

PHOTO-ENHANCED VOC SENSING PROPERTIES OF THE PN JUNCTION DIODE COMPOSED OF WIDE-GAP OXIDE SEMICONDUCTORS

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Introduction

From the viewpoint of maintenance of safe environment, there is currently great interest in the R&D of compact sized with lower power consumption VOC (volatile organic compounds) monitoring systems. Combustible gas sensing devices are major application field for oxide semiconductors and their simple structures with low running costs are appropriate for the application to compact sized environmental monitoring systems.

The reliable sensing system for aromatic VOCs, benzene, toluene, etc. are in great demand because these are etiological compounds for serious disease, sick building syndrome[1]. However, due to their thermodynamic stability, aromatic VOCs are difficult to be detected by traditional gas sensing devices based on oxide semiconductors even at elevated temperatures. In the present study, we will propose a new concept for detecting aromatic VOCs in atmosphere by using an oxide semiconductor pn heterojunction diode. The point to be devised is how to activate aromatic VOC adsorbates over a junction interface. Here, it is examined whether the photo-excitation of aromatic VOCs is giving rise to the current response of a pn junction diode. Photo-driven electron transfer from π^* excited states of aromatic ring adsorbate to the pn junction interface would be deeply related to the novel VOC sensing mechanism in this system.

Experimental Procedure

A Sn/*n*-ZnO/*p*-NiO:Li/Ni structure, a pre-structure of a *p*-NiO:Li/*n*-ZnO heterojunction sensor element was fabricated by continuous preparation of NiO:Li (NiO doped with 2at% of lithium), ZnO and Sn films over a optically flat Ni metal substrate by rf-magnetron sputtering (*p*-NiO:Li and *n*-ZnO) and vacuum evaporation techniques (Sn). The current-voltage (*I*-*V*) characteristics of this structure had been checked in advance and it showed good rectifying character, whose rectifying ratio was over 4×10^2 at ± 2 V.

Next, the Sn/*n*-ZnO/*p*-NiO:Li/Ni structure was processed into a *p*-NiO:Li/*n*-ZnO heterojunction sensor element whose junction interface was exposed to the atmosphere. After drawing the interdigital electrode pattern by photolithography technique, the heterojunction element was chemically etched in 0.1M HNO₃ at 21°C. After 15 sec. etching, Sn and ZnO layer are completely removed leaving the electrode patterns intact, then the *p*-NiO:Li-*n*-ZnO interface was completely exposed to the atmosphere. The total process for manufacturing the sensor element was

summarized in Figure 1.

The *p*-NiO:Li/*n*-ZnO sensor element prepared by the above mentioned process was set on the sample stage of an atmosphere controlled micro-probing system and the current passing through the junction interface was continuously monitored by an electrometer. The 50ml of benzene or other VOC sources was directly injected into the gas flow system and it traveled to the sample chamber with a carrier gas of dried air. Deep UV-light was irradiated to the sensor element using a 17W mercury vapor lamp which was set over the sample stage.

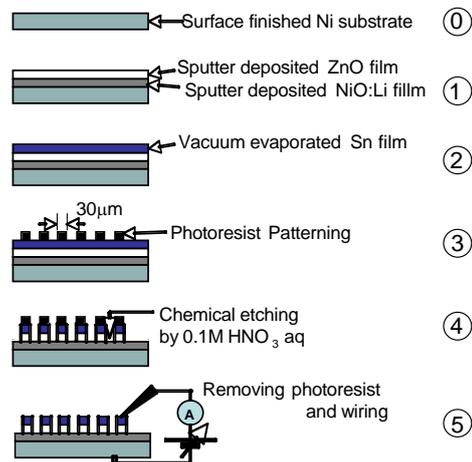


Figure 1 Schematic illustrations of the fabrication process of a *p*-NiO:Li/*n*-ZnO heterojunction sensor element.

Results and Discussions

The good diode performance of the original Sn/*n*-ZnO/*p*-NiO:Li/Ni structure was once spoiled by processing it into a sensor element (The inset of Figure 2: Curve 1), however its leaky *I*-*V* response is able to be recovered by low temperature ($T=200^\circ\text{C}$) annealing in Ar-O₂ (20%) atmosphere. After annealing process, the *I*-*V* response of the sensor element shows large hysteresis under both forward and reverse bias (Figure 2: Curve 2). This result indicates that an additional capacitance with long relaxation time is added in the *p*-NiO:Li-*n*-ZnO interface region, whose origin is charge/discharge process in long-lived surface adsorption states, probably oxygen adsorption states. The *p*-NiO:Li/*n*-ZnO heterojunction sensor element shows extremely small response to acetone or ethanol vapor introduction under dark, and no response to aromatic VOCs, benzene or toluene. Aromatic VOCs will physically adsorb over a metal oxide surface, but never activated or positively charged at room

temperature[2]. If benzene adsorbate over a p -NiO- n -ZnO junction was positively charged due to the external cause such as light irradiation or d.c. bias application, the current passing through the junction would be strongly modified and it worked as an aromatic VOC sensor.

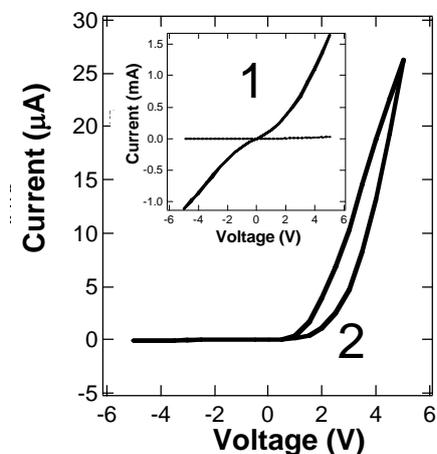


Figure 2 The I-V response of a p -NiO:Li/ n -ZnO sensor element, whose junction region is exposed to the atmosphere before (1) and after (2) annealing in Ar-O₂ 20% at 200°C. The measurement is conducted under dark.

The effect of benzene vapor introduction on the I-V response of a p -NiO:Li/ n -ZnO heterojunction sensor element is shown in Figure 3. Under the UV light irradiation, the photocurrent flows both forward and reverse directions and its rectifying junction properties are spoiled again. When benzene vapor is introduced in the junction interface, both forward and reverse current rapidly decreases in proportion to the square root of the benzene concentration, thereby its rectifying character is still spoiled during the exposure to the benzene vapor. The current response is rapid and reversible and it recovered to the initial value when the benzene vapor is completely removed. Here, we will discuss the necessary condition for benzene sensing by a p -NiO:Li/ n -ZnO sensor element. The characteristic emission-lines of a mercury lamp are λ (wavelength)=254, 295,302,313 and 365nm in the UV region and λ =254nm line is coincide in wavelength with the absorption maximum of aromatic ring, which is located around 255nm(4.90eV)[3]. The full spectrum of the irradiating UV light can excite not only the valence electrons of NiO and ZnO but also π conjugated electrons of adsorbed benzene, while emission lines at λ =295,302,313 and 365nm can excite only valence electrons of NiO and ZnO.

When the λ =254nm emission-line is completely cut by a Pyrex glass filter, the photocurrent still flows through the junction but the current response to benzene vapor introduction is dramatically suppressed. Photo-generated carriers at the NiO:Li/ZnO interface dose not directly promote the activation and reaction of aromatic VOCs. That is, λ =254nm deep UV light incidence is essential for aromatic VOC sensing operation and it might cause the activation of aromatic ring of benzene. Photo-activated adsorbed benzene would easily interact with

photo-generated holes concentrated at the junction interface and possibly, molecularly adsorbed benzene would be charged positively. As is shown in Figure 3, the current decreases by the introduction of benzene vapor. Positive space charge is suggested to be generated by the interaction between photo-activated benzene adsorbates and photo-generated holes and such extra cahrg would enhance the potential barrier height of p -type side (p -NiO:Li) of the junction. That would be the origin of the current response of a p -NiO:Li/ n -ZnO heterojunction sensor element under UV light irradiation.

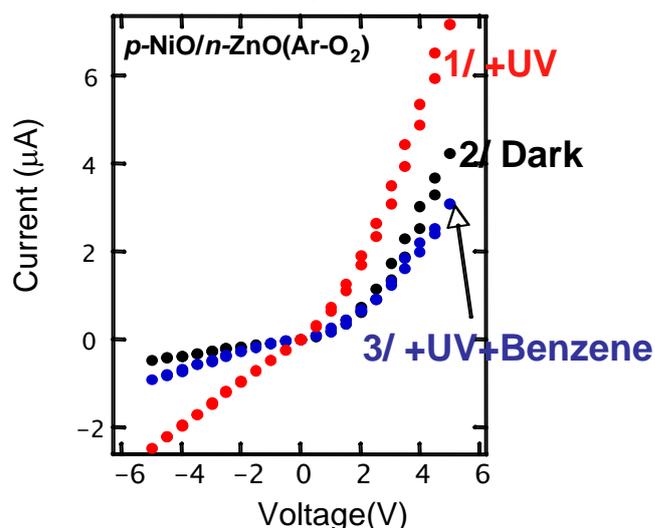


Figure 3 The effect of benzene vapor introduction on the I-V characteristics of a p -NiO:Li/ n -ZnO sensor element. The benzene concentration in the sample chamber is 3300ppm. The necessary condition for benzene sensing is deep UV light (λ <254nm) incidence.

CONCLUSION

The authors succeeded to detect aromatic VOCs by using p -NiO:Li/ n -ZnO heterojunction sensor element at room temperature. The core mechanism for aromatic VOC detection by such a wide gap pn junction diode would be photo-driven oxidation (positive ionization) of aromatic ring, which was triggered by remarkable UV irradiation of λ =254nm by a mercury lamp. Another novel function, molecular recognition was expected and molecular recognition of π conjugated electron systems would be possible by tuning the wavelength of excitation light source.

References

1. Norbaeck D, Michel I, and Widstroem J, Indoor air quality and personal factors related to the sick building syndrome, *Scand J. Work Environ. Health*, **16** (1990) 121-28.
2. Petittio S.C., Marsh E.M, and Langell M.A., Adsorption of bromobenzene on periodically stepped and nonstepped NiO(100), *J.Phy. Chem. B*, **110** (2006) 1309-18.
3. Hashimoto.T, Nakamno. H, and Hirao K., *J. Chem. Phys.*, **104**, (2004) 6244-58.