Gate-refreshable nanowire chemical sensors

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(Received 8 November 2004; accepted 25 January 2005; published online 17 March 2005)

ZnO nanowire field effect transistors were implemented as highly sensitive chemical sensors for detection of NO₂ and NH₃ at room temperature. Due to a Debye screening length comparable to the nanowire diameter, the electric field applied over the back gate electrode was found to significantly affect the sensitivity as it modulates the carrier concentration. A strong negative field was utilized to refresh the sensors by an electodesorption mechanism. In addition, different chemisorbed species could be distinguished from the "refresh" threshold voltage and the temporal response of the conductance. These results demonstrated a refreshable field effect sensor with a potential gas identification function. © 2005 American Institute of Physics. [DOI: 10.1063/1.1883715]

Semiconducting quasi-one-dimensional (Q1D) systems are natural candidates for chemical sensing applications due to their large surface-to-volume ratio and finite charge carrier concentration which can be significantly influenced by the chemical surroundings. It has been well accepted that this electrical property change is the consequence of charge transfer between the Q1D systems and the chemisorbed species. Based on this mechanism, various Q1D systems have been configured as chemical sensors for detection of toxic and flammable gases such as NO₂, CO₂, CO, NH₃, etc. Most of the previous reports are based on two terminal measurements treating Q1D systems simply as resistance wires. Very little effort has been devoted to study the effect of gate potential on the sensing performance of Q1D systems. In fact, gate potential plays a crucial role in Q1D systems since their diameters are comparable to the Debye screening length thus a small change on the gate potential can affect the electronic property of the entire channel. In this letter, ZnO nanowire field effect transistors (FETs) are presented as chemical sensors for detection of NO₂ and NH₃. It was observed that the detection sensitivity can be tuned by the back gate potential and large negative gating could significantly expedite the desorption process at room temperature. Furthermore, the gate potential variation induced time-dependent behavior demonstrated a potential gas distinguishing mechanism.

The remarkable optical, electrical, and mechanical properties of ZnO nanostructures have been intensively studied. N-type ZnO nanowires were grown via catalytic chemical vapor deposition method. Fabrication of nanowire FETs and electrical transport studies are reported elsewhere. To conduct chemical sensing experiments, NW FETs were loaded into a clean chamber with electrical feedthrough. The chamber was pumped down to 10⁻⁷ Torr and the sample was baked at 200 °C for half an hour to remove the surface adsorbents such as O₂ and H₂O. After the system was cooled down to room temperature, it was filled with 760 Torr diluted target gas balanced with Ar. Figures 1(a) and 1(b) plot the I–V curves obtained under different NO₂ concentrations at V₉=0 and −5 V. The minimum NO₂ concentration detected with this particular NW is 200 ppb. It has been reported that thinner metal-oxide NWs and NWs network could demonstrate lower detection limit. The inset of Fig. 1(a) indicates a linear decrease of the NW conductance with increasing NO₂ concentration up to 10 ppm. It is evident that lowering gate potential increases the detection sensitivity, which is also observed in O₂ sensing. In fact, the dependence of gas detection sensitivity on the gate potential can be obtained from curves acquired under different target gas concentrations and the corresponding derivation is presented as following. It can be seen that the threshold voltage V₉ shifts from V₉₀(−7.9 V) in 0 ppm NO₂ to V₉₁(−5.2 V), or ΔV₉₂=2.7 V in 5 ppm NO₂. This shift can be correlated with the change of electron concentration ∆n using

\[ n = C(V_9 - V_t)/e \pi R^2 L, \]  

where C is the nanowire capacitance with respective to the back gate, e is the electronic charge, and R and L are radius and length of nanowire channel, respectively. Hence

\[ \Delta n = -C \Delta V/e \pi R^2 L. \]  

Relative sensitivity is defined as \( S = \left| G_{\text{gas}} - G_0 \right|/G_0 \), where the \( G_{\text{gas}} \) and \( G_0 \) are the NW conductance in the presence of target gas and pure Ar, respectively. Since \( G = n \mu e \pi R^2 /L \), therefore

\[ S = \left| n_{\text{gas}} - n_0 \right|/n_0 = |\Delta n|/n_0. \]  

The combination of Eqs. (1)–(3) gives

\[ S(V_9) = \Delta V/(V_9 - V_{t0}). \]  

The derived \( S(V_9) \propto (V_9 - V_{t0})^{-1} \) relationship is depicted in the inset of Fig. 1(c). Apparently, maximum sensitivity can be achieved when gate potential approaching \( V_{t0}(−7.9 \, \text{V}) \). This relationship can be also interpreted by the increased Debye screening length with decreasing electron concentration. Furthermore, \( S(V_9) \) is related with the partial pressure of the target gas. Let the surface density of chemisorbed molecules be \( N_r \), hence for Q1D system

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The probability of the chemisorbed states is 15. This concept is utilized in catalytic activity on the surface, determining the occupation of the surface by adsorbed molecules. According to the theory of chemisorption, the chemical potential controls the adsorption, and thus the occupation of the surface. The chemical potential is related to the electronic structure of the metal-oxide NW.

In this work, we propose a self-contained sensor which can electrically desorb the chemisorbed gas molecules using gate potential. As shown in Fig. 2, after a NW was first exposed to 10 ppm NO₂ gas pulse, then again to 760 Torr pure Ar, a −60 V gate voltage pulse (much below the threshold value $V_g = -25$ V in 10 ppm NO₂ for this NW) pulse with 60 s duration was applied. This voltage pulse accounts for a complete NW conductance turnoff. Interestingly, about 4 min after the voltage pulse, NW conductance was recovered to the initial level before NO₂ exposure. Therefore, the large negative gate pulse efficiently refreshed the NW sensor. The possible mechanism accounts for this phenomenon is proposed as following. Although the binding energy between the adatoms and adsorption sites is usually much larger than the room-temperature thermal energy, a negative gate potential depletes the electrons in the metal-oxide NW and reduces the number of electrons available at vacancy sites, thus lowering the chemisorption rate. However, it is not convenient to integrate a UV source with a chemical sensor and this method suffers from a relative long recovery time due to the large number of electron-hole pairs generated and the low recombination rate. Hence we propose a self-contained sensor which can electrically desorb the chemisorbed gas molecules using gate potential.

FIG. 1. ZnO NW I-V curves obtained in different NO₂ concentration at $V_d = 0$ V (a) and $V_d = -5$ V (b). Inset: NW conductance vs NO₂ concentration at $V_d = -5$ V. (c) NW FET I-V curves obtained in pure Ar (0 ppm), 5 and 10 ppm NO₂. Inset: detection sensitivity as a function of gate voltage.

The conductance recovery process caused by a −60 V gate voltage pulse is shown in the inset of Fig. 1(a). Consequently, Eqs. (2), (4), and (5) yield

$$\Delta n = -\frac{2}{R} \alpha N_s,$$

where $\alpha$ is a charge transfer coefficient denoting the number of electrons captured by one chemisorbed molecule. In the low pressure limit of Langmuir isotherm, $N_s$ can be expressed as $N_s = \beta P_{gas}$, where $\beta$ is a proportionality coefficient, thus $\Delta n \propto P_{gas}$. This is consistent with the linear concentration dependence of conductance shown in the inset of Fig. 1(a).

Equation (6) clearly demonstrates the tunability of the chemical sensitivity using gate potential. In addition, it has been observed that a large gate voltage induced field is capable of affecting gas adsorptivity on the ZnO NW significantly. In this case, the chemical potential in the NW is altered by the external field. According to the electron theory of chemisorption, the chemical potential controls the catalytic activity on the surface, determining the occupation probability of the chemisorbed states.

This concept is utilized in this work to implement an electrically recoverable gas sensor which operates at room temperature. As known, chemical sensing at room temperature is hardly reversible because the thermal energy is usually lower than the activation energy for desorption. This leads to a long recovery time. UV illumination is a common method to refresh the sensor. However, it is not convenient to integrate a UV source with a chemical sensor and this method suffers from a relative long recovery time due to the large number of electron-hole pairs generated and the low recombination rate. Hence we propose a self-contained sensor which can electrically desorb the chemisorbed gas molecules using gate potential.

In addition, if the chemisorption is "weakly" associated with the adsorbed gas molecules, then the thermal energy is usually much larger than the room-temperature thermal energy, a negative gate potential depletes the electrons in the metal-oxide NW and reduces the number of electrons available at vacancy sites, thus lowering the chemisorption rate.

Hole migration to the surface driven by the negative field leads to the discharge of gas molecules. In addition, if the chemisorption is "weakly" associated with an appreciable dipole moment, it is likely that the negative gate induced repulsive field stretches and weakens the bonding between these adatoms and adsorption sites. Conclusively, these factors lead to the electrodeposition process and the fast conductance recovery at room temperature.

Using gate potential to refresh the nanowire chemical sensor takes advantage of the FET device structure and greatly simplifies the design of chemical sensors. Besides NO₂, NH₃ was also used for sensing study and exposure of NH₃ reduced the NW conductance as reported. Experiments showed that the gate voltage required to refresh the adsorbed NH₃ molecules was lower than that for NO₂. For example, the “refresh” voltage for 1% NH₃ is ~30 V as compared with ~60 V for 10 ppm NO₂. Using the same gate pulse duration (60 s), the minimum gate “refresh” voltage is determined to be concentration dependent, as plotted in Fig. 3(a). In addition, the time domain response for NO₂ and NH₃ shows clear difference. As shown in Fig. 3(b), NW conductance dropped when a negative gate voltage pulse (~20 V, slightly higher than $V_d$) was applied at the back gate. In the...
duration of the pulse, NW conductance shows a quick transient followed by a relative steady recovery process, as expected from the dynamic adsorption-desorption process. The slopes ($k$) of the linear recovery regions for NO$_2$ and NH$_3$ at different concentrations are shown in Figs. 3(b) inset and 3(c), respectively. It was observed that this slope was concentration independent and different for NO$_2$ and NH$_3$, specifically, $k_{\text{NH}_3} = 2k_{\text{NO}_2}$. These results lead to the conclusion that NH$_3$ is much easier to be electodesorbed than NO$_2$. The theoretical investigation on the mechanism behind these phenomena is still open. We believe that the difference in the recovery rate is due to the weaker surface binding for NH$_3$ than NO$_2$. According to the Volkenstein model, acceptor-like chemisorption state ($E_a$) formed in the forbidden band if chemisorbed gas molecules capture electrons. Qualitatively, the depth of $E_a$ in the forbidden band is related with the conductance activation energy $E_A$ [Fig. 3(d)], in which $E_a(\text{NH}_3) < E_A(\text{NO}_2)$. This condition yields two consequences: (1) the total chemisorption coverage of NH$_3$ is less than that of NO$_2$, which has been confirmed by the observation that NW FETs tend to be less sensitive to NH$_3$ than to NO$_2$ (data not shown) and (2) the desorption energy needed for NO$_2$ is greater than that for NH$_3$. This indicates the higher surface binding strength for NO$_2$ than for NH$_3$ and also accounts for the differences on their refresh voltage and recovery rate.

In conclusion, we present a ZnO NW field effect chemical sensor, showing their sensing properties for NO$_2$ and NH$_3$ target gases. It was observed that the gate potential can affect the detection sensitivity, and the adsorbed gas molecules could be electrically desorbed by applying a large negative gate voltage. In addition, the studies on the “refresh” threshold gate voltage and time dependent response demonstrate a potential gas distinguishability. These findings indicate that ZnO NW FET is a highly promising candidate for smart chemical sensing.

This work was supported by the National Science Foundation Grant No. ECS-0306735 and performed at the Integrated Nanosystem Research Facility in UC Irvine. The authors thank Dawei Wang and Paichun Chang for technical assistance.

\[\text{References}\]