

Gate-refreshable nanowire chemical sensors

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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 electrodesorption 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.^{1–3} Based on this mechanism, various Q1D systems have been configured as chemical sensors for detection of toxic and flammable gases such as NO₂,^{1–3} CO,⁴ NH₃,^{1,3} ethanol,^{2,5} 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.⁶ 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,⁷ electrical,⁸ and mechanical properties⁹ of ZnO nanostructures have been intensively studied. *N*-type ZnO nanowires were grown via catalytic chemical vapor deposition method.¹⁰ Fabrication of nanowire FETs and electrical transport studies are reported elsewhere.^{11,12} To conduct chemical sensing experiments, NW FETs were loaded into a clean chamber with electrical feedthrough. The chamber was pumped down to 10⁻³ 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 *V*_g=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.^{11,13} 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.¹¹ In fact, the dependence of gas detection sensitivity on the gate potential can be obtained from *I*–*V*_g curves acquired under different target gas concentrations and the corresponding derivation is presented as following. *I*–*V*_g curves are obtained under 0 (pure Ar) and 5 ppm NO₂ [Fig. 1(c)]. It can be seen that the threshold voltage *V*_t shifts from *V*_{t0}(–7.9 V) in 0 ppm NO₂ to *V*_{t1}(–5.2 V, or Δ*V*_{t1}=2.7 V) in 5 ppm NO₂. This shift can be correlated with the change of electron concentration Δ*n* using

$$n = C(V_g - V_t)/e\pi R^2L, \quad (1)$$

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

$$\Delta n = -C\Delta V_t/e\pi R^2L. \quad (2)$$

Relative sensitivity is defined as $S \equiv |G_{\text{gas}} - G_0|/G_0$, where the *G*_{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

$$S = |n_{\text{gas}} - n_0|/n_0 = |\Delta n|/n_0. \quad (3)$$

The combination of Eqs. (1)–(3) gives

$$S(V_g) = \Delta V_t/(V_g - V_{t0}). \quad (4)$$

The derived $S(V_g) \propto (V_g - V_{t0})^{-1}$ relationship is depicted in the inset of Fig. 1(c). Apparently, maximum sensitivity can be achieved when gate potential approaching *V*_{t0}(–7.9 V). This relationship can be also interpreted by the increased Debye screening length with decreasing electron concentration.¹⁴ Furthermore, *S*(*V*_g) is related with the partial pressure of the target gas. Let the surface density of chemisorbed molecules be *N*_s, hence for Q1D system

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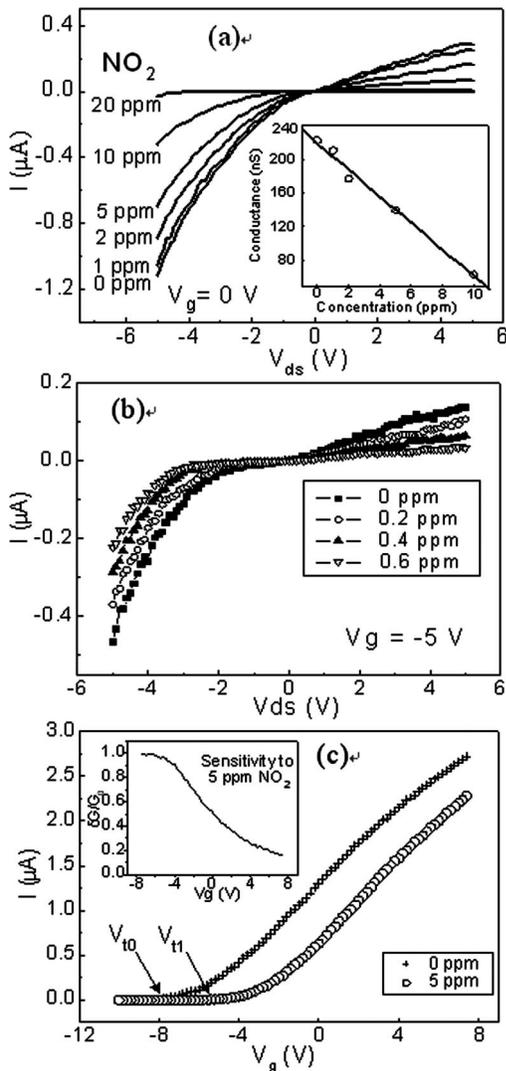


FIG. 1. ZnO NW I - V curves obtained in different NO_2 concentration at $V_g = 0$ V (a) and $V_g = -5$ V (b). Inset: NW conductance vs NO_2 concentration at $V_{ds} = -5$ V. (c) NW FET I - V_g curves obtained in pure Ar (0 ppm), 5 and 10 ppm NO_2 . Inset: detection sensitivity as a function of gate voltage.

$$\Delta n = -\frac{2}{R} \alpha N_s, \quad (5)$$

where α 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 $N_s = \beta P_{\text{gas}}$ where β is a proportionality coefficient, thus $\Delta n \propto P_{\text{gas}}$. This is consistent with the linear concentration dependence of conductance shown in the inset of Fig. 1(a). Consequently, Eqs. (2), (4), and (5) yield

$$S(V_g) = \frac{2e\alpha\pi RL}{C(V_g - V_{t0})} \beta P_{\text{gas}}. \quad (6)$$

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.^{15,16} 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.¹⁵ This concept is uti-

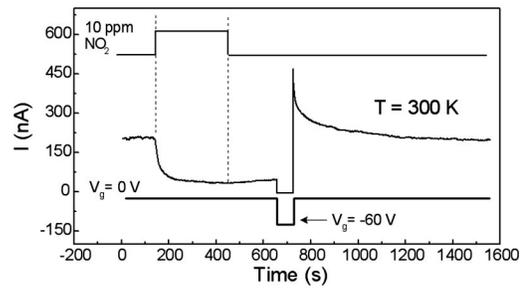


FIG. 2. NW sensing response to 10 ppm NO_2 and the conductance recovery process caused by a -60 V gate voltage pulse.

lized 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.¹⁷ This leads to a long recovery time. UV illumination is a common method to refresh the sensor.¹ However, it is not convenient to integrate a UV source with a chemical sensor and this method suffers from 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. As shown in Fig. 2, after a NW was first exposed to 10 ppm NO_2 gas pulse, then again to 760 Torr pure Ar, a -60 V gate voltage (much below the threshold value $V_t = -25$ V in 10 ppm NO_2 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 NO_2 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 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.⁶ 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,¹⁴ 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 electrodesorption 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 NO_2 , NH_3 was also used for sensing study and exposure of NH_3 reduced the NW conductance as reported.¹⁸ Experiments showed that the gate voltage required to refresh the adsorbed NH_3 molecules was lower than that for NO_2 . For example, the “refresh” voltage for 1% NH_3 is -30 V as compared with -60 V for 10 ppm NO_2 . 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 NO_2 and NH_3 shows clear difference. As shown in Fig. 3(b), NW conductance dropped when a negative gate voltage pulse (-20 V, slightly higher than V_t) was applied at the back gate. In the

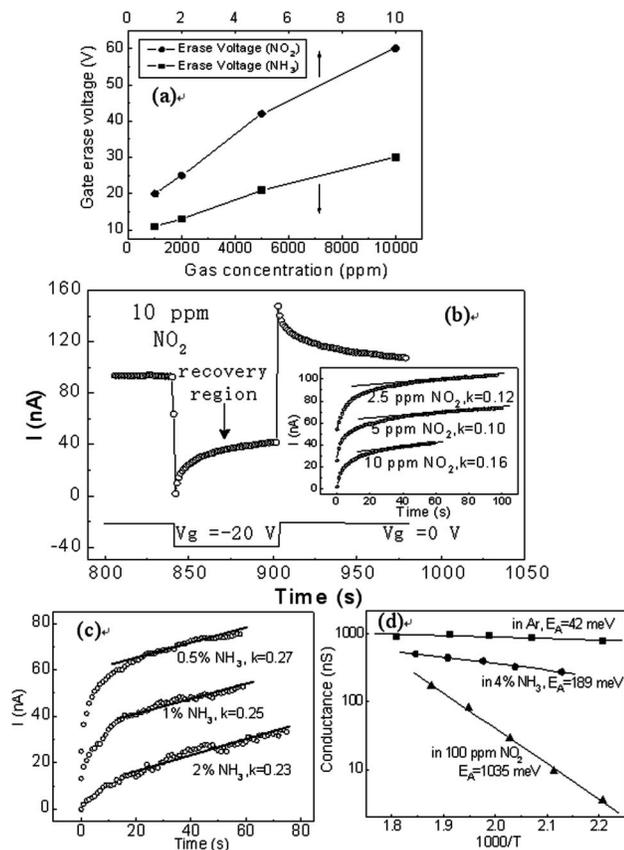


FIG. 3. (a) Gate “refresh” voltage magnitude as a function of NO₂ and NH₃ concentration. (b) NW conductance recovery under $V_g = -20$ V pulse in 10 ppm NO₂. Inset: recovery curves at different NO₂ concentrations. The solid lines represent the linear fits in the recovery region. (c) Conductance recovery curves for NH₃ under $V_g = -20$ V pulse. (d) Temperature dependence of the nanowire conductance show different activation energies, E_A , obtained in Ar, NH₃, and NO₂.

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 NO₂ and NH₃ 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 NO₂ and NH₃, specifically, $k_{\text{NH}_3} \approx 2k_{\text{NO}_2}$. These results lead to the conclusion that NH₃ is much easier to be electrodesorbed than NO₂. The theoretical investigation on the mechanism behind these phenomena is still under way. We believe that the difference in the recovery rate is due to the weaker surface binding for NH₃ than NO₂. According to the Volkenstein model, acceptorlike chemisorption state (E_a) formed in the forbidden band if chemisorbed gas molecules capture electrons.¹⁵ 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 conse-

quences: (1) the total chemisorption coverage of NH₃ is less than that of NO₂, which has been confirmed by the observation that NW FETs tend to be less sensitive to NH₃ than to NO₂ (data not shown) and (2) the desorption energy needed for NO₂ is greater than that for NH₃. This indicates the higher surface binding strength for NO₂ than for NH₃ 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 NO₂ and NH₃ 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.

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