

The Electronic Nose: The Effect of Metal Oxide Modifications to Well-Aligned ZnO Nanowire Arrays for Highly Sensitive and Selective Gas Detection

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Abstract:

To mimic biological olfactory receptor arrays, a three dimensional (3D) "electronic nose" was fabricated by using well-aligned ZnO nanowire arrays modified with different metal oxides. Metal oxide nanowire arrays share 3D structures similar to mammalian olfactory receptor arrays, with thousands of vertically aligned nanowires providing a high reception area which can significantly enhance the sensors' sensitivity. Meanwhile, with different material decorations, each array of nanowires can produce a distinguishable response for each separate analyte, which would provide a promising way to improve the selectivity. We have successfully fabricated gas sensors based on SnO₂, In₂O₃, and WO₃ coatings which have discriminated five gases which are NO₂, H₂S, H₂, NH₃, and CO. The sensitivity to NO₂ and H₂S has reached down to the ppb level.

Key words: Electronic nose, ZnO nanowire, Metal oxide, Gas sensor arrays.

Introduction

Highly sensitive and selective chemical agent detectors have important applications in the areas of environmental emission control, public security, automotive applications, workplace hazard monitoring, medical diagnosis, and so on [1-2]. Among most of the detection technologies, including conductive polymer sensors, metal oxide conductometric sensors, and microcantilever sensors, metal oxide conductometric sensors comprise a significant part of the gas sensor component market. The reason is that metal oxides possess a broad range of electronic, chemical, and physical properties that are often highly sensitive to changes in their chemical environment. As nanotechnology has developed, metal oxide nanostructures have attracted much attention for applications in highly sensitive and selective gas sensors due to their high aspect ratio, large surface area, and availability of versatile structures as compared to their thin film counterparts [3-4]. For example, in gas sensors formed with individual In₂O₃ nanoparticles, a nanowire or nanowire networks can detect NO₂ down to the ppb level at room-temperature [5-6].

For the purpose of mimicking the biological olfactory system with a diversity of receptor

arrays, vertically aligned 3D nanowire arrays have great potential for sensor applications, due to their extremely large surface area which provides a much stronger capability of capturing target molecules in the atmosphere [7-8]. To realize multiple receptor arrays, different metal oxides were coated onto well-aligned ZnO nanowire arrays, which can be readily grown by hydrothermal synthesis [8-9]. The electrical and gas-sensing properties of individual nanowire arrays were characterized. The electronic nose was fabricated with ZnO nanowire arrays decorated with the different metal oxides (SnO₂, In₂O₃, and WO₃) and the gas discrimination of this electronic nose was studied in detail.

Experimental

The fabrication of vertically aligned semiconductor core-shell nanowire arrays generally starts with well-aligned ZnO nanowires grown by hydrothermal synthesis [10]. Fig.1 shows the schematic of the fabrication procedures for 3D sensor devices. The substrate was cleaned by a standard process, followed by the well aligned growth of ZnO nanowire arrays by hydrothermal synthesis [8]. Common thin film techniques, such as sputtering, PLD, or CVD, can be used to deposit the shell layers [8]. In this experiment, 50 nm SnO₂, In₂O₃, and WO₃ were sputtered in

a Lesker PVD75 system and a metal mask was employed to ensure selective deposition. Finally, the top electrodes connecting the nanowire arrays were prepared by microfabrication processes [8].

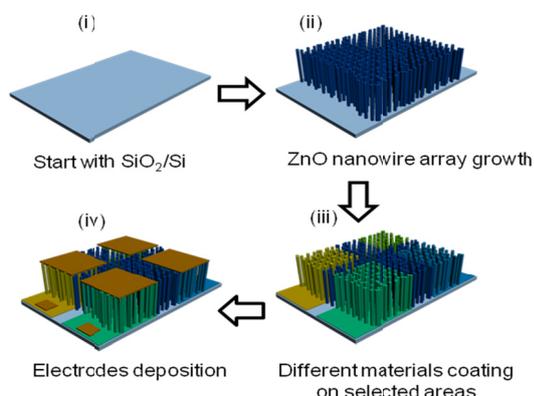


Fig. 1. Schematic diagrams showing the procedures of metal oxide coatings on ZnO nanowire arrays for selective detection. (i) The procedures start with a cleaned substrate; (ii) Followed by well aligned ZnO nanowire array growth; (iii) Different material coatings on selected areas; (iv) Electrode deposition.

To test the sensor performance, the nanowire array sensors were loaded onto the gas sensor testing system and the conductance for all the devices was continuously monitored when different air-diluted chemicals were introduced. The devices were connected by 0.02 mm gold wires and silver paste. The Keithley 2400 source measurement unit cooperating with a 7001 switch module can continuously monitor the conductivity of all the nanowire array devices. The gas sensors were recovered by flushing with a constant dry air flow.

Results and Discussion

Fig.2 (a) and (b) shows FESEM images of ZnO nanowire arrays. The pristine ZnO nanowires have 100 ~ 400 nm diameters and are 5µm in length.

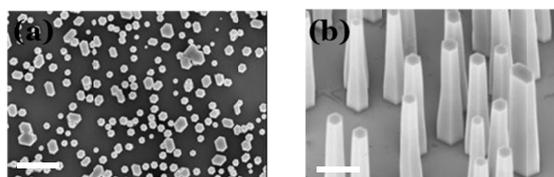


Fig. 2. FESEM images. (a) Top view; (b) View by 30° tilting. (Scale bar is 1µm.)

After different metal oxide coatings, I-V characteristics were obtained when the sensor arrays (ZnO/SnO₂, ZnO/In₂O₃, and ZnO/WO₃) were loaded into testing systems. The linear I-V plots in Fig.3 indicate that the contact between the electrodes and nanowires are all ohmic.

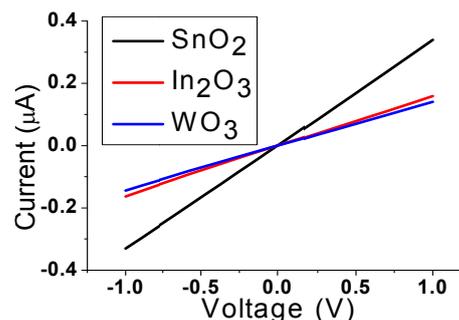


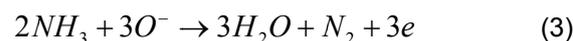
Fig. 3. I-V curves for nanowire arrays coated by different metal oxides.

The sensing responses were measured with air-diluted NO₂, H₂S, NH₃, CO, and H₂ of different concentrations at room-temperature. All normalized sensing responses, $(G_{\text{gas}} - G_{\text{air}}) / G_{\text{air}}$, are plotted in Figure 4 (a-e). The devices show high sensitivity to NO₂ and H₂S at room temperature, and the lowest detection limits are as low as 20 ppb and 50 ppb, respectively.

The sensing responses of metal oxide conductometric gas sensors can be explained by the processes of oxygen absorption and desorption onto the metal oxide surfaces [2]. Trapping of electrons at adsorbed molecules and band bending induced by these charged molecules are responsible for a change in the conductivity. When O₂ molecules are adsorbed onto the surface of metal oxides, they would extract electrons from the conduction band E_c and trap the electrons at the surface in the form of ions which will lead to a bending of the band and an electron depleted region which can be described by



Reducing gases (H₂S, NH₃, CO, and H₂) can react with these oxygen species, which will release the electrons back to the metal oxides and reverse the band bending. This results in an increased in conductivity. As described by



On the contrary, oxidizing gases like NO₂ would decrease the device conductance. As described by this reaction:



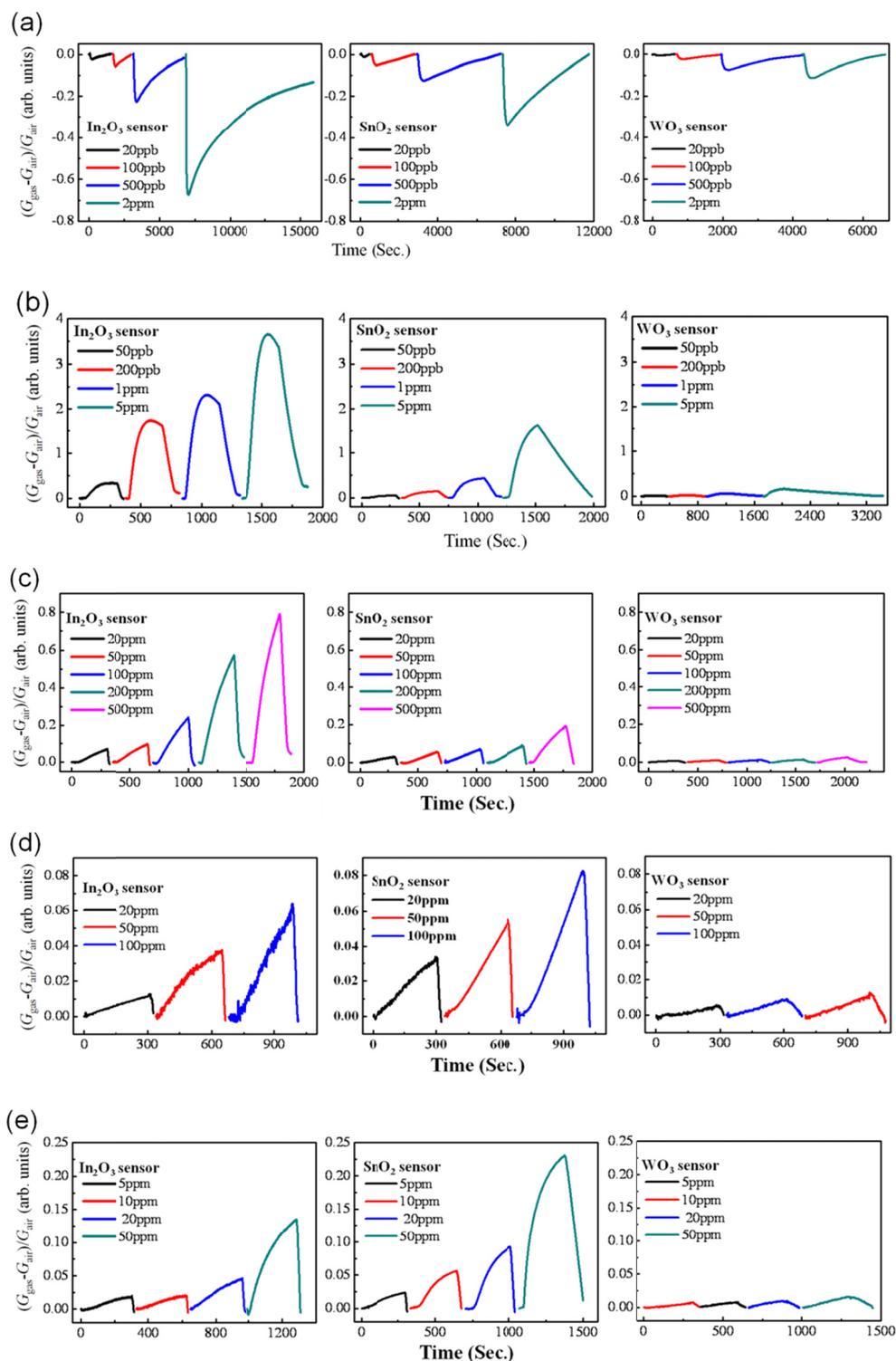


Fig.4. Sensing responses to different gases. (a) NO_2 ; (b) H_2S ; (c) H_2 ; (d) CO ; (e) NH_3 .

As one of the statistical methods, principal component analysis (PCA) is widely used to display the sensing responses of sensor arrays because it is a linear unsupervised method that requires little or no prior knowledge. Furthermore, in most cases only response

variables (i.e. response strength, speed) are needed [11]. Fig. 4 is the PCA analysis of the sensing responses from the sensor arrays. Both H_2S and H_2 are easily distinguished from the plot. Since NO_2 is an oxidizing gas, it is readily picked up from the signal trend. So far, NH_3 and

CO are overlap at the low concentration region. However, by judging the response speed and sensitivity from Fig.4 (d) and (e), they can also be discriminated. We are currently exploring more metal oxide materials to discriminate them directly at low concentration.

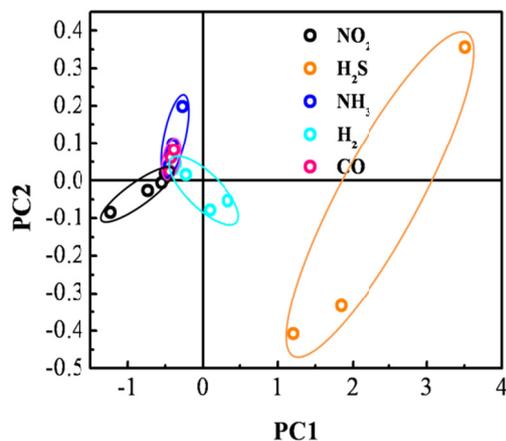


Fig. 4. PCA analysis of sensing responses from the sensor arrays.

Conclusions

An electronic nose system based on ZnO nanowire arrays with different gas sensing metal oxide coatings has been demonstrated for the gas discrimination of NO₂, H₂S, H₂, NH₃, and CO at room temperature assisted with principal components analysis (PCA). The SnO₂, In₂O₃, and WO₃ coated ZnO sensors show responses to NO₂ and H₂S with concentrations as low as 20 ppb and 50 ppb, respectively. These results demonstrate a strong potential for highly sensitive sensor fabrication. Our method for engineering ZnO 3D nanowire arrays with different metal oxides provides a promising way to adapt more semiconductive materials on the novel route towards 3-D nanosensors for various gas detections.

Acknowledgements

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References

- [1] G. Shen, P. Chen, K. Ryu, C. Zhou, Devices and chemical sensing applications of metal oxide nanowires, *J. Mater. Chem.*, 19, 828-839 (2009); doi: 10.1039/B816543B
- [2] C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Metal oxide gas sensors: sensitivity and influencing factors, *sensors*, 10, 2088-2106(2010); doi:10.3390/s100302088
- [3] A. Kolmakov, M. Moskovits, Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures, *Annual Review of Materials Research* 34, 151-180 (2004); doi:10.1146/annurev. matsci.34.040203.112141
- [4] B. Cao, J.Chen, X. Tang, W. Zhou, Growth of monoclinic WO₃ nanowire array for highly sensitive NO₂ detection, *J. Mater. Chem.*, 19, 2323-2327(2009), doi: 10.1039/B816646C
- [5] 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 and multiple In₂O₃ nanowire devices, *Nano Letters* 4, 1919-1924 (2004); doi: 10.1021/nl0489283
- [6] K. Yao, D. Caruntu, Z. Zeng, J. Chen, C. O'Connor, W. Zhou, Parts per billion-level H₂S detection at room temperature based on self-assembled In₂O₃ nanoparticles, *J. Phys. Chem. C* 113, 14812-14817 (2009); doi: 10.1021/jp905189f
- [7] K. Albert, N. Lewis, C. Schauer, G. Sotzing, S. Stitzel, T. Vaid, D. Walt, Cross-reactive chemical sensor arrays, *Chem. Rev.* 100, 2595-2626 (2000); doi: 10.1021/cr980102w
- [8] J. Chen, K. Wang, W. Zhou, Vertically aligned ZnO nanorod arrays coated with SnO₂/noble metal nanoparticles for highly sensitive and selective gas detection, *IEEE Transactions on Nanotechnology* 10, 968-974 (2011); doi: 10.1109/TNANO.2010.2091423
- [9] L. Vayssieres, Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions, *Adv. Mater.* 15, 464-466 (2003); doi: 10.1002/adma.200390108
- [10] S. Xu, Y. Wei, Z. Wang, Patterned growth of vertically aligned ZnO nanowire arrays on inorganic substrates at low temperature without catalyst, *J. Am. Chem. Soc.*, 130, 14958-14959(2008), doi: 10.1021/ja806952j
- [11] S. Jha, R. Yadava, Pattern recognition methods for SAW sensor array based electronic nose, *2011 IEEE*, 1-4(2010), doi: 10.1109/ICCIC.2010.5705774