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PAPER

Sensing properties of different classes of gases based on the nanowire-electrode junction barrier modulation†

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The role of contact between semiconducting nanowire and metal electrodes in a single nanowire field effect transistor (NW-FET) is investigated for the sensing of different types of gases. Two different types of In₂O₃ nanowire devices, namely; Schottky contact device (SCD) and Ohmic contact device (OCD) are evaluated. SCD has shown a superior response to the reducing gas (CO) compared to oxidizing gas (NO), while OCD has shown high sensitivity towards oxidizing gas (NO) compared to the reducing gas (CO) under similar working conditions. The sensing mechanism is dominated by the contact resistance at the metal-semiconductor junction in SCD and the change in nanowire channel conductance dominates in OCD. The Schottky barrier height (SBH) was extracted using low temperature current voltage measurement which provided direct evidence for the notion that the barrier height plays a crucial role in the sensing of different types of gases. The sensing mechanism is illustrated in this work for both devices.

1. Introduction

Semiconducting metal oxides (MO_x) as chemical sensing materials have been extensively studied for a long time due to their advantageous features, such as good sensitivity to the ambient conditions and simplicity in fabrication.^{1,2} Among MO_x, In₂O₃ has been found to have a pronounced sensitivity to gases such as NO_x, NH₃, CO, and other species.³⁻⁷ For highly sensitive nanosensors, devices based on one dimensional oxide semiconductor nanostructures have shown promising results^{3,4,8,9} because of their desirable large surface to volume ratio, single crystalline nature, ease of fabrication on various substrates by different techniques^{10,11} and controlled charge carriers flow along a small cross sectional area of the nanowire. Single nanowire field effect transistor (NW-FET) based conductometric sensors have shown the capability of room temperature operation¹²⁻¹⁴ mainly due to the fact that gas molecules directly interact on the single crystalline nanowire (with a small cross sectional area) surface with simple device geometry which alters their electronic properties and reflects as a change in the conductance of the device. Development of room-temperature gas sensors has very important advantages such as low power consumption, simple system

configuration, reduced explosion hazards and longer device lifetime.

Most past efforts on nanosensors have been focused on improving the sensitivity by modifying the nanowire channel; mainly by surface modification using polymer or metal nanoparticle functionalization to the nanowire channel,¹⁵⁻¹⁷ doping of nanowire *etc.*^{5,14} Recently there has been work done on the utilization of the contact resistance at the nanowire-electrode interface to improve the sensitivity.¹⁸⁻²¹ In a conductometric sensor, the sensor response is the relative change in the conductance of the device before and after exposure to the species to be detected. There are two main components in a single nanowire sensor which directly contribute to the sensor response; the nanowire channel and the contact resistance between electrode and nanowire [metal-semiconductor (MS) contact]. These contacts may be either ohmic or Schottky type, and both types of contact are important in sensing. In a single nanowire FET based sensor, the devices are usually designed to have ohmic contacts to enhance sensor performance. However, it may not always be advantageous to have an ohmic contact. Schottky contact devices are interspersely reported to be highly sensitive devices for gas sensing.¹⁸⁻²¹ The contact resistance contribution towards sensor response may vary significantly for different types of gases; as a result SBH modulation takes place during sensing due to the gas molecule interaction at the MS interface which plays an important role in the sensor response. Wei *et al.*¹⁹ have reported a four orders of magnitude higher sensor response for 400 ppm CO gas at 275 °C by using an one end Schottky contact device made of ZnO nanowire operated in reverse biased mode in comparison to that obtained using an ohmic contact device

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under the same conditions. The gas sensing mechanism of such devices is mainly dominated by the SBH modulation through adsorption and desorption of the negatively charged oxygen ions at the MS interface.

The goal to realize sensors at room temperature with a high response remains unfulfilled with critical challenges. Past research efforts on contact resistance utilization for gas sensing did not reveal any clear trend in sensing behavior toward two different classes of gases (*e.g.* oxidizing and reducing). A systematic study is required to investigate the sensing behavior of both Schottky and ohmic devices toward oxidizing and reducing gases. This work provides insight on the contact junction modulation to achieve improved sensor response at room temperature and selectivity for a particular class of gas. We have used two different types of devices (OCD and SCD) for the sensing of two different classes of gases [namely; CO (reducing gas) and NO (oxidizing gas)] by differentiating control of the contact resistance of the device to improve the sensor response at room temperature. In SCD we have used Schottky contact at both ends of the nanowire which gives the advantage to operate the device in both reverse and forward bias mode. In OCD, the nanowire channel plays a dominate role. The results presented here represent a step forward in the understanding on the utilization of the contact resistance in room temperature gas sensing of different class of gases and pave the way toward the future development of better sensor device at room temperature.

2. Results and discussion

In order to improve the sensitivity at room temperature, we have investigated sensing on two types of devices. In the first device, Schottky contacts at both ends of In_2O_3 NWs were made by placing NW on the Cr/Au electrode. In the second type of device In_2O_3 NWs were placed underneath the Cr/Au electrode for the ohmic contacts at the two ends. Sensing towards 5 ppm CO and NO gases using both types of devices were studied.

The as-synthesized In_2O_3 nanowires were found to be single crystalline with preferred orientation along (111). Details regarding the morphology and crystallinity of the vapor-liquid-solid (VLS) grown circular nanowires can be obtained from our

previous work.²² Electrical measurements on the single nanowire OCD and SCD are shown in figure 1 (a) and (b) respectively with devices consist of similar channel lengths of $\sim 4 \mu\text{m}$ and nanowire diameter of 165 nm respectively. The corresponding electrical behavior of the nanowire device can be observed clearly from the families of I-V plots. The OCD shows linear current-voltage (I-V) characteristics (Figure 1a). In case of SCD an asymmetric and non-linear characteristics in both reverse and forward bias voltage was observed (Figure 1b). These two above-mentioned device characteristics show that the change in electrical contact behavior has been achieved by placing the nanowire on top (SCD) or underneath (OCD) the electrode. When the nanowire is placed on top of the electrode, the contact material is gold and when the nanowire is underneath the electrode, the contact material is Cr (20 nm). Due to the different work functions of Cr (4.5 eV) and Au (5.1 eV–5.47 eV), these devices form different potential barrier for the migration of electrons which results in the change of the contact resistance to In_2O_3 NW. If a Schottky barrier (SB) of arbitrary height exists at the MS interface, current can be modulated by the gate electrode by changing the SB thickness and the tunneling probability through this barrier. Higher currents are expected for thinner barriers. However, it is well known that the tunneling does not play an important role in conventional semiconductor/metal structures at room temperature especially for undoped or low doping levels. I_d - V_g characteristics at a constant drain voltage $V_d = 0.5 \text{ V}$ have shown a threshold voltage of -13.6 V with a high on/off ratio of 1.5×10^6 and an electron mobility of $49.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured from OCD (shown in supporting information S1).[†] The details regarding formula used in mobility calculations can be found in our previous work.¹⁴

Low temperature I-V measurements were performed on SCD to extract the estimated activation barrier energy at the NW-electrode junction for thermionic electron current in the temperature range from 150 K to 297 K, with 0 V applied to the gate electrode. Figure 2(a) shows the I_d - V_d characteristics at different temperature under a pressure of 10^{-6} mbar. The conductance of the device decreased drastically by several orders of magnitude as the temperature was reduced. Arrhenius equation $I_d \sim \exp[-E_a/kT]$ where E_a is the activation energy, k is

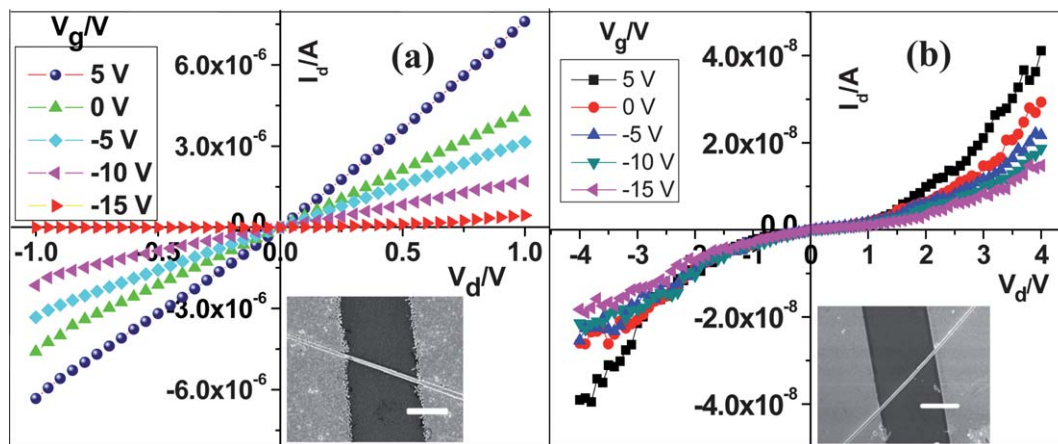


Fig. 1 I_d - V_d characteristics of, (a) single In_2O_3 nanowire device with nanowire underneath the electrode shows ohmic nature of the contacts between the nanowire and electrode, (b) single In_2O_3 nanowire device with nanowire on top of the electrode, shows Schottky nature of the contacts between nanowire and electrode. Inset in both plots show the respective SEM images of the single nanowire device, the scale bar is 2 μm in both images.

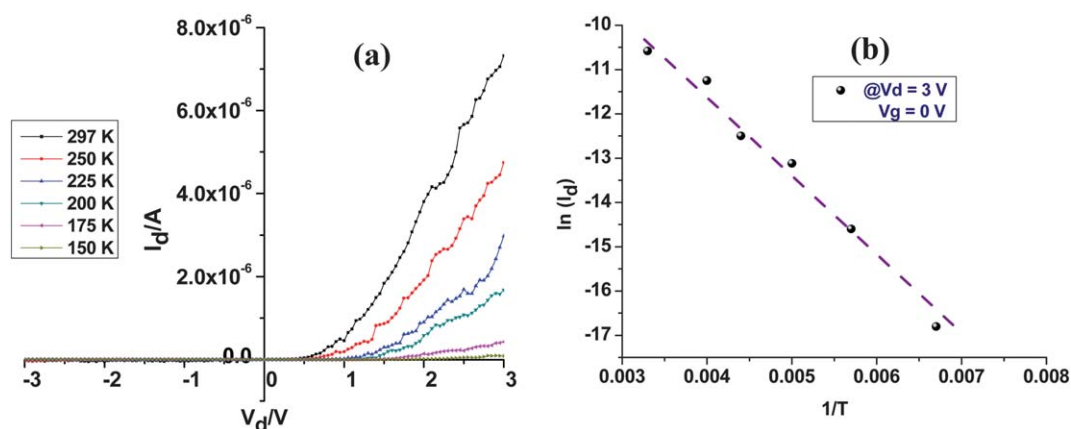


Fig. 2 (a) I_d - V_d characteristics measured on the single In_2O_3 nanowire device with nanowire on top of the electrode (Schottky device) at low temperature, (b) Arrhenius plot for the extraction of activation energy (0.35 eV in this case).

the Boltzmann constant and T is the temperature, was used for the activation barrier energy extraction.^{23–25} A typical Arrhenius plot in figure 2(b) between I_d and $1/T$ at $V_d = 3\text{ V}$ and $V_g = 0\text{ V}$ was used to extract the negative slope for the barrier activation energy in the SCD. Activation barrier energy (E_a , for electrons) of 0.35 eV was obtained from the slope of Arrhenius plot for $\text{Au}/\text{In}_2\text{O}_3$ NW FET, which was sufficient to produce rectifying behavior at room temperature. The dominant mechanism for current injection into the semiconductor in this case is thermal emission which gives an apparent height of the Schottky barrier. At lower temperature range, where $k_B T$ has smaller value, thermally activated transport through the system was quenched and therefore larger V_d brought the device to conductive state. Previously, $\text{Ti-Au}/\text{In}_2\text{O}_3$ has revealed a small barrier height of 6.90 meV,²⁵ it is mainly due to the use of smaller work function of the contact metal Ti (4.33 eV) and a low k -gate dielectric SiO_2 . *S.N. Das et al.*²⁰ have found Schottky barrier height (SBH) of 0.42–0.67 V for Pt/ZnO single nanowire which exhibited a good rectifying behavior. The magnitude of the SBH is not solely dependent on the work functions of the materials used; other factors such as the contact area between semiconductor NW and metal electrode, and preparation of the metal-semiconductor interface also play a role in determining the magnitude of the SBH. We have observed that high vacuum (10^{-6} mbar during low temperature I-V measurement) can dramatically improve the conduction of our In_2O_3 nanowires due to desorption of the oxygen ions from the nanowire surface.

The gas sensing characteristics of the OCD and SCD towards CO and NO (which are reducing and oxidizing gases, respectively) were investigated under similar device conditions for both gases. The SCD was operated at a forward bias of $V_d = 3\text{ V}$ and $V_g = -10\text{ V}$ whereas OCD was operated at a forward bias of $V_d = 0.5\text{ V}$ and $V_g = -10\text{ V}$ for both types of gases. In the previous reports^{18–21} most of the devices were composed of one end Schottky contact and were therefore operated in reverse bias mode. In this work we have operated the device in forward bias mode because the device consist Schottky barrier at both ends of the nanowire. Figure 3 (a and b) shows the sensor response towards 5 ppm CO by the OCD and SCD respectively. An increase in the sensing current was measured for several cycles of

5 ppm CO gas for both types of devices, but the sensor response of SCD was found to be nearly 4 times higher than OCD towards CO gas (Figure 3). The response and recovery time of OCD towards 5 ppm CO gas (52 and 10 seconds respectively) was slightly faster compared to 70 and 18 seconds of SCD correspondingly. Figure 4 (a and b) shows the sensor responses at room temperature towards 5 ppm NO gas using OCD and SCD respectively. The current in the device was found to be decreased for each cycle of 5 ppm NO gas. It can be observed from figure 4(a) that the OCD shows high response (sensor response of 30), which is almost 22 times higher than the SCD towards 5 ppm NO gas at room temperature. A response and recovery time of 160 and 25 seconds respectively was observed towards 5 ppm NO gas using OCD, indicating slow reaction kinetics. The low signal to noise ratio (S/N of 1.7) of SCD towards NO gas does not allow an accurate measurement of the response and recovery time. Surface chemical reaction kinetics strongly influences the response and recovery time constants of devices.²⁶ The response towards any chemical species is on account of their molecules chemisorption on the NW surface and the resistance recovery is originated from desorption of these compounds. Thus, in this case, the mean adsorption and desorption times of molecules from the surface will determine the fastest recovery and response time.

The schematic illustration of both types of devices and band diagrams before and after CO and NO exposure is shown in Figure 5. In each case, the increased barrier height after NO exposure is shown with the solid dash line and the lowering of barrier height after CO exposure is shown in dotted dash line. The equivalent resistance circuit for a single nanowire in contact with the metal electrode at two ends was shown in figure 5. Single NW FETs based sensor devices can be considered as three resistances made of R_{c1} , R_{ch} and R_{c2} connected in series (Figure 5c), where R_{c1} and R_{c2} are the contact resistances at the interface between metal/semiconductor at the two ends of the nanowire and R_{ch} is the nanowire channel resistance. The contact resistances R_{c1} and R_{c2} are large initially in the SCD devices which give a large equivalent resistance for the device, as a result small current flows across the interface. All three resistances dropped when CO gas was introduced into the chamber and increased for NO gas exposure resulting in a large change in the

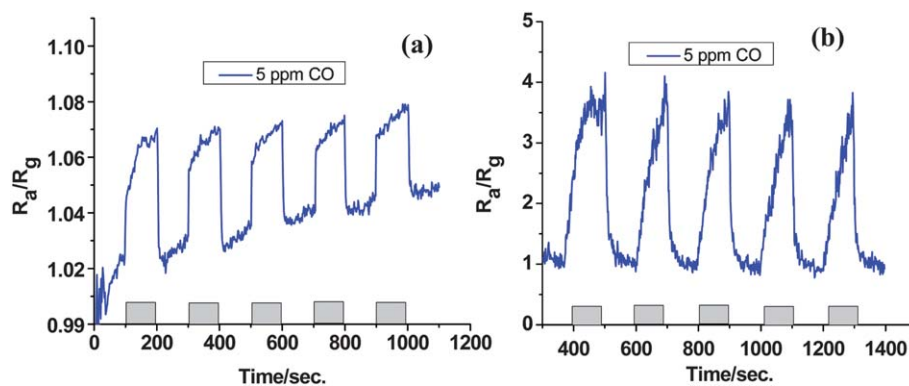


Fig. 3 Sensor response plots for 5 ppm CO gas at room temperature using, (a) OCD, shows weak response, (b) SCD, shows better response.

final value of equivalent resistance ($R_{c1} + R_{ch} + R_{c2}$) as they are connected in series.

2.1 Sensing mechanism

The response of a conductometric nano-sensor is the change in the relative conductance of the device before and after the exposure to the detecting species. In order to obtain a better response it is advantageous to start with a device which can give a higher relative change in the device conductance. In a single NW device there are mainly two components (nanowire channel conductance and contact resistance at the two junctions) which play a major role in the output of the device. If the contacts are rectifying type (SCD) then the modulation in the SBH due to the gas molecules interaction at the MS interface during sensing plays an important role in the sensor response. For the non-rectifying type of contacts (OCD), main contribution comes from the change in nanowire channel conductance during sensing due to the electronic exchange between channel and adsorbed gas molecule on the channel.

Reducing gases (*e.g.* CO) are electron donating in nature, their exposure led to enhanced conductivity of the n-type semiconductor channel device. In the exposure of CO gas to the OCD (where SBH is nearly zero) the sensor response was found to be mainly due to the change in the channel conductivity which is expected to be smaller due to limited surface chemical reaction kinetics at room temperature.^{26,27} However if CO is

exposed to SCD (with an arbitrary SBH) the sensor response is contributed by both the change in the channel conductance and reduction in SBH (due to the adsorption of the gas molecule at MS interface) which show a larger response than the previous case. Due to the lowering of barrier height when CO gas was exposed to SCD, a larger change in conductance of the device was observed.

On the other hand, after the exposure of another class of gases *e.g.* NO (oxidizing gas, which has an electron withdrawing nature) to an OCD, it is expected that a drop in the device conductance occurs due to its electron withdrawing nature of the gases of this class. In OCD, due to the small contact resistance the sensor response is mainly dependent on the change in channel conductance. With the electron withdrawing nature of the oxidizing gas molecules, a small down shift in the Fermi level occurs as a result a slow decrease in the device conductance was observed. In the undoped In_2O_3 nanowires due to the low charge carrier concentration, exposure to NO gas forms an electron depletion region near the surface. Adsorption of gas molecules on the nanowire surface induces charge transfer which may affect the carrier concentration and mobility of the nanowire.²⁸ As NO gas was exposed to the SCD a low response was shown by the sensor (Figure 4b) compared to the previous case (Figure 4a). In SCD, there is an arbitrary SBH before the commencement of sensing operation. When NO gas is exposed to such devices, there is a further increase in the barrier height at the junction, which allows even lesser charge carriers to migrate

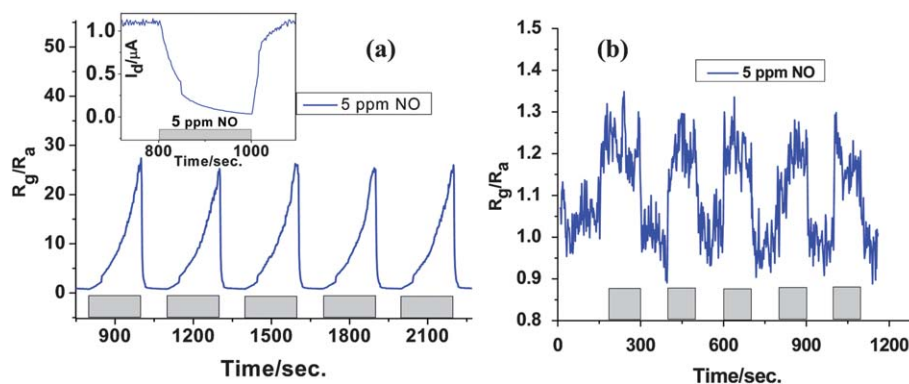


Fig. 4 Sensor response plots for 5 ppm NO gas at room temperature using, (a) OCD shows high response and inset shows the I_d -time plot for one cycle of 5 ppm NO gas, (b) SCD, shows poor response.

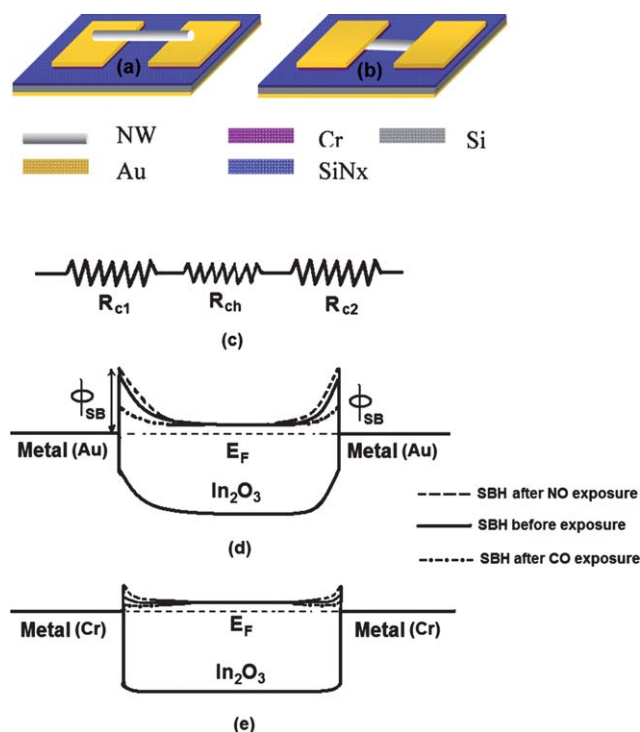


Fig. 5 Schematics of (a) SCD (b) OCD (c) electrical resistance equivalent circuit of the device (d) band banding in SCD with SBH modulations after the NO and CO gas exposure and (e) band diagram of the OCD, at zero bias voltage.

through the barrier. As a result, the SCD shows poor response to NO gas.

In the schematic of the band diagram of OCD (Figure 5e), a small resistance barrier is shown for OCD, this may exist because of the surface oxygen adsorption on the undoped In_2O_3 NW which withdraws electrons from the nanowire and form negatively charged oxygen ions which results in a small depletion region formation on the nanowire surface. When NO gas is exposed to the OCD, the electron depletion region extends more into the nanowire bulk which results in a further increase in potential barrier. For a smaller fixed applied voltage (0.5 V) during sensing, it is difficult for the charge carriers to overcome the barrier and the current gradually reduces with increasing NO exposure time. In the case of CO gas exposure to OCD, there is an increase in the electron concentration in the nanowire channel due to the conversion of CO into CO_2 ($\text{CO} + \text{O}_2^- = \text{CO}_2 + \text{e}^-$) resulting in a slight decrease in the depletion region with a lowering of the barrier height. However, the change in relative current is very small due to the nearly saturation current flowing in the OCD. As a result, the relative change in current before and after CO exposure in the OCD is smaller compared to the relative change in current during NO gas exposure.

In SCD there are large resistance barriers at the two ends of the nanowire, electrons required a larger energy to overcome the barrier, consequently, a larger voltage is required to initiate the flow of electrons in the device. When CO gas is exposed to the SCD (with larger voltage ~ 3 V) there is a large increase in the current. In such initial conditions even a small lowering of the barrier height can make the electrons travel across the barrier

resulting in drastic current change. On the other hand, NO gas exposure further increases the resistance barrier in SCD, leading to a small noisy decrease in current.

The modulation of contact resistance during gas exposure at the MS interface plays a crucial and dominant role to define the gas mechanism in SCD; meanwhile the kinetics of gas–surface chemical reactions at the solid–gas interface governs the electronic interaction between gas molecule and NW. Surface reaction kinetics depend strongly on temperature,²⁶ partial pressure of the gas in the chamber,²⁷ surface properties and surface oxygen vacancies of the material used.²⁹ Considering that both the devices contain similar surface and structural properties [*e.g.* nanowire channel area made of the same material, surface properties (oxygen vacancies and other defects)], with the same operational parameters [*e.g.* temperature, humidity, gas flow rate (300 sccm)] similar surface kinetics can be considered. The key difference is the contact resistance at the two ends of the devices and hence operating voltages. Higher operating voltage of SCD (3 V compared to 0.5 V of OCD) makes a difference in the electric field (voltage per unit length). Despite a higher electric field (in SCD) that will sweep electron faster ($F = qE$) in the SCD, the larger energy barriers at the junction in a SCD does not allow instantaneously fast response as an output. The surface chemical kinetics play a dominant role in the OCD, as there are small energy barriers at the MS junction. Therefore, any change in the carrier concentration instantly reflects as an output in OCD giving a fast response. The larger energy barriers at the MS interface in SCD dominate the device output response.

3. Experimental section

The preparation of the In_2O_3 NWs followed the similar procedure reported in our previous work,²² where the In_2O_3 nanowires were grown using VLS mechanism in a horizontal double quartz tube furnace at a source temperature of 900 °C using Au as catalyst and In_2O_3 powder as the precursor. OCD and SCD were fabricated using In_2O_3 nanowires from the same production batch. For the fabrication of OCDs, In_2O_3 NWs were first placed on the highly doped Si substrate deposited with 100 nm SiN_x which serves as the gate dielectric layer. Then the electrodes were selectively designed on top of the nanowires using conventional photolithography, where a positive photo resist (AZ 5312) layer of ~ 1 μm thickness was used to transfer the photo-mask patterns on an aligned nanowires on Si/ SiN_x substrate followed by the Cr (20 nm)/Au (50 nm) deposition in a dc sputtering system. The fabrication of SCDs followed the similar procedure except the nanowires were placed after the electrode deposition and formed on top of the electrode.

The electrical and gas sensing characterizations in both type of devices were performed on a Keithley 4200-SCS semiconductor characterization system, attached with an optical microscope and sensing gases with gas controller. The testing gases employed in this work were N_2 , CO (reducing) and NO (oxidizing). All the sensing experiments were performed at room temperature under 50% humidity. Sensor response towards NO gas was defined as the ratio of the electrical resistance in the testing gases (R_g) to that in air (R_a) and for CO gas it was defined as R_a/R_g due to the opposite changes of resistance. The response time is defined as

resistance change up to 90% of the initial saturated value upon introduction of testing gas, while the time it takes for the resistance to come to 90% of the initial saturated value is recovery time.

4. Conclusions

In conclusion, utilization of contact resistance has been demonstrated as an effective way to improve the sensor response for two different classes of gas at room temperature. When nanowires placements are located on top of the electrodes, it showed SCD characteristics. Temperature-dependent I-V measurements revealed thermal emission as the dominant transport mechanism with an activation barrier of 0.35 eV. In contrast, when nanowires were placed underneath the electrodes, it showed OCD characteristics. These two different types of devices have been found useful for two different classes of gases; OCD exhibits a large response for the oxidizing gases (e.g. NO) and SCD devices shows better response for reducing gases. In OCD, main contribution to sensor response comes from the nanowire channel and in SCD, modulation of SBH dominates the contribution. Achieving high sensor response by utilizing contact resistance at the MS interface suggests the possibility of using these devices at room temperature for a particular class of gases with distinct response. This work delineates the importance of device type selection for a particular class of gas with higher response.

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