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Enabling selectivity and fast recovery of ZnO nanowire gas sensors through resistive switching

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ABSTRACT

Nanomaterial based chemical sensors promise exceedingly high sensitivity with ultra-small form factors. However, fundamental limitations in selectivity and recovery speed have largely hindered their application in real-life scenarios. We report on a unique approach to improving the key performance of ZnO nanowire sensors by leveraging their resistive switching properties. By manipulating the resistive states of the nanowire, we were able to achieve excellent selectivity along with a significant improvement in recovery speed by more than 8 times. We attributed the enhancement to the switching between different electron transport mechanisms and redistribution of oxygen vacancies inside the one-dimensional channel. The innovative concept of incorporating sensing and resistive switching properties of nanostructures is particularly inspiring to the development of nanosensors to meet the versatile needs of real world applications.

1. Introduction

Gas sensors are playing an increasingly important role in civil applications, such as environmental monitoring [1], industrial process control [2], disease diagnostics [3–5], and traffic safety. They have been widely used for detection of toxic environmental pollutant [6] and prevention of hazardous gas leaks from manufacturing processes [7]. Recently, incorporating gas sensors into portable systems including smart phones and wearable devices [9–11] has attracted considerable interest from both academia and industry. However, the task is extremely challenging given the stringent requirements on device size, performance and power consumption, which largely limit the selection of sensor technologies.

Ever since Seiyama et al. [12] discovered that the electrical conductivity of ZnO could dramatically change in response to reactive gases, there have been tremendous efforts on the development and applications of metal-oxide semiconductor gas sensors. [13–19] Among them, one-dimensional (1D) semiconductive nanostructures such as ZnO [11–14], SnO_2 [16], NiO [17], and In_2O_3 [18,19] nanowires are one of the most promising candidates for realizing ultrasensitive sensors because of their large surface-to-volume ratio, polarized crystal orientation and high carrier mobility. Most importantly, sensors based on semiconductive nanostructures are fully compatible with CMOS integration to achieve extremely small form factors and ultralow power consumption. In fact, sensor chips based on thin film metal-oxides have been commercially available [2,7,8], which are expected to take a very rapid growth in market share in the next few years.

However, semiconductor gas sensors have a number of fundamental drawbacks at the same time, including relatively low sensitivity at room temperature, lack of selectivity and poor recoverability. [20] For example, long recovery time and unstable baseline may reduce sensitivity and lead to inconsistent measurements, which largely hinder the adoption of the sensors for practical applications. Researchers have investigated various approaches to enhancing the recovery speed. For instance, a widely adopted method is to operate the sensors at elevated temperature to promote gas desorption (150 °C–300 °C) [21,22]. However, the high temperature activates sensitivity to a wide variety of gases therefore resulting in lower selectivity. In addition, this approach increases fabrication complexity and power consumption, which are particularly undesirable given the tight budgets of cost and power in most portable systems. Another approach reported in previous work was to exploit Schottky barrier [23,24] between

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nanowire and metal electrode (instead of the nanowire itself) to detect gas adsorption. In spite of limited improvements in sensitivity and recovery speed, the solution was unable to provide sufficient selectivity. At the same time it brings substantial difficulty in device fabrication as multiple lithography steps are required to form a functional diode. A comprehensive solution able to deliver satisfactory performance in all three aspects, room temperature sensitivity, selectivity and recovery speed is well needed.

In this work, we propose a unique approach to meeting the above needs by exploiting the resistive switching (RS) behavior of ZnO nanowires. We have systematically evaluated the sensing performance of the nanowire devices and explained the mechanism via experiments and modeling. Specifically, we found that different resistive states of the nanowire could respond to various gases differently, providing an effective means to differentiate target analytes. The selectivity presumably results from distinct electron transport mechanisms of the two resistive states. In addition, we have considerably shortened the recovery time through a set of switching operations, which triggered redistribution of the oxygen ions along the nanowire and effectively promoted gas desorption from the surface. At the same time, the RS nanowire sensor exhibited excellent sensitivity comparable to those of heated nanowire and thin film gas sensors. Our proof-of-concept experiments brought new insights into the fields of chemical and biological sensing. The idea would also open up new opportunities for RS devices to be applied to a wide variety of sensing applications.

2. Experimental section

2.1. Materials and methods

Single-crystalline ZnO nanowires were synthesized via vapor-liquid-solid deposition process. Details of the nanowire growth have been discussed in a previous report [25]. Typical length of the wires is 10 μm and the diameters range from 50 to 100 nm. RS devices were fabricated on highly doped silicon substrate with 300 nm thermal oxide. Metal electrodes were patterned via ebeam lithography followed by evaporation of Ti (150 nm)/Au (50 nm) and liftoff. Typical channel length is 500 nm.

2.2. Characterization

Morphology and crystallinity of the ZnO nanowires were evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Semiconductor parameter analyzer (Agilent B1500) was used to characterize the electron transport and RS behaviors at room temperature.

2.3. Gas sensing

Sensing measurements were carried out by exposing the RS devices to NO_2 and NH_3 gases diluted in ultrahigh purity nitrogen. Gas concentrations were adjusted by modulating the flow rates of both the target and carrier gases. The total flow rate was kept constant. The gas chamber was flushed with nitrogen to recover the device after each measurement.

3. Results and discussion

Fig. 1a shows the SEM image of ZnO nanowires grown on Si/SiO_2 substrate. The inset TEM image confirms wurtzite structure and growth direction ([0001]) of the nanowire. An SEM image of the RS device is shown in Fig. 1b. The channel length is defined as the separation between two adjacent electrodes and is 500 nm long typically. Each individual nanowire is sufficiently long to be configured into multiple RS devices in series. Comparisons between these devices allow us to decouple wire-to-wire variations from the experimental results.

Typical RS behaviors of the device are demonstrated in Fig. 2. All measurements were carried out in air at room temperature. The diameter of the nanowire used in the measurements was 100 nm. According to our previous studies and other reports [26–31], the RS mechanism can be understood to first order by considering oxygen ion migrations along the nanowire, as illustrated in Fig. 2a. In a pristine nanowire, the oxygen ions and intrinsic oxygen vacancies are uniformly distributed along the one dimensional channel. When we apply positive voltage bias on one electrode (defined as Anode) while grounding the other end (defined as Cathode), the electric force drives the migration of oxygen ions towards the anode side, leaving oxygen vacancies in the channel as n-type dopants. The oxygen ions accumulated near the anode form a large Schottky barrier (SB), leading to very low conductance under small voltage bias. This constitutes the OFF state of the device. When a higher bias is applied, the electric field reduces the width of the SB junction and increases the doping level of oxygen vacancy in the bulk portion of the wire at the same time. At the moment when the junction is thinned to a threshold width, electron tunneling is turned on and leads to dramatic increase in current density, resulting in ON state of the device. We define the transition from OFF to ON state as the SET operation. Reversely, when a sufficiently negative bias

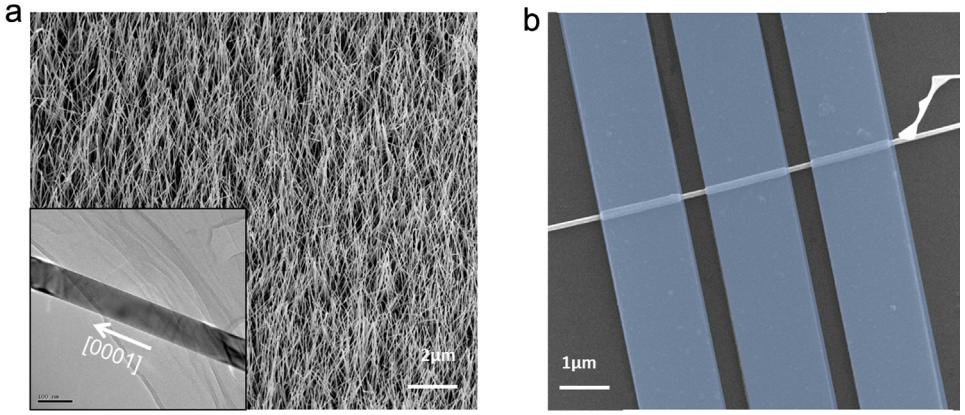

Fig. 1. SEM and TEM images of nanowire structures (a)SEM image of ZnO nanowires grown on the substrate. Inset: TEM image of a nanowire with wurtzite structure and crystal orientation along [0001] direction. (b) SEM image of typical RS devices with channel lengths of 500 nm. All I–V characteristics were measured by using two adjacent electrodes.