

Porous Nickel Oxide Film Sensor for Formaldehyde

U Cindemir, Z Topalian, L Österlund, C G Granqvist and G A Niklasson

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Uppsala, Sweden

E-mail: umut.cindemir@angstrom.uu.se

Abstract. Formaldehyde is a volatile organic compound and a harmful indoor pollutant contributing to the “sick building syndrome”. We used advanced gas deposition to fabricate highly porous nickel oxide (NiO) thin films for formaldehyde sensing. The films were deposited on Al₂O₃ substrates with prefabricated comb-structured electrodes and a resistive heater at the opposite face. The morphology and structure of the films were investigated with scanning electron microscopy and X-ray diffraction. Porosity was determined by nitrogen adsorption isotherms with the Brunauer-Emmett-Teller method. Gas sensing measurements were performed to demonstrate the resistive response of the sensors with respect to different concentrations of formaldehyde at 150 °C.

1. Introduction

The development of low-cost, sensitive, selective and reliable sensors for detecting volatile organic compounds (VOCs) is gaining importance, and there is great need for monitoring environmental health risks. It is important to quantify the concentration of aldehyde pollutants in indoor environments, since it is well documented that they can have adverse health effects. For example, acetaldehyde and formaldehyde can be generated from building materials such as laminates, furniture, wood ceilings, emulsion paints, etc. The well-known effect of VOCs is the “sick building syndrome”, a term used to describe situations where in building inhabitants develop diffuse disease symptoms and discomfort connected with time spent inside the building but without acquiring any specific illness [1]. Furthermore high concentrations (>50 ppm) of VOCs are extremely irritating and probably carcinogenic [2]. Since people in industrialized countries spend 80 to 90% of their time indoors, in buildings or vehicles, the monitoring of these compounds is of large significance [3].

Nanostructured metal oxides can exhibit semiconducting properties and are attractive as low-cost chemical detectors. Nanocrystalline nickel oxide is of special interest for gas sensing at low operating temperatures [4]. The mechanism for gas detection relies on a change of resistance due to gas adsorption on the surface of a thin film. Different production techniques, such as sputtering and evaporation are being used to manufacture nano-crystalline porous thin film for gas sensing purposes [5–7]. However, those techniques normally yield a rather uncontrolled, broad distribution of particle sizes that may be disadvantageous for sensing applications. However, a technique called Advanced Gas Deposition (AGD) allows the production of thin films with well-controlled, log-normal particle size distributions [8–11]. AGD uses thermal evaporation and comprises two chambers connected via a pipe. The first chamber where the nanoparticles are produced is called the evaporation chamber and has a higher pressure than in the second chamber (referred as the deposition chamber), where the film is deposited onto the substrate by a spray.



2. Materials and methods

2.1. *Synthesis of NiO nanoparticles and thin film sensors*

The pressures in the AGD chambers to produce nanoparticle films were set to 86.5 mbar and 8.45 mbar for the evaporation and deposition chamber, respectively. During the process, Ni metal was melted and vaporized by use of 2.5 kW of RF power. To produce NiO during the process, 20 l/min of He and 100 ml/min of O₂ were injected into the evaporation chamber. NiO nanoparticles were deposited onto glass and also onto silicon substrates in order to allow material characterization. To manufacture sensor devices, the films were deposited onto aluminium oxide (Al₂O₃) substrates with prefabricated comb-structured platinum–silver alloy (C4729) electrodes (0.3 mm spacing) on one side and a resistive heater at the opposite side. The dimensions of the ceramic substrates were 25×5×0.5 mm. The thickness of films on single crystal Si substrates was 1.5 μm, measured by a profilometer (Bruker DektakXT). Thicker films are needed to facilitate accurate resistance measurements. However, the decreased resistance is related to decreasing the film porosity and a possible lowering of sensor performance.

2.2. *X-ray diffraction (XRD)*

For XRD measurements, a glass substrate coated with NiO nanoparticles was loaded into a Philips D5000 diffractometer equipped to detect with CuK_α (λ=1.54 Å) radiation. A continuous scan was performed in the 30–80° range of diffraction angles (2θ) using an integration step width of 0.05°. The measuring time per step was 12 seconds. Structural parameters were extracted from θ–2θ scans, and Scherrer's formula [12] was used to calculate average crystallite size.

2.3. *Scanning electron microscopy (SEM)*

Samples for SEM analysis were deposited on Si wafer pieces. SEM images were acquired using a Zeiss LEO1550 instrument with InLens detector and a working distance of 2.7 mm. Due to the low electrical conductivity of NiO, the acceleration voltage was kept at 5 kV thereby limiting the resolution and magnification.

2.4. *Brunauer-Emmett-Teller (BET) measurements of surface area*

The specific surface area was determined with the BET method using NiO powder collected from thick layers of NiO nanoparticles coated onto the glass substrates and then the powder was removed mechanically. BET isotherm measurements were done using nitrogen gas as adsorbing agent, and the temperature was set to -195.8°C. The sample mass employed, after degassing, was measured to be 122.4 mg.

2.5. *X-ray photo-electron spectroscopy (XPS)*

Samples for XPS measurements were coated on Si wafer substrates. In the XPS spectra, oxygen 1s features (O1s) were analysed in order to determine the chemical composition of the nanoparticles. XPS analyses were performed using a PHI Quantum 2000 instrument, equipped with an Al x-ray source having an energy of 1486.7 eV. The carbon peak at 284.3 eV due to residual aliphatic carbon was used as a reference for the energy scale.

2.6. *Gas sensing measurements*

The gas sensing setup consisted of a 300 ml cylindrical chamber, connected to a gas handling system via mass flow controllers. The sensor's resistance response to formaldehyde was recorded at a substrate temperature of 150°C and dry synthetic air (80% N₂ and 20% O₂) was used as carrier gas. Three cycles of exposure to formaldehyde (30 min) and synthetic air (30 min) were performed. The sensors were biased with a battery and a 200 MΩ load resistor, and sensor resistances were extracted from the voltage on the sensor and the load resistor.

3. Results and discussion

3.1. Material characterization

The porosity and the particle size of the NiO films were characterized via SEM analysis. The SEM image in figure 1 shows a highly porous surface comprised of particles with sizes less than 10 nm together with voids among the particles.

XRD analysis revealed a film structure consistent with the cubic phase (fcc) of NiO (JCPDS–ICDD No. 47–1049), with a cell parameter of 4.17 Å (figure 2). The crystallite size was calculated by Scherrer's formula and found to be approximately 3.7 nm. The specific surface area of the NiO particles deposits was determined to be 184 m²/g. The average pore size was found to be 4.3 nm, using the Barrett-Joyner-Halenda method [13]. XPS data of the O1s feature showed two peaks: a predominant one due to NiO located at ~530 eV binding energy and a minor contribution of Ni₂O₃, around 532 eV binding energy.

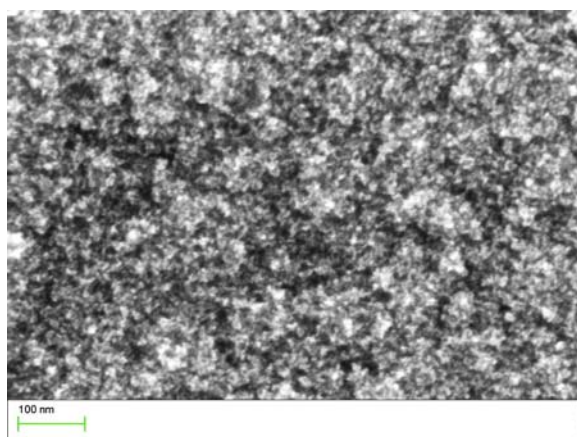


Figure 1. SEM image of NiO film showing a porous surface with particles sizes less than 10 nm.

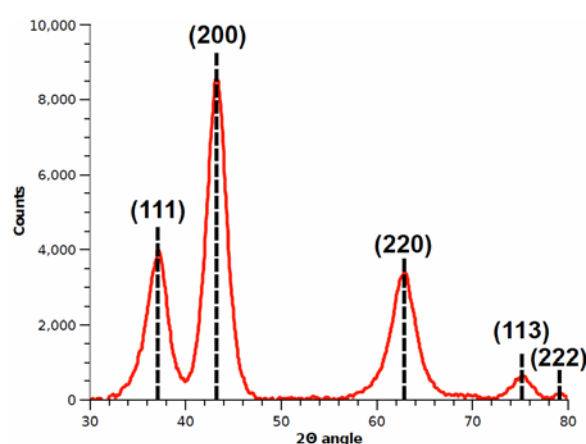
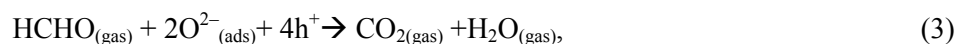
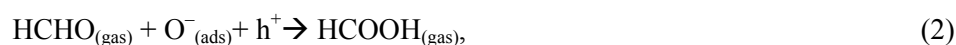


Figure 2. XRD spectra of a NiO film with (*hkl*) indices pertinent to the fcc NiO structure.

3.2. Gas sensing measurements

Resistance changes were employed as the sensing mechanism for formaldehyde detection in the NiO sensor devices. Gas sensing measurements were done at a total gas flow rate of 200 ml/min. Sensor resistances were recorded with formaldehyde diluted in synthetic air at formaldehyde concentrations of 50, 25, 10 and 5 ppm. The underlying mechanism for the resistance change in the NiO film is mainly governed by oxygen adsorption in the film and ensuing electron transfer reactions following oxidation of formaldehyde at the NiO surface [14]. Oxygen is adsorbed on the surface of NiO (*p*-type semiconductor) and dissociates into atomic O fragments, as explained elsewhere [14]. Bonding of O fragments results in the formation of Ni³⁺ centres which increase the concentration of charge carriers (holes). Formaldehyde reacts with O atoms which results in reduction of Ni³⁺ sites, and hence in a decreasing concentration of hole carriers (h⁺) in the NiO film, and in an increased film resistance. The relevant chemical reactions at the NiO surface were proposed to be [5]:



The sensitivity S can be defined as the change in resistance upon exposure to formaldehyde, divided by the initial resistance, according to

$$S = \frac{R_{gas} - R_{air}}{R_{air}} \times 100\% \quad (4)$$

where R_{gas} and R_{air} are the resistance after exposure to formaldehyde and synthetic air, respectively. An average was taken over three measurement cycles. The resistance drift is defined as the ratio of the time-averaged resistance in synthetic air, after and before the three cycles of gas exposure, *i.e.*

$$R_{drift} = \frac{R_{air_{start}} - R_{air_{end}}}{R_{air_{end}}} \times 100\% \quad (5)$$

Here $R_{air_{start}}$ stands for time-averaged resistance of the sensor in synthetic air before exposure to formaldehyde for three cycles, whereas $R_{air_{end}}$ is the corresponding measure after exposure.

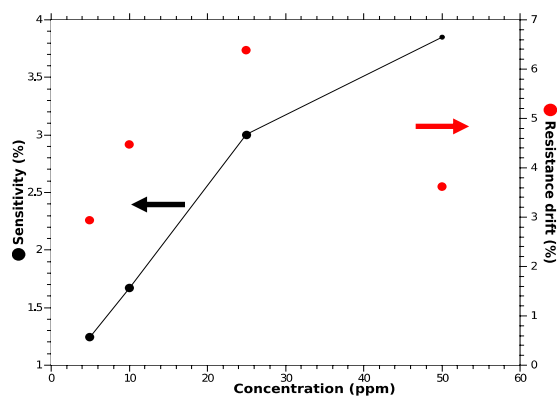


Figure 3. Dependence of Sensitivity, S , and resistance drift, R_{drift} , of a NiO sensor exposed to different concentrations of formaldehyde.

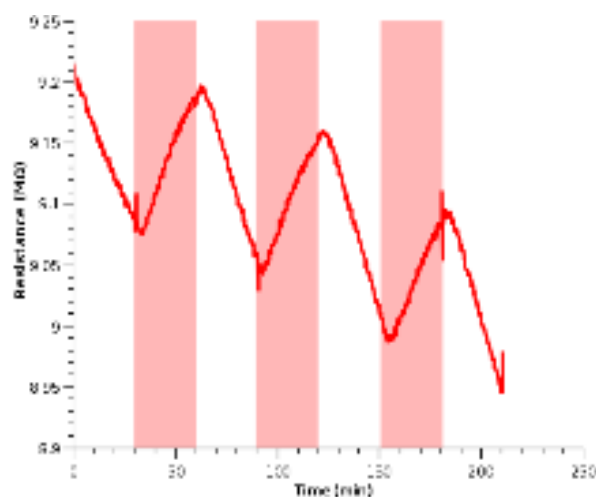


Figure 4. Transient resistance response of a NiO sensor at 150°C when exposed to 5 ppm of formaldehyde with synthetic air as a carrier gas. Shaded regions refer to inlet of formaldehyde.

The resistivity measurements yielded a turn-on time between gas exposure and sensing of 2.5 minutes and a saturation time (time to reach 90% of the resistance change before the end of exposure) of around 20 minutes at 50 ppm. The NiO films showed sensitivity values for formaldehyde detection in the range from 1.2 to 3.8% for 5 and 50 ppm of formaldehyde, respectively (figure 3). The resistance drift, as defined in equation 5, was measured to be between 2.9 and 6.4% depending on gas concentrations (figure 4).

4. Conclusion

It is shown that nanoporous NiO particle films produced by AGD are sensitive to low levels of formaldehyde (of the order 1 ppm) at a sensor temperature of 150°C. The results are promising for further development of inexpensive indoor gas sensing devices. It would be desirable to further increase the sensitivity, as well as to decrease the operating temperature and the response time.

Acknowledgements

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References

- [1] Murphy M 2006 *Sick Building Syndrome and the Problem of Uncertainty: Environmental Politics, Technoscience and Women Workers* (Duke University Press, Durham, USA)
- [2] Giberti A, Carotta M C, Fabbri B, Gherardi S, Guidi V and Malagù C 2012 *Sensors Actuat. B* **174** 402–405
- [3] Godish T 2000 *Indoor Environmental Quality* (CRC Press, Boca Raton, USA)
- [4] Luyo C, Ionescu, R, Reyes L F, Topalian Z, Estrada W, Llobet E, Granqvist C G and Heszler P 2009 *Sensors Actuat. B* **138** 14–20
- [5] Castro-Hurtado I, Herrán J, Mandayo G G and Castaño E 2011 *Thin Solid Films* **520** 947–952
- [6] Kemmler J A, Pokhrel S, Birkenstock J, Schowalter M, Rosenauer A, Bârsan N, Weimar U and Mädler L 2012 *Sensors Actuat. B* **161** 740–747
- [7] Du Y, Wang W, Li X, Zhao J, Ma J, Liu Y and Lu G 2012 *Mater. Lett.* **68** 168–170
- [8] Granqvist C G and Buhrman R A 1976 *J. Appl. Phys.* **47** 2200–2219
- [9] Hayashi C, Uyeda R and Tasaki A, editors 1997 *Ultra-Fine Particles: Exploratory Science and Technology* (Noyes, Westwood, USA)
- [10] Söderlund L, Kiss L B, Niklasson G A and Granqvist C G 1998 *Phys. Rev. Lett.* **80** 2386–2388
- [11] Reyes L F, Saukko S, Hoel A, Lantto V and Granqvist C G 2004 *J. European Ceramic Soc.* **24** 1415–1419
- [12] Cullity B D and Stock S R 2001 *Elements of X-ray Diffraction*, 3rd edition (Prentice-Hall, Upper Saddle River, USA)
- [13] Barrett E P, Joyner L G and Halenda P P 1951 *J. American Chem. Soc.* **73** 373–380
- [14] Kohl D 2001 *J. Phys. D: Appl. Phys.* **34** R125–R149