

Photo-assisted Aromatic VOC Sensing by a p -NiO:Li/ n -ZnO Transparent Heterojunction Sensor Element

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Abstract

p -NiO/ n -ZnO transparent heterojunction diode is prepared by the continuous film deposition using RF magnetron sputtering technique and processed into a chemical sensor element by photolithography patterning and chemical etching. This structurally designed p -NiO/ n -ZnO junction diode, whose junction interface is exposed to the atmosphere, has a response to VOCs (volatile organic compounds) in atmosphere. Furthermore, its VOC sensing performance is extremely enhanced when the sensor element is operated under deep UV light irradiation (<300nm). Independent of the polarity of the applied bias, the current passing through the junction interface rapidly decreases by the introduction of benzene or other aromatic VOCs. Photo-driven electron transport between photo-excited VOC adsorbates and valence band (VB) of p -NiO plays an important role for this sensor operation.

Key words: Heterojunction, Sensor, Photocurrent, VOC, Benzene, Photolithography

Introduction

From the viewpoint of maintenance of safe environment, there is currently great interest in the R&D of compact-sized VOC (volatile organic compounds) monitoring systems with high reliability, rapid response and lower power consumption. Since the first proposal of a gas sensor device based on oxide semiconductors, their simple structures have been attractive candidate for VOC monitoring systems for the use of air quality monitoring.

Recently, sick building syndrome is recognized as a serious social problem [1]. Benzene, toluene or other aromatic VOCs are etiological compounds for this strange disease. For preventing the indoor air pollution by these compounds, the reliable sensing system for aromatic VOCs is in great demand. However, aromatic VOCs are thermodynamically stable and they are difficult to be detected by traditional gas sensing devices. If it were possible, the sensor operation would require elevated temperatures. High stability in aromatic ring prevents the full or partial

oxidation of aromatic compounds under the moderate temperature conditions. For this reason, traditional gas sensor materials are not so sensitive to aromatic VOCs.

In the present study, we will propose a new concept for detecting aromatic VOCs by using 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 photo-activation or electro-activation of aromatic VOCs is giving rise to the VOC sensing performance of the pn junction diode. Through the careful evaluation of the VOC sensing performance, we will discuss the VOC sensing mechanisms of the pn junction diode under d.c. bias. Both photo and electro activation processes are suggested to be required for VOC sensing in this system. 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

p-NiO:Li (NiO doped with 2 mol% lithium) and *n*-ZnO, wide-gap semiconductors with high chemical stability, were chosen for heterojunction sensor element. A Sn/*n*-ZnO/*p*-NiO:Li/Ni structure, a „pre-structure“ of a *p*-NiO:Li/*n*-ZnO heterojunction sensor element was fabricated on an optically flat Ni metal substrate by stacking NiO:Li, ZnO and Sn films using rf-magnetron sputtering technique (Process (2) in Fig.1).

Next, the Sn/*n*-ZnO/*p*-NiO:Li/Ni „pre-structure“ was processed into a chemical sensor element whose junction interface was exposed to the atmosphere. After drawing the interdigital electrode pattern over the „pre-structure“(Process (3) in Fig.1), it was chemically etched in 0.1M HNO₃ aqueous solution at 21°C. After 15 sec. etching, Sn and ZnO layer were completely removed leaving intact electrode patterns, 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 Fig. 1 (0)-(6).

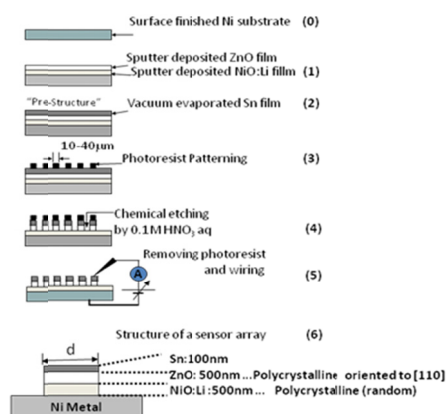


Fig.1 Schematic illustrations of the fabrication process of a *p*-NiO:Li/*n*-ZnO heterojunction sensor element. (2) is „Pre-structure“ of a sensor element, whose junction interface is not exposed to the atmosphere.

Experimental setup for the evaluation of sensor performance was illustrated in Fig.2. A *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. The current under constant d.c. bias was continuously monitored by a precision electrometer. The 50µl of benzene or other VOC sources was directly injected into the gas flow system and traveled to the sample chamber with a carrier gas of dried air. The concentration of VOC around the sample stage was checked in advance using a gas detection system. For the enhancement of the VOC

sensitivity, deep UV-light was irradiated to the sensor element using a 17W mercury vapor lamp. The UV light intensity was 1.1mW/cm at the wavelength of 254nm.

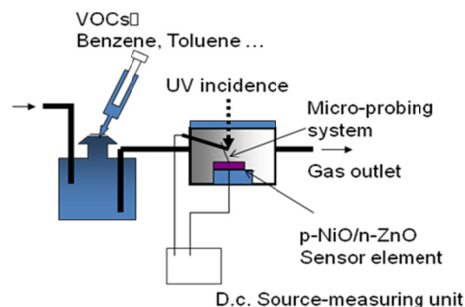


Fig.2 Experimental setup for the evaluation of the VOC sensing performance.

Results and Discussion

Prepared NiO and ZnO thin films are polycrystalline ones with random crystal axis orientation for NiO and weak (110) orientation for ZnO. The *p*-NiO:Li/*n*-ZnO junction device has polycrystalline-polycrystalline interface and it shows rectifying character with the rectifying ratio of 4×10^2 and ideality factor of $n=6.2$. No hysteresis is observed in its I-V response. The carrier concentrations for *p*-NiO:Li and *n*-ZnO were checked by Hall effect measurement in advance and $p=1.2 \times 10^{17}$ for NiO and $n=1.0 \times 10^{19} \text{ cm}^{-3}$ for ZnO were obtained.

The basic electrical properties of a *p*-NiO/*n*-ZnO epitaxial junction had already reported by Ohta et.al.[2] A *p*-NiO-*n*-ZnO epitaxial junction shows good rectifying character with ideality factor of $n=2$, that is, the dominant current transport process is the recombination current via interface states. Therefore, the current passing through the junction is suggested to be strongly modified by the nature of the interface states.

The diode performance of the Sn/*n*-ZnO/*p*-NiO:Li/Ni structure is once spoiled by processing it into a sensor element as is shown in the inset of Fig. 3: Curve 1. The leaky I-V response is able to be recovered by low temperature ($T=200^\circ\text{C}$) annealing in Ar-O₂ (20%) atmosphere. Simultaneously, the I-V response shows characteristic hysteresis under both forward and reverse bias (Fig.3: Curve 2). This result indicates that 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.

In our previous study, the authors suggested that adsorbed oxygen or other adsorbed species over an oxide semiconductor junction interface would be ionized by the carrier injection from the junction interface and found out that the catalytic activity of oxidation

reaction of combustible gas is modified as a function of applied bias [3].

In the case of the present p -NiO:Li/ n -ZnO heterojunction diode, the „electro-activation“ of interface layers would not be effective in the VOC detection at room temperature. From the data of the current-time behavior ($V=+4.5V$), the electric current passing through the junction is judged to show no characteristic change as a function of benzene vapor concentration (Fig.4). Rise and decay of the benzene vapor concentration is superposed in current data in Fig.4. The p -NiO:Li/ n -ZnO heterojunction sensor element shows extremely small response to acetone or ethanol vapor introduction under dark.

Under forward applied bias, majority carriers would concentrate in the junction region but they would not strongly interact with the adsorbed species of VOCs under dark. Aromatic VOCs will physically adsorb over a metal oxide surface, but never activated or positively charged at room temperature[4]. If benzene adsorbate over a p -NiO- n -ZnO junction was positively charged due to the

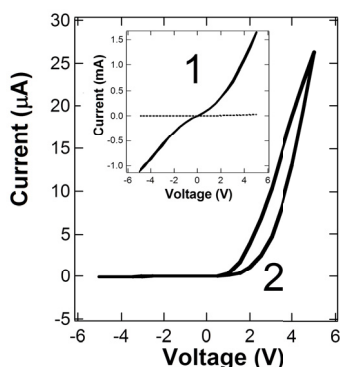


Fig.3 The I-V response of a p -NiO:Li/ n -ZnO sensor element, whose junction region is exposed to the atmosphere before (1) and after (2) annealing in Ar-O₂ 20% at 200°C. The measurement is conducted under dark.

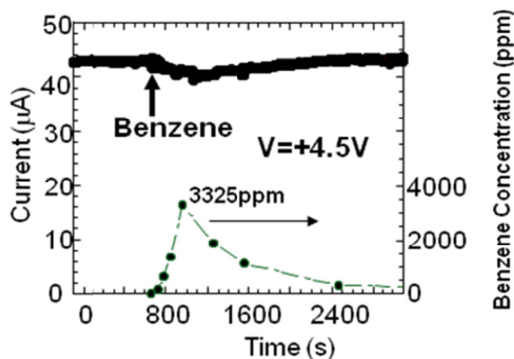


Fig.4 The effect of benzene vapor introduction on the forward current ($V=+4.5V$) through p -NiO:Li/ n -ZnO heterojunction sensor element. Rise and decay of benzene vapor concentration is superposed in the current data.

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. From the data of Fig.4, electric activation is not effective by itself. No response in the current by the introduction of aromatic VOC can be guessed by using very simple energy diagram in Fig.5. The ground states of π electrons in benzene molecule is located 9.24eV below the vacuum level, while the valence band (VB) of p -NiO is located -5.5eV vs. vacuum level. From the simplistic discussion, holes in VB of p -NiO cannot interact with π electrons in benzene due to far large difference between the VB of p -NiO and the π electron states of aromatic ring. On the other hand, the excited state (π^*) of aromatic ring is -4.13eV vs. vacuum level and it could interact with holes in VB of p -NiO, if the lifetime of the excited states is sufficiently long.

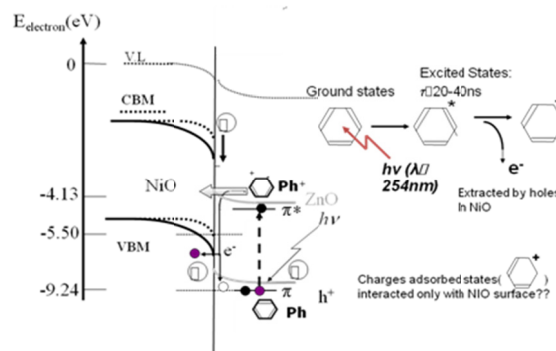


Fig.5 Energy diagram of p -NiO/ n -ZnO heterojunction. If the electron transfer between VB of p -NiO and excited states (π^*) electrons of benzene. Possible photo-driven oxidation process for aromatic VOC (benzene) would be possible under $\lambda=254nm$ UV light irradiation.

The effect of benzene vapor introduction on the I-V response of a p -NiO:Li/ n -ZnO heterojunction is shown in Fig.6. 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 into 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. 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 $\lambda=254nm$ line is coincide in wavelength with the absorption maximum of aromatic ring, which is

located around 255nm(4.90eV)[5]. 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 $\lambda=295,302,313$ and 365nm can excite only valence electrons of NiO and ZnO.

As is shown in Fig.7, when the $\lambda=254$ nm 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, $\lambda=254$ nm 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 charge 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.

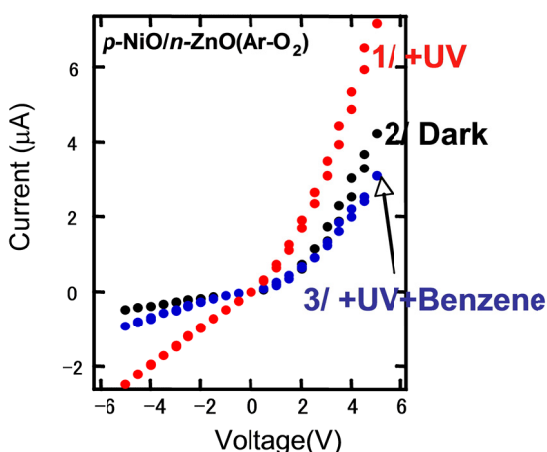


Fig.6 The effect of benzene vapor introduction on the I-V characteristics of a p -NiO:Li/ n -ZnO sensor element. The benzene concentration in the sample chamber is 3300ppm. The necessary condition for benzene sensing is deep UV light ($\lambda < 254$ nm) incidence.

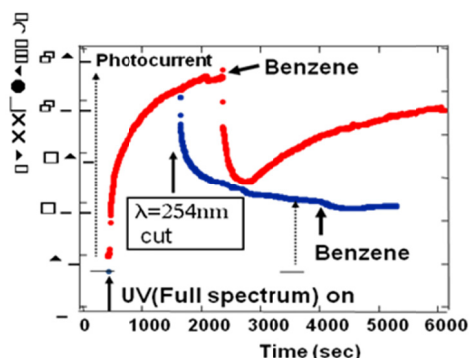


Fig.7 Effect of wavelength of UV light source on the benzene sensing characteristics of a p -NiO:Li/ n -ZnO heterojunction sensor element. When $\lambda=254$ nm line is cut by a glass filter, the current becomes insensitive to benzene vapor.

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 $\lambda=254$ nm 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.

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