

Chemical Sensing With ZnO Nanowire Field-Effect Transistor

Zhiyong Fan and Jia G. Lu

Abstract—Zinc oxide nanowires are configured as n-channel FETs. These transistors are implemented as chemical sensors for detection of various chemical gases. It is observed that the nanowire conductance is reduced when it is exposed to oxygen, nitrogen dioxide, ammonia gases at room temperature. Its ammonia sensing behavior is observed to switch from oxidizing to reducing when temperature is increased to 500 K. This effect is mainly attributed to the temperature dependent Fermi level shift. In addition, carbon monoxide is found to increase the nanowire conductance in the presence of oxygen. Furthermore, the detection sensitivity dependence on the nanowire radius is presented.

Index Terms—Field-effect transistor (FET), nanotechnology, semiconductor device, semiconductor–metal interface, sensitivity.

I. INTRODUCTION

IN THE LAST decade, semiconducting quasi-one-dimensional (Q-1D) structures have received enormous attention for their promising potential in nanoscale electronic and optoelectronic devices, and much progress has been achieved towards these objectives [1]–[4]. In fact, the downscaling of material dimension does not only imply an increase in device packing density and a decrease in power consumption, but also it renders superior sensitivity to surface adsorption related chemical processes. As it has been reported, chemical sensing with nanowires and nanotubes is usually realized by monitoring their conductance change upon exposure to the target chemicals [5]–[7]. Compared with their bulk and thin-film counterparts, in addition to a larger surface-to-volume ratio, the Q-1D structure has radius comparable to the Debye screening length, so that chemisorption induced surface states effectively alter the electronic property of the entire system, yielding enhanced sensitivity.

In this paper, we report chemical sensing studies with zinc oxide (ZnO) nanowires configured as FETs. It is noteworthy that this device configuration can not only facilitate the monitoring of conductance change, but also utilize a transverse electric field to modulate the chemical sensing behavior of the nanowires, since the external field regulates the surface chemisorption activity [8].

II. NANOWIRE SYNTHESIS AND DEVICE FABRICATION

Single-crystalline ZnO nanowires were synthesized via a vapor trapping chemical vapor deposition method [9]. Using

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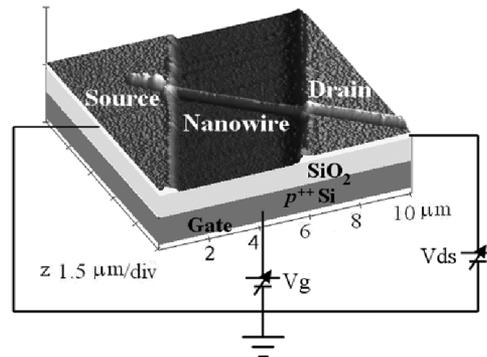


Fig. 1. Schematic of ZnO nanowire FET combined with the electrical transport measurement circuit.

this method, ZnO nanowires with high aspect ratio were obtained. The details of nanowire FET fabrication were reported elsewhere [10] and can be briefly described as follows. The as-synthesized ZnO nanowires were suspended in alcohol and deposited onto p^{++} Si substrates capped with an SiO_2 layer. Photolithography or electron beam lithography was conducted on such chips to define electrode patterns. The contacts were then fabricated using ebeam evaporation. Fig. 1 illustrates an atomic force microscopy image of a ZnO nanowire FET combined with the schematic of the measurement circuit. The three-terminal electrical transport study showed that the ZnO nanowires are n -type semiconductors, owing to the presence of oxygen vacancies and Zn interstitials. The measured room temperature Q-1D electron concentration is on the order of 10^7 cm^{-1} [10], corresponding to a volume concentration of $\sim 10^{19} \text{ cm}^{-3}$, and the electron mobility is on average $40 \text{ cm}^2/\text{V} \cdot \text{s}$.

III. CHEMICAL SENSING EXPERIMENTS AND RESULTS

In conducting chemical sensing experiments, nanowire FET samples were loaded into a vacuum chamber with electrical feedthroughs. The chamber was then pumped down to 10^{-3} torr and the sample was baked at 200°C for 30 min to remove the surface adsorbents such as O_2 and H_2O . After the system was cooled down to room temperature, it was first purged with 760 torr pure Ar. Then target gas mixed with Ar was introduced via mass flow controllers. The concentration of the target gas was controlled by setting its flow rate as well as the Ar flow rate to a desired ratio.

Various gases have been used in the chemical sensing study, such as O_2 , NO_2 , NH_3 , and CO . The monitoring of these gases in the environment is of paramount importance. As is known, chemisorbed gas molecules on a metal–oxide surface withdraw

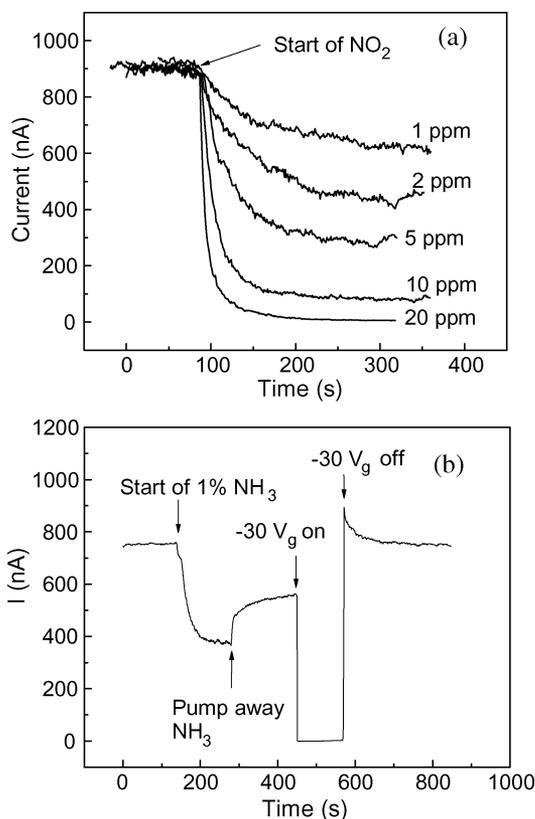


Fig. 2. (a) ZnO nanowire sensing response to different concentrations of NO_2 . (b) Nanowire sensing response to 1% NH_3 at 300 K, and the negative gate field induces a surface refresh process.

or donate electrons to the conduction channel, giving rise to a conductance change. Experiments have demonstrated that ZnO nanowire exposure to O_2 , NO_2 , and NH_3 at room temperature show decreased conductance. As shown in Fig. 2(a), nanowire conductance decreased when it was exposed to different concentrations of NO_2 varying from 1 to 20 ppm, and the sensing response increases with under higher concentration.

Fig. 2(b) plots the time-domain response of the nanowire conductance to 1% NH_3 at room temperature. In this case, a refresh process is also demonstrated. As reported in [11], a large negative gate field assists the surface desorption process, and thus leads to a fast recovery of nanowire conductance. It can be seen from Fig. 2(b) that a negative 30-V gate voltage was applied to efficiently recover the nanowire conductance in about 1 min.

NO_2 and NH_3 sensing experiments showed that even though both of them resulted in a conductance decrease, semiconducting nanowires were much more sensitive to NO_2 than to NH_3 . As shown in Fig. 2(a) and (b), 2-ppm NO_2 causes 50% conductance decrease while 1% NH_3 yields the same effect. This difference is due to the higher binding strength between NO_2 molecules and the nanowire surface. Interestingly, it was observed that NH_3 sensing at 500 K has the opposite effect compared to that at room temperature, i.e., the ZnO nanowire conductance increased upon exposure to NH_3 at 500 K, as illustrated in Fig. 3(a), indicating that the chemisorbed NH_3 molecules donate electrons to ZnO nanowire. Oxidizing and

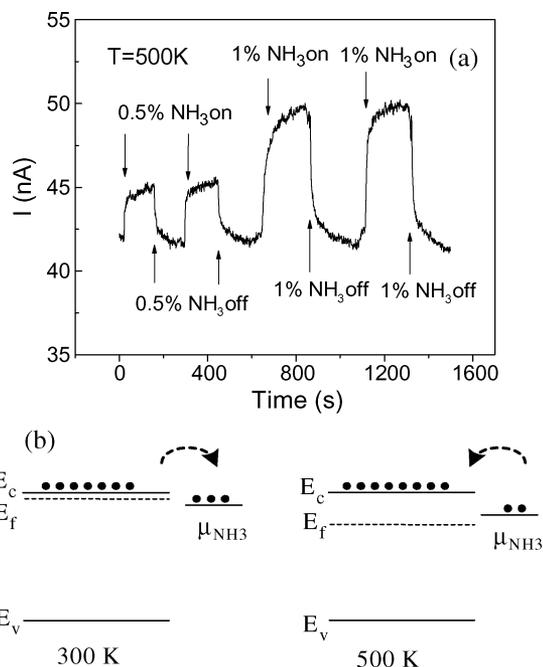


Fig. 3. (a) ZnO nanowire reducing sensing to NH_3 at 500 K. (b) Schematic of Fermi level shift from 300 K to 500 K and the resulted reversal of electron transfer direction.

reducing sensing of NH_3 with In_2O_3 nanowires at room temperature has been reported and attributed to a doping dependent Fermi level shift [12]. In our work, both oxidizing and reducing sensing to NH_3 were measured on the same ZnO nanowire sample. We attribute the change in the sensing response to a temperature-dependent Fermi level shift [13], [14].

As is known, n-type behavior of ZnO originates from donors such as oxygen vacancies and Zn interstitials. Some form shallow donor levels at about 30–60 meV below the conduction band edge E_c [10]. These donor states can be easily ionized, and the Fermi level is close to E_c as shown in Fig. 3(b). When the gas molecules adsorb onto the nanowire surface, electrons transfer from the material with higher chemical potential to that with lower chemical potential until the system reaches equilibrium. At room temperature, the Fermi level E_F lies above the chemical potential of ammonia gas μ_{NH_3} . Thus, electrons are withdrawn from the nanowire channel to the NH_3 molecules, causing a reduction in the conductance of the ZnO nanowire. When the temperature is increased, the Fermi energy level of the nanowire is downshifted; at the same time, the chemical potential of the NH_3 gas is also reduced [15]. At 500 K, we believe that the reduction of E_F is much larger than the reduction of μ_{NH_3} , resulting in E_F lying below μ_{NH_3} , as depicted in Fig. 3(b). As a consequence, electrons transfer from the NH_3 molecules to the nanowire, yielding a nanowire conductance increase. Thus, the reversal of electron transfer direction represents the switch of the sensing response from oxidizing to reducing behavior. There are other mechanisms which could also contribute to the conductance change at elevated temperature, such as an increased adsorption and desorption rates of the chemical molecules on the nanowire surface. However, we believe that the change in chemisorption

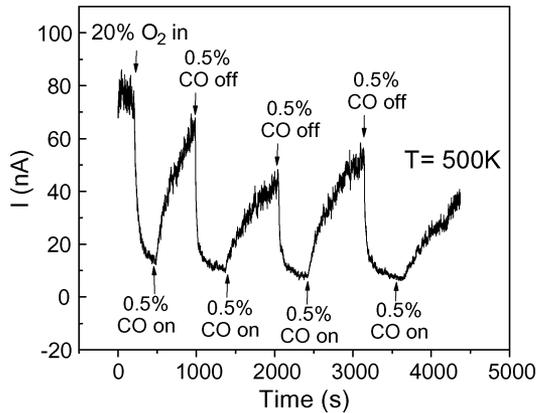
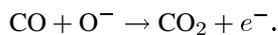


Fig. 4. The response of nanowire conductance to 0.5% CO in 20% O₂ at 500 K. The drain-source voltage here is 0.5 V.

rate will not explain the steady reversal in the electron transfer direction, but rather, it affects the sensitivity. As observed in our experiment, under the same concentration of NH₃ gas (1%), the relative conductance change is considerably smaller at 500 K [Fig. 3(a)] as compared to that at room temperature [Fig. 2(b)]. In order to gain a thorough understanding of such chemical sensing system, theoretical simulations which incorporate both the temperature dependence of the energy levels as well as the dynamic process of the nanowire surface chemisorption are necessary.

In addition to the sensing response to O₂, NO₂, and NH₃, we have also investigated the response of ZnO nanowires to CO gas in the presence of O₂. It is observed that the nanowire conductance is increased at 500 K. Fig. 4 demonstrates the time-domain measurement of nanowire conductance when the nanowire is exposed to 0.5% CO in 20% O₂ at 500 K. It can be seen that nanowire conductance first decreases upon admittance of 20% O₂; however, the subsequent admittance of CO increases the nanowire conductance. It is known that CO is a combustible gas; the sensing of CO is based on the reaction between CO and the preadsorbed oxygen species to form CO₂ [6]



Thus, an electron will be released back to the nanowire conduction band, resulting in the increase in the conductance.

As mentioned above, the large surface-to-volume ratio of the Q-1D systems enhances sensitivity to the chemical environment. Therefore, the nanowires' radius should significantly affect their chemical sensitivity. Fig. 5 plots the ZnO nanowire sensitivity to O₂ on seven samples with different radii [10]. Here, we define sensitivity as the relative conductance change after exposing nanowire to a target gas, i.e., $\Delta G/G_0 = |G_{\text{gas}} - G_0|/G_0$, where G_0 is the conductance before exposure under inert environment. In fact, this dependence of sensitivity on the nanowire radius can be simply derived using the Drude model. In such a model, assuming uniform

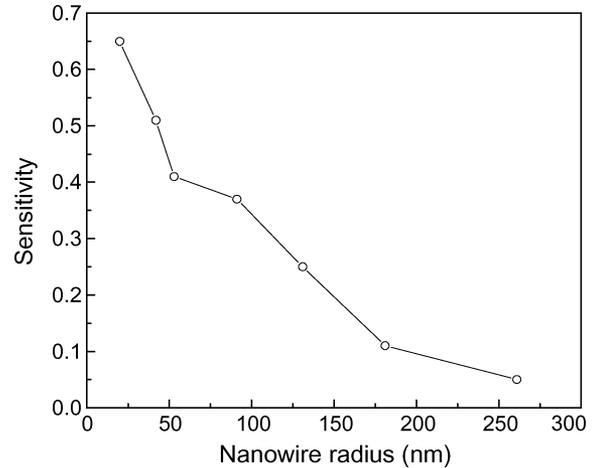


Fig. 5. Nanowire radius dependence of the sensitivity to O₂.

current density, the conductance G of a cylindrical wire with radius r and length l is expressed as

$$G = \frac{\pi r^2}{l} n_e e \mu_e \quad (1)$$

where n_e and μ_e are the electron concentration and mobility. According to [11]

$$n_e = n_0 - \frac{2\alpha N_s}{r} \quad (2)$$

where n_0 is electron concentration before nanowire exposure to target gas and N_s and α represent the surface density of chemisorbed molecules and the charge transfer coefficient, respectively. Therefore, upon chemisorption

$$\Delta G/G_0 = \frac{2}{r} \cdot \frac{\alpha N_s}{n_0}. \quad (3)$$

Apparently, the obtained $1/r$ relationship resembles the plot in Fig. 5 and clearly demonstrates that as the radius shrinks, the nanowire becomes more sensitive to chemical adsorption on the surface.

IV. CONCLUSION

In conclusion, ZnO nanowires FETs were implemented as chemical sensors for detection of various gases including NO₂, NH₃, CO, and O₂. It was observed that nanowire FET demonstrated oxidizing sensing property to NO₂, NH₃, and O₂ at room temperature. However, it showed reducing sensing property for NH₃ at 500 K. This behavior was attributed to the shift in Fermi energy at elevated temperature. In addition, the nanowire shows a conductance increase when exposed to CO gas mixed with O₂. Finally, sensitivity dependence on nanowire radius was demonstrated using O₂ sensing as an example. The result manifests that thinner nanowire achieves higher sensitivity.

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