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, mainly attributed to the temperature dependent Fermi level shift. 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 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-type 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$^{-2}$ [10], corresponding to a volume concentration of $\sim 10^{19}$ cm$^{-3}$, and the electron mobility is on average 40 cm$^2$/V·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 $10^{-5}$ torr and the sample was baked at 200 °C for 30 min to remove the surface adsorbents such as O$_2$ and H$_2$O. 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...
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 reducing sensing of NH$_3$ with In$_2$O$_3$ 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 lies above the chemical potential of ammonia gas $\mu_{\text{NH}_3}$. 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 $\mu_{\text{NH}_3}$, resulting in $E_F$ lying below $\mu_{\text{NH}_3}$, 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...
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]

\[
CO + O^- \rightarrow CO_2 + e^-.
\]

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., \( \Delta G / G_0 = |G_{gas} - G_0| / G_0 \), 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 current density, the conductance \( G \) of a cylindrical wire with radius \( r \) and length \( l \) is expressed as

\[
G = \frac{\pi r^2}{l} n_e \mu_e \mu_e (1)
\]

where \( n_e \) and \( \mu_e \) are the electron concentration and mobility. According to [11]

\[
n_e = n_0 - \frac{2 \alpha N_S}{r} (2)
\]

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

\[
\Delta G / G_0 = 2 \alpha N_S / n_0 (3)
\]

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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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.

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


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