO thick films were found to be sensitive for CO gas. Among all other additives 5 wt. % Cu-doped NiO thick film was found to be optimum and showed highest response to CO gas at 230 $^{\circ}$ C. The 0.1 wt. % Pt incorporated 5 wt.% Cu doped NiO lowers the operating temperature from 230 to 180 $^{\circ}$ C. Response to CO gas increases with increase in operating temperature attains 89 % at 180 $^{\circ}$ C and then decreases further with an increase the temperature. The 0.1 wt. % Pt incorporated 5 wt.% Cu doped NiO thick films sensor has good selectivity to CO gas against LPG, NH₃, H₂S & Ethanol vapours at 180 $^{\circ}$ C.

Acknowledgements

The authors are indebted to Principal, Dr.M.S Ali, Principal, Prof Ram Meghe College of Engineering & Management, Badnera- Amravati, India for his kind cooperation during this research work

References

- J.Q. Xu, Q.Y. Pan, Y.A. Shun, Z. Li, Emulsion synthesis structure and gas sensing properties of nanometer ZnO, J. Inorg. Chem. 14, 355 (1998)
- [2]. A.A. Tomchenko, G.P. Harmer, B.T. Marquis, J.W. Allen, Semiconducting metal oxide sensor array for the selective detection of combustion gases, Sens. Actuators B, 93, 126 (2003)
- [3]. J. Liu, X. Wang, Peng, Y. Li, Vandium pentoxide nanobelts: highly selective and sTable ethanol sensor materials, Adv. Mater. 17,764 (2005)
- [4]. D. Zhang, Z. Liu, C. Li, T. Tang, X. Liu, S. Han, B. Lei, C. Zhou, Detection of NO2 down to ppb levels using individual & multiple In2O3 nanowires devices, Nanoletters, 4, 1919 (2004)
- [5]. J. Polleux, A. Gurlo, N. Barsan, V.Wiemer, M. Antonietti, M. Niedeberger, Template free synthesis & assembly of single crystalline tungsten oxide nanowires&their gas-sensing properties, Angew. Chem. Int. Ed. 45,261 (2005)
- [6]. H.T. Wang, B.S. Kang, F. Ren, L.C. Tein, P.W. Sadik, D.P. Norton, S.J. Pearton, J. Lin, Hydrogen-selective sensing at room temperature with ZnO nanorods, Appl. Phys. Lett. 86, 243503 (2005)
- [7]. C.S. Rout, K. Ganesh, A. Govindaraj, C.N.R. Rao, Sensors for the nitrogen oxides, NO2, NO and N2O, based on In2O3 and WO3 nanowires, Appl. Phys. A 85, 241 (2006)
- [8]. C.S. Rout, A. Govindaraj, C.N.R. Rao, High-sensitivity hydrocarbon sensors based on tungsten oxide nanowires, J. Mater. Chem. 16,3936 (2006)



- [9]. H. Huang, O.K. Tan, Y.C. Lee, T.D. Tran, M.S. Tse, X. Yao, Semiconductor gas sensor based on tin oxide nanorods prepared by plasma-enhanced chemical vapor deposition with post-plasma treatment, Appl. Phys. Lett. 87,163123 (2005)
- [10]. Y.J. Chen, L. Nie, X.Y. Xue, T.H. Wang, Linear ethanol gas sensing of SnO2 nanorods with extremely high sensitivity, Appl. Phys. Lett. 88, 83105 (2006)
- [11]. J.X.Wang,X.W. Sun,Y.Yang, H. Huang,Y.C. Lee, O.K.Tan, L.Vayssieres, Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications, Nanotechnology 17, 4995 (2006)
- [12]. I. Hotovy, J. Huran, L. Spiess, S. Hascik, V. Rehacek, Preparation of nickel oxide thin films for gas sensors applications, Sens. Actuators B 57,147(1999)
- [13]. C. Imawan, F. Solzbacher, H. Steffes, E. Obermeier, TiOx-modified NiO thin films for H2 gas sensors: effects of TiOx-overlayer sputtering parameters, Sens. Actuators B 68,184 (2000)
- [14]. I. Hotovy, J. Huran, P. Siciliano, S. Capone, L. Spiess, V. Rehacek, The influences of preparation parameters on NiO thin film properties for gassensing application, Sens. Actuators B, 78,126 (2001)
- [15]. J. Dirksen, K. Duval, T. Ring, NiO thin-film formaldehyde gas sensor, Sens. Actuators B 80, 106 (2001)
- [16]. C. Cantalini, M. Post, D. Buso, M. Guglielmi, A. Martucci, Gas sensing properties of nanocrystalline NiO and Co3O4 in porous silica sol-gel films, Sens. Actuators B 108,184 (2005)
- [17]. N. Miura, J. Wang, M. Nakatou, P. Elumalai, S. Zhuiykov, M. Hasei, High-temperature operating characteristics of mixed-potential-type NO2 sensor based on stabilized-zirconia tube and NiO sensing electrode, Sens. Actuators B 114,903 (2006)
- [18]. C. Lee, C. Chiang, Y. Wang, R. Ma, A self-heating gas sensor with integrated NiO thin-film for formaldehyde detection, Sens. Actuators B 122,503 (2007)
- [19]. L. Zbroniec, A. Martucci, T. Sasakil, N. Koshizaki, Optical CO gas sensing using nanostructured NiO and NiO/SiO2 nanocomposites fabricated by PLD and sol-gel methods, Appl. Phys. A 79,1303 (2004)
- [20]. N. Yamazoe, New approaches for improving semiconductor gas sensors, Sens. Actuators B: Chem. 5,7 (1991)
- [21]. X. Wang, S.S. Yee, W.P. Carey, Transition between neck-controlled and grain-boundarycontrolled sensitivity of metal-oxide gas sensors, Sens. Actuators B: Chem. 24/25,447 (1995)
- [22]. J. Tamaki, Z. Zhang, K. Fujimori, M. Akiyama, T. Harada, N. Miura, N. Yamazoe, Grain-size effects in tungsten oxide-based sensor for nitrogen oxides, J. Electrochem. Soc. 141,2207 (1994)
- [23]. H.-M. Lin, C.-H. Hsu, H.-Y. Yang, P.-Y. Lee, C.-C. Yang, Nanocrystalline WO3-based H2S sensors, Sens. Actuators B: Chem. 22,63 (1994)





- [24]. M. Ando, S. Suto, T. Suzuki, T. Tsuchida, C. Nakayama, H2S and CH3SH sensor using a thick film of gold-loaded tungsten oxide, Chem. Soc. Jpn., Chem. Lett.45,335 (1994)
- [25]. R.S. Niranjan, Y.K.Hwang, D.-K. Kim, S.H. Jhung, J.-S. Chang, I.S. Mulla, Nanostructured tin oxide: Synthesis and gas-sensing properties, Mater. Chem. Phys. 92,384 (2005)
- [26]. B. D. Cullity, Elements of X-ray diffraction, 2nd Edition, Addison Wesley, 155 (1978)
- [27]. J.L. Gunjakar, A.M. More, C.D. Lokhande, Chemical deposition of nanocrystalline nickel oxide from urea containing bath and its use in liquefied petroleum gas sensor, Sensors and Actuators B, 131,356 (2008)