

# Comparative study of spin coated and AACVD deposited NiO films for detecting VOCs

Sai Kiran Ayyala<sup>1</sup>, Jone Him Tsang<sup>2</sup>, Chris Blackman<sup>2</sup>, and James A. Covington<sup>1</sup>

<sup>1</sup> School of Engineering, University of Warwick, Coventry, CV4 7AL, United Kingdom

<sup>2</sup> Department of Chemistry, University College London, London, WC1H 0AJ, United Kingdom

**Abstract**—Nickel oxide (*p*-type) sensors were developed to detect volatile organic compounds (VOCs). Here, NiO films were deposited onto alumina substrates using both spin-coating (SC) and vapour deposition (AACVD) methods. In the presented work, we tested the fabricated sensors towards acetone, ethanol, toluene, hexane, methanol, and n-propanol vapours between 5 to 25 parts-per-million concentrations, under both dry and humid conditions. The measured thickness of the spin coated and AACVD NiO films were approximately comparable at 10.3  $\mu\text{m}$  and 6.7  $\mu\text{m}$ , respectively. Both SC and AACVD sensors showed maximum response at 350°C. No significant influence of humidity was observed on sensor response and baseline resistance for either SC or AACVD sensors. The sensitivity was found to be highest for alcohol groups.

**Keywords**—metal oxides; spin coating; NiO; volatile organic compounds; gas sensors

## I. INTRODUCTION

Air pollution is an ever-increasing worldwide problem. The everyday activity of humans results in the emission of toxic gases and organic compounds, particularly due to the increase in industrial processes. According to the World Health Organisation there are more than 4.2 million deaths every year as a result of air pollution [1]. Consequently, the impact of volatile organic compounds on air quality is becoming of increasing concern. Several major environmental safety agencies, such as National Institute of Occupational Safety and Health (NIOSH), Environmental Protection Agency (EPA) and European Agency for Safety and Health at Work (EU-OSHA), have established guidelines to limit the exposure of humans to VOCs, indoor and outdoor because of their adverse effects on health, which can effect individuals even at low PPM (parts per million) concentrations [2].

Volatile organic compounds can be broadly defined as a set of organic compounds that consist of at least one carbon atom and a hydrogen atom. Typical examples of VOCs include acetone ( $\text{C}_3\text{H}_6\text{O}$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), benzene ( $\text{C}_6\text{H}_6$ ), formaldehyde ( $\text{HCHO}$ ), methanol ( $\text{CH}_3\text{OH}$ ), toluene ( $\text{C}_7\text{H}_8$ ) and n-propanol( $\text{C}_3\text{H}_8\text{O}$ )[3]. VOCs are very complex to detect,

in particular when separating VOCs of similar chemical structure, but which have very different exposure limits (sometimes by a factor of a 1000). Chemo-resistive type gas sensors, based on metal oxide semiconductors (MOX), are one of the most used sensing modalities for monitoring harmful VOCs. These type of sensors have a number of advantages including, fast response and recovery times, high sensitivity to target gases, simple design, small dimensions, portability, simple and cost-effective fabrication, ease of use, real-time detection, low detection limits and can have low cross-sensitivity [4].

In this work, nickel oxide (*p*-type) devices were fabricated by spin-coating (SC) and aerosol assisted chemical vapour deposition (AACVD) methods to detect a range of VOCs. It is proposed that the effect of humidity is less on *p*-type MOX materials compared to *n*-type [5]. NiO is an attractive material due to its physical properties such as phase dimensions and, as a gas sensing material, it is highly dependent on the surface morphology. This is due to its high surface to volume ratio and its lower charge carrier recombination rate [6].

## II. EXPERIMENTAL

Fig. 1 shows a drawing of the cross-section of the device used in this work. Gold electrodes were deposited using screen printing method on an alumina tile of 2x2 mm size with a platinum heater below. The sensor materials were deposited by photolithography assisted spin coating (SC) and aerosol assisted chemical vapour deposition (AACVD) techniques [7].

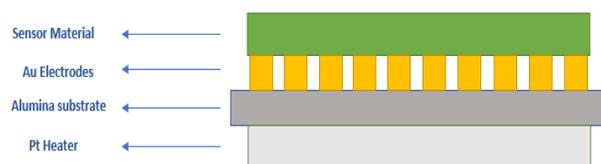


Fig. 1. Schematic of a NiO coated device in cross-section

### A. Sensor Fabrication

Spin coated – NiO was deposited using a photolithography-assisted technique. NiO (99.99% trace metal basis) material was purchased from Sigma Aldrich Ltd and used without further treatment. The spin coating ink was prepared by mixing the NiO with Dirasol-916 (negative photoresist, purchased from Sigma Alrich). A 1:5 weight ratio of NiO and photoresist was used to get a smooth and consistent ink along with 10ml of De-ionised (DI) water added to this ink to maintain its viscosity. Then the substrates were washed with acetone, IPA and DI water and were subjected to pre-baking for 2 min at 60°C. The prepared ink was poured on to the alumina substrates and spun at 3000 RPM for 30 sec to achieve a homogenous layer. Then the substrate was exposed to UV for 2 min. DI water was used as a developer. Then the substrates were post-baked at 60°C for 2 min. After this, the whole process was repeated twice to increase the thickness of the sensing material before firing them at 800°C for an hour at a ramping rate of 5°C per min [8].

AACVD – NiO films were fabricated with nickel(II) bis(acetylacetonate) ( $\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2$ ) dissolved in methanol. An aerosol was generated from this precursor solution using a Johnson Matthey Liquifog, which was passed through the reaction chamber at a nitrogen carrier flow rate of 1500 standard-cubic-centimeters-per minute (sccm). NiO was deposited at a substrate temperature of 340°C.

### B. Gas Testing

Both SC and AACVD sensors were tested with acetone ( $\text{C}_3\text{H}_6\text{O}$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), toluene ( $\text{C}_7\text{H}_8$ ), hexane ( $\text{C}_6\text{H}_{14}$ ), methanol ( $\text{CH}_3\text{OH}$ ), n-propanol ( $\text{C}_3\text{H}_8\text{O}$ ) and isobutylene ( $\text{C}_4\text{H}_8$ ) gases at concentrations between 5 and 25 parts-per-million (ppm). A pre-calibrated sealed bottle for each of the vapours was developed in such a way to get the desired concentrations. The gas experiments were performed using a gas rig with 2 mass flow controllers (MFCs) with a flow rate of 500ml/min which is capable of supplying both the target gas and reference gas at defined flow rates simultaneously [5]. Here, one of the gas lines runs through the pre-calibrated VOC bottle while the other with zero air runs directly on to the sensor holder. The humid air was generated by a water bubbler with relative humidity between 80% - 85% [8].

The sensors were mounted onto an AS-330 Sensor management system, produced by Atmospheric Sensor Ltd, UK. The system is controlled by a software that allows the set up the desired input parameters including heater temperature, heater resistance and duration of the gas test while the output data includes temperature, resistance and current through the sensors.

## III. RESULTS AND DISCUSSION

Initially, all sensors were tested at sensor heater temperatures ranging from 50°C to 400°C towards Isobutylene

at concentrations between 2 and 10 ppm. It was found that at 350°C the gas response was maximum for both types of sensors and thus the same temperature was used for all further sensor testing. The SC - NiO sensors showed a fast, and stable response without any baseline drift for all the vapours in dry conditions. The response and recovery time of SC - NiO for all the vapours were <80 sec and <150 sec respectively while AACVD-NiO were <300 sec and <900 sec respectively.

SEM topography analysis as given in Fig. 2 showed that the thickness of SC and AACVD films were 10.3 micron and 6.7 micron respectively. The thickness of AACVD films are thinner when compared to SC and thus, we would have expected higher resistance, however, the opposite was found. Since AACVD is a reactive deposition technique, there is less control on the density of the deposited material. The SEM images suggests that SC – NiO films has more holes in the microstructure and denser NiO deposition, hence having the lower resistance than AACVD – NiO.

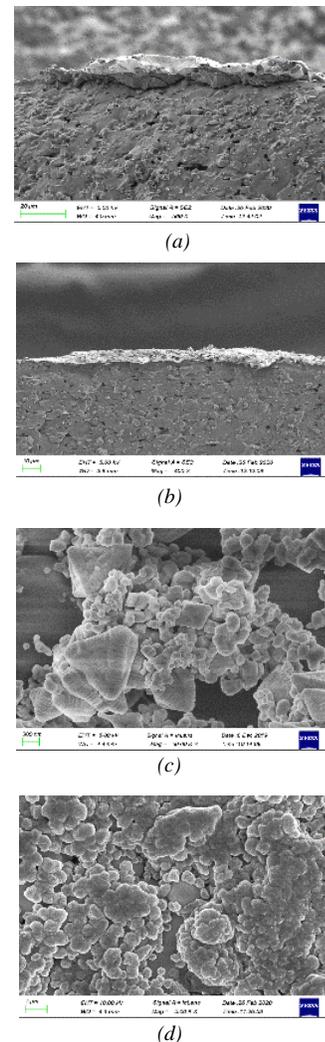


Fig. 2. (a): Cross-section of SC NiO; (b): Cross-section of AACVD NiO; (c): Surface topography of SC - NiO; (d): Surface topography of AACVD – NiO;

Fig. 3 and Fig. 4 illustrates sensitivity versus concentrations (PPM) to target VOCs. Here  $R_g/R_a$  represents ratio of

resistance in gas to resistance in air, with hash lines representing the slope of the response curve. Both the type of NiO gas sensors were possessing higher responses towards ethanol, methanol, and 2-propanol vapours. In other words, response was higher for hydroxyl (-OH) functional groups than the rest of the vapours at the given concentrations.

Fig. 5 and Fig. 6 illustrates the response curves under 40% RH (dry conditions) and 85% RH (humid conditions) of SC - NiO and AACVD - NiO when subjected to isobutylene gas at concentrations between 2 and 10 ppm, respectively. NiO, being a *p*-type semiconductor material, shows an increase in resistance when subjected to reducing gases (as in this case). There was no significant effect of humidity on the baseline resistance or the sensor responses between dry and humid conditions. This indicates that NiO (*p*-type) as a material is more humidity tolerant irrespective of the thickness and deposition techniques used here [9].

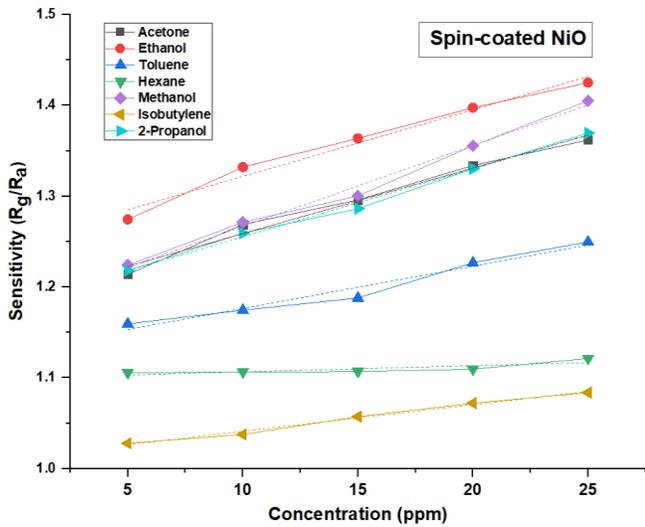


Fig. 3: Sensitivity verses concentration of Spin coated NiO

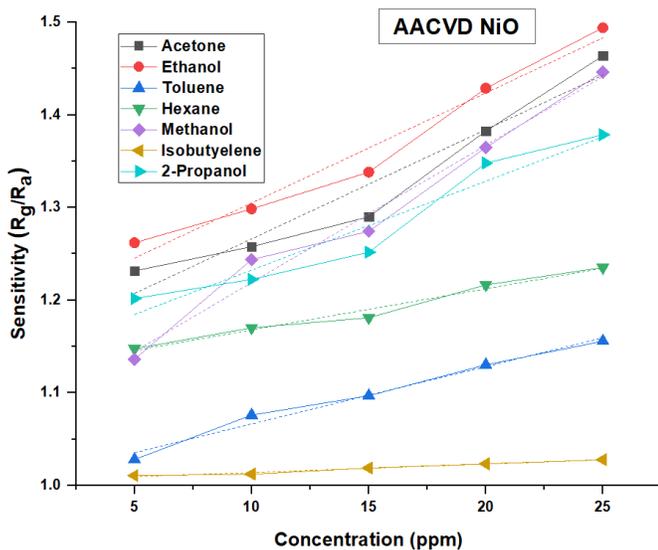


Fig. 4: Sensitivity verses concentration of AACVD NiO

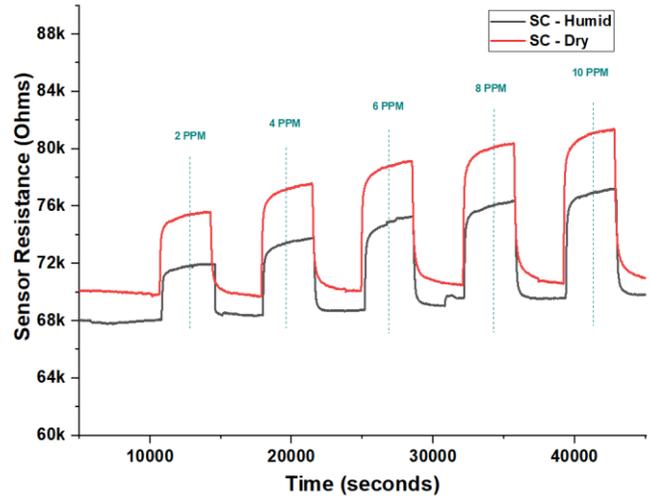


Fig. 5: Humid and dry conditions of Spin coated NiO for a Isobutylene

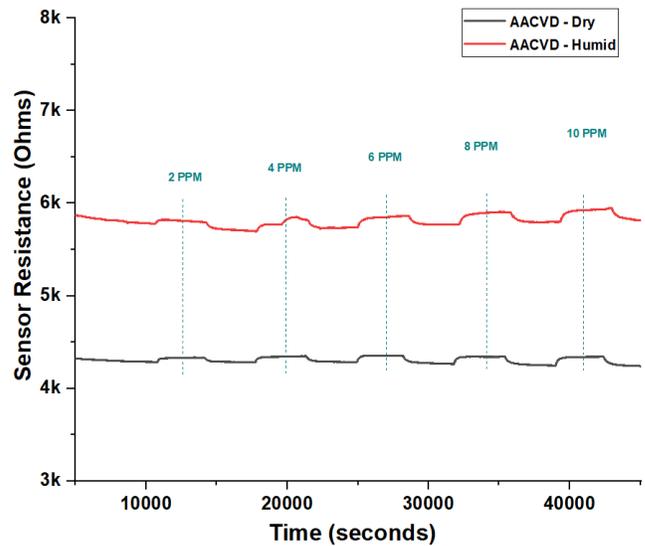


Fig. 6: Humid and dry conditions of AACVD NiO for a VOC

#### IV. CONCLUSIONS

In this paper we achieved our aim of developing a fast and stable chemo-resistive NiO-based sensor for a number of VOC vapours. Fabrication of photolithography-assisted spin coated NiO and AACVD deposited NiO devices were discussed. All the sensors were tested at an operating temperature from 50°C to 400°C and found that the maximum gas response was at 350°C. SEM analysis suggest that SC-NiO is more porous than AACVD-NiO. Comparatively, responses are better for SC-NiO at lower concentrations while responses are better for AACVD-NiO at relatively higher concentrations. Sensitivity ( $R_g/R_a$ ) of the sensors was relatively higher for ethanol and acetone vapours at the tested concentrations than the remaining vapours. Both the type of NiO sensors was subjected to dry and humid conditions while testing with VOC vapors and found to be no significant effect of humidity on sensor response and baseline resistance.

## REFERENCES

- [1] G. Korotcenkov, *Handbook of Gas Sensor Materials*, vol. 1, 2014.
- [2] P. Kumar, A. Deep, K. H. Kim, and R. J. C. Brown, "Coordination polymers: Opportunities and challenges for monitoring volatile organic compounds," *Prog. Polym. Sci.*, vol. 45, pp. 102–118, 2015.
- [3] A. Mirzaei, S. G. Leonardi, and G. Neri, "Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review," *Ceram. Int.*, vol. 42, no. 14, pp. 15119–15141, Nov. 2016.
- [4] V. Balouria *et al.*, "Nano-crystalline Fe<sub>2</sub>O<sub>3</sub> thin films for ppm level detection of H<sub>2</sub>S," *Sensors Actuators, B Chem.*, vol. 181, pp. 471–478, 2013.
- [5] J. Wang, P. Yang, and X. Wei, "High-performance, room-temperature, and no-humidity-impact ammonia sensor based on heterogeneous nickel oxide and zinc oxide nanocrystals," *ACS Appl. Mater. Interfaces*, vol. 7, no. 6, pp. 3816–3824, 2015.
- [6] W. Zeng, B. Miao, L. Y. Lin, and J. Y. Xie, "Facile synthesis of NiO nanowires and their gas sensing performance," *Trans. Nonferrous Met. Soc. China (English Ed.)*, vol. 22, no. SUPPL. 1, pp. s100–s104, 2012.
- [7] S. Vallejos, F. Di Maggio, T. Shujah, and C. Blackman, "Chemical vapour deposition of gas sensitive metal oxides," *Chemosensors*, vol. 4, no. 1, pp. 1–18, 2016.
- [8] W. Sari, P. Smith, S. Leigh, and J. Covington, "Oxygen Sensors Based on Screen Printed Platinum and Palladium Doped Indium Oxides," *Proceedings*, vol. 1, no. 10, p. 401, 2017.
- [9] R. L. Wilson *et al.*, "Humidity-Tolerant Ultrathin NiO Gas-Sensing Films," *ACS Sensors*, 2020.