DOI 10.5162/IMCS2018/GS3.2

Temperature-Modulated pn-Transition Gas Response of ZnO Nanorod Arrays for Selective Detection of CO

Tingqiang Yang, Wei Jin, Wen Chen
State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China
E-mail: chenw@whut.edu.cn (Wen Chen)

Abstract
It has been problematic to selectively detect CO by metal oxide semiconductor (MOS) gas sensors, due to gas response to CO is normally much lower than volatile organic compounds (VOCs). In this work, an abnormal pn-transition gas response of ZnO nanorod arrays is discovered. At relatively low temperature (463 K), resistance of ZnO nanorod arrays increases when CO is injected into testing chamber, suggesting a “p-type” gas response; while, at relatively high temperature (643 K), resistance decreases after CO injection, meaning a usual “n-type” response. Density functional theory (DFT) simulation reveals that the abnormal p-type response at 463 K is attributed to CO molecule facilitating the dissociation of absorbed O_2 molecule. This peculiarity can be applied to selective detection of CO.

Key words: pn-transition, ZnO nanorod arrays, temperature-modulated, gas sensing, CO

CO gas is extremely dangerous, not only due to deadly poisonousness, easy combustion and explosion, but also because of colorless and odorless peculiarities. It is definitely necessary to detect CO. Metal oxide semiconductor (MOS) gas sensors have drawn extensive attention in gas sensing domain due to their high gas responses, simple synthesis process and low cost. However, their gas responses to CO are generally much lower than volatile organic compounds (VOCs), leading to a difficulty in selective detection of CO.

The gas sensing process is generally believed that reducing gases consume absorbed oxygen pieces, thus, give electrons back to surface layers. For n-type MOSs, these processes result in decline of resistance. However, some abnormal phenomena have been reported that resistance of n-type MOSs increases after injection of reducing gas under specific conditions, which is a performance of p-type MOSs [1]. Hence, the abnormal gas response was referred as “p-type” gas response.

In this work, an unprecedented phenomenon is discovered that ZnO nanorod arrays show p-type gas response to CO at relatively low temperature and show n-type gas response at higher temperature. The mechanism is revealed by density functional theory (DFT) simulation.

Synthesis of ZnO nanorod arrays and device fabrication are totally same with our previous works [2]. The gas sensing properties were measured by commercial gas sensing measurement system (WS-30A, Zhengzhou Winsen Technology Corp., China). In the response process, a certain amount of gas was injected into the test chamber, and signals were collected after five minutes to ensure sufficient diffusion of gas molecule. In the recovery process, gas sensor device was exposed to air by opening the chamber for five minutes. After the exposure, the chamber was sealed again, and it was still five minutes before signals acquisition to avoid effects of flow disturbance. Gas response (S) was defined as R_{air}/R_{gas}, where R_{air} and R_{gas} are values of resistance in air and goal gas, respectively.

Fig. 1 shows resistance response curves and gas response curves to CO at 463 K and 643 K, respectively. The resistance curve of 463 K is peculiar. Resistance decreases slightly when ZnO nanorod arrays are exposed to low concentration of CO, whereas resistance increases if concentration is higher than 50 ppm. This results in descent of gas response, shown in Fig. 1c. In contrast, gas sensing properties at 643 K is normal. Resistance declines obviously upon injection of CO, and gas response rises with enhancement of concentration.

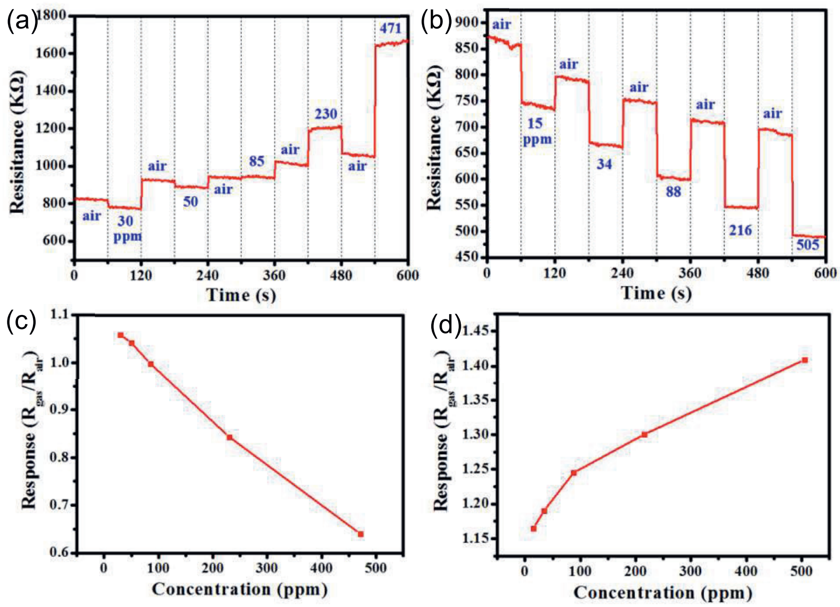

Fig.1. (a, b) Resistance response curves and (c, d) gas response curves to CO of different concentrations at 463 K and 643 K, respectively.

Density functional theory (DFT) simulation is utilized to explain the abnormal phenomenon. According to previous research, it is O adatom that plays role at 643 K. While 463 K is around the temperature at which absorbed O_2 molecule begins to dissociate [2]. Therefore, it is likely that CO facilitates the dissociation of absorbed O_2 molecule. In that case, more electrons will be extracted from ZnO surface layers, leading to improvement of resistance. Fig.2 illustrates the dissociation process of absorbed O_2 molecule on ZnO ($10\bar{1}0$) with the presence of CO. The activation energy is 342.70 kJ/mol, which is slightly lower than that (351.71 kJ/mol) without CO molecule [2]. This confirms the speculation. The facilitation of CO on dissociation of O_2 molecule is also discovered at Au_x clusters [3].

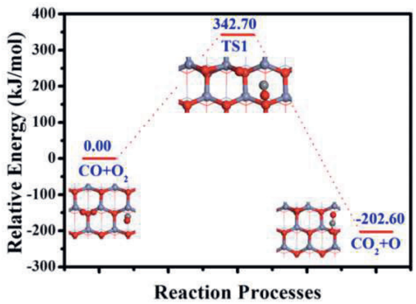

Fig.2. Dissociation process of absorbed O_2 molecule with presence of CO on ZnO ($10\bar{1}0$) surface.

This peculiar gas sensing properties can be utilized to detect CO selectively and quantitatively by modulating working temperature. When the device works at 463 K, it can distinguish CO from other reducing gases because of abnormal p-type response; when it works at 643 K, concentration of CO can be determined according to the correlation between gas response and concentration.

In conclusion, it is discovered that ZnO nanorod arrays show abnormal pn-transition gas response to CO, which is modulated by temperature. The mechanism of p-type response at relatively low temperature is that CO facilitates the dissociation of absorbed O_2 molecule. The peculiarity can be applied to selective detection of CO.

References

[1] Y. Qin, G. Tao, K. Liu, M. Hu, Vanadium Pentoxide Hierarchical Structure Networks for High Performance Ethanol Gas Sensor with Dual Working Temperature, Sensors and Actuators B: Chemical 190, 141-148 (2014); doi: 10.1016/j.snb.2013.08.061

[2] T. Yang, Y. Liu, W. Jin, Y. Han, S. Yang, W. Chen, Investigation on the Transformation of Absorbed Oxygen at ZnO {$10\bar{1}0$} Surface Based on a Novel Thermal Pulse Method and Density Functional Theory Simulation, ACS Sensors 2, 1051-1059 (2017); doi: 10.1021/acssensors.7b00363

[3] C. Liu, Y. Tan, S. Lin, H. Li, X. Wu, L. Li, Y. Lei, X. Zeng, CO Self-Promoting Oxidation on Nanosized Gold Clusters: Triangular Au_3 Active Site and CO Induced O−O Scission, Journal of the American Chemical Society 135, 2583-2595 (2013); doi: 10.1021/ja309460v