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A novel gas sensor based on field ionization from ZnO nanowires: moderate working voltage and high stability

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Abstract

We report a kind of gas sensor using ZnO nanowires as the field ionization anode. The sharp tips of nanowires generate very high electric fields at relatively low voltages. The sensors show good sensitivity and selectivity. Moreover, the detection limitation of the field ionization based ZnO nanowire gas sensors is about 5%. More importantly, a sensor with ZnO nanowires as the anode exhibits an impressive performance with respect to stability and anti-oxidation behavior, which are significantly better than those of carbon nanotubes (CNTs) as electrodes. Therefore, the simple, low-cost, sensors described here could be deployed for a variety of applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Gas sensors can be classified into a chemical type operated by gas adsorption and a physical type operated by ionization. Most gas sensors are the gas adsorption type, in which metal-oxide, polymer, porous silicon [1] and carbon nanotubes (CNTs) [2–5] have been used as the active layer. The chemical types of gas sensor usually utilize an electrical response by the adsorption of gas molecules on the surface of the active layer, which leads to a large change in its electrical resistance [6–8]. But most of these sensors (except for the CNTs-based sensors) need high working temperatures, for example 300–500 °C. Meanwhile, structures with large surface area may be required for distinguishable detection, which cause problems like high power consumption and pre-heating time. Besides, these sensors have potential difficulties in detecting gases with low adsorption energies or low electronegativity such as inert gases.

On the other hand, ionization sensors as a physical type gas sensor, which work by fingerprinting the ionization characteristics of distinct gases, are mainly used as the gas detector in advanced gas analyzers such as the chromatograph and mass spectrograph to realize the high-precision measurement of gas concentration after the gas mixture is separated. However, this kind of instrument has high power consumption and risky high-voltage operation, and thus cannot be used on site.

Recently a physical type of gas sensor using CNT arrays has been reported [9] as a novel sensor which can detect many gases regardless of the magnitude of the gas adsorption energy and the electronegativity. For example, NH₃, CO₂, N₂, O₂, He, air and gas mixtures were detected by ionization of gas molecules under low voltage [9]. However, CNTs could be oxidized and degraded easily under an oxygen-contained atmosphere and high electric current as a light element nanostructure [10]. Thereby ZnO nanowires entered our thoughts as a wide band gap semiconductor. ZnO has a wide band gap of 3.37 eV at room temperature [11]. Due

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to their chemical stability and sharp nanotips, ZnO nanowires can be used for stable field emission sources instead of carbon nanotubes [12, 13]. Therefore, ZnO nanowires could be used as the anode of an ionization gas sensor.

In this paper, we introduce a physical type of ZnO nanowire gas sensor with simplicity, compactness and reliability in the sensing process, examining them to detect inert gases including air, and comparing with the use of carbon nanotubes. With the promising properties such as good sensitivity and selectivity, and being unaffected by extraneous factors such as temperature, humidity and gas flow, such ionization sensors could be deployed for a variety of applications, such as environmental monitoring, sensing in chemical processing plants, and gas detection for counter-terrorism. This work is a continuation of our ongoing efforts toward the applications of ZnO nanowires [6, 7, 12–14].

2. Experimental details

Vertically aligned ZnO nanowire arrays were selectively grown on the areas of the substrate where ZnO seeds were pre-coated via a thermal evaporation and vapor phase transport, as in a previous report [15]. Briefly, a 200 nm ZnO film was first deposited on a Si(100) substrate at a temperature of 500 °C with oxygen pressure of 0.02 Pa by pulsed laser deposition (PLD). After the film deposition, a powder mixture of ZnO (99.99%) and graphite (99.9%) with a molar ratio of 1:1 was placed in the closed end of a one-end-sealed small quartz tube. The ZnO-coated silicon substrates were placed definite distances away from the evaporation source in the small quartz tube. Then, the small tube was pushed into the tube furnace with the source positioned at the center of the furnace, while the open end was put against the gas flow direction. The furnace was heated at a rate of 25 °C min⁻¹ and held at 950 °C for 8 min. The local temperature of the substrate was about 850 °C. During the whole synthesis process, a constant flow of 100 cm³ (STP) min⁻¹ of Ar gas was introduced to the furnace and the pressure in the tube was kept at about 200 Pa. Finally, the substrates were naturally cooled to room temperature under Ar flow in the furnace.

Well-aligned carbon nanotubes were synthesized on Si(100) substrates by bias-assisted hot filament chemical vapor deposition. Briefly, Ni film (20 nm)/silicon wafers were used as the substrates, and the flow rates of N₂ and CH₄ were kept at 75 and 25 sccm as the precursors. When the filament was heated to about 1700 °C, a bias of 600 V was applied to produce the glow discharge plasma, and the growth started at 2.0 kPa. The growth duration was fixed to 20 min [16].

The morphologies and microstructures of the samples were characterized with a Sirion FEG scanning electron microscope (SEM). As shown in figure 1, the apparatus for a field ionization gas sensor consists of two electrodes, anode (sample) and cathode (copper), the gap between the cathode and the anode is adjusted by a micrometer caliper. As a result, the gap between these two electrodes can be controlled from 5 to 500 μm accurately; in the present experiments, the space between them is 100 μm. The voltage of the two electrodes can be varied from 20 V to 1 kV (Keithley 2400), and the current is measured by a picoammeter (Keithley 6485). The pressure in the chamber could be controlled from 0.1 to 10⁵ Pa.

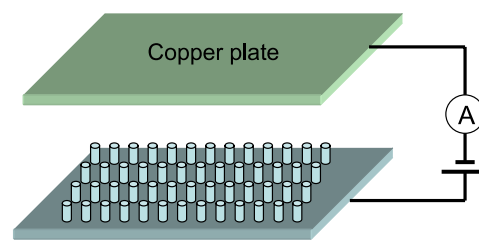


Figure 1. The nanowire sensor device. Exploded view of the sensor showing a ZnO nanowire film as the anode and a Cu plate as the cathode.

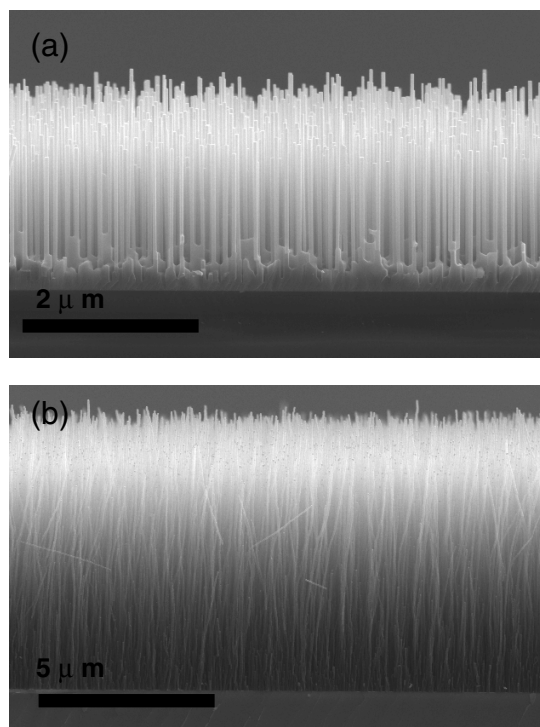


Figure 2. SEM images of (a) ZnO nanowire arrays and (b) carbon nanotube arrays.

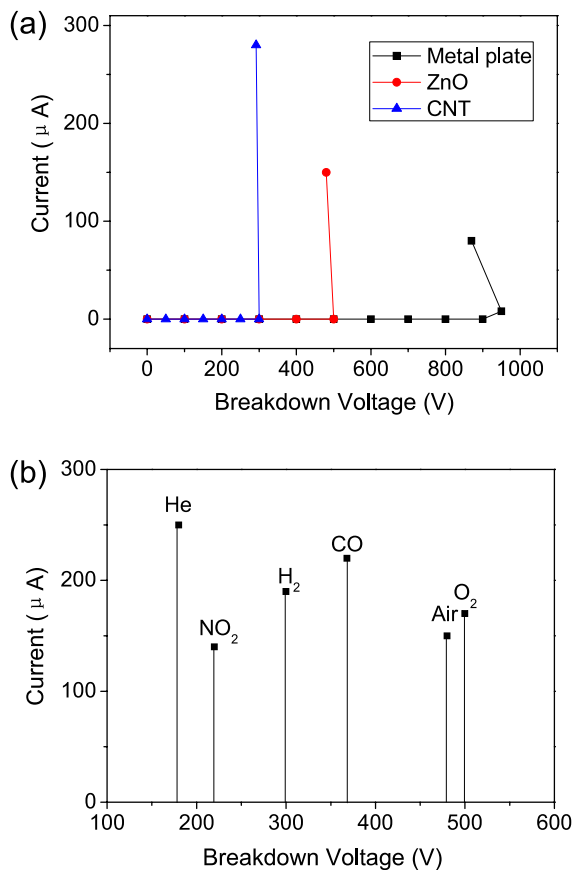
3. Discussion and results

Figure 2(a) shows the SEM image of the ZnO nanowires grown on Si(100) substrate. The ZnO nanowires are several microns in length, and about 150–200 nm in diameter. Figure 2(b) shows a typical SEM image of a carbon nanotube array. As can be seen from the side view, the nanotubes are all straight, uniform and relatively vertical to the silicon substrate. Their length is about 10 μm and the diameter is about 50 nm.

The device was first tested in air (figure 3(a)) with anode–cathode separation of 100 μm and pressure of 10³ Pa. A continuous current discharge of 150 μA was generated by using ZnO nanowires as the anode at 480 V. The same tests were performed by replacing the ZnO nanowires by carbon nanotubes and a Cu plate. For the carbon nanotubes, the breakdown voltage of air occurred at 292 V with a current discharge of 280 μA; however, for the metal electrodes, the breakdown voltage of air occurred at 870 V with a current discharge of 72 μA. This shows that by the use of ZnO

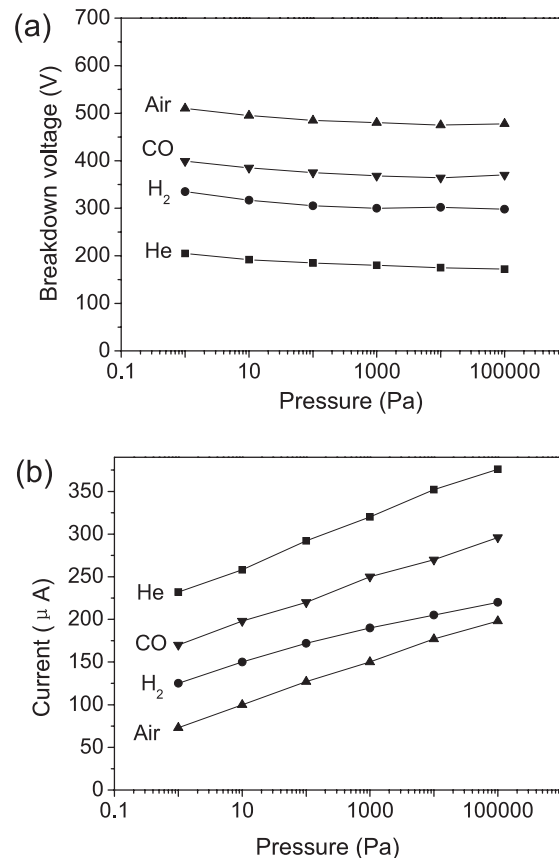
Table 1. The working voltage of different type field ionization gas sensors.

Type	ZnO nanowires	Carbon nanotubes [17]	Carbon nanotubes [9]	Field ionization mass spectrometry [18]	Field ionization mass spectrometry [19]
Working voltage	About 500 V	About 300 V	About 400 V	About 10 kV	About 2000 V

**Figure 3.** Current–voltage (I – V) curves for electrical breakdown. (b) I – V curves for He, NO₂, CO, H₂, air and O₂, showing distinct breakdown voltages.

nanowires as the anode, compared with metal electrodes, the breakdown voltage of air could be moderated, though that of carbon nanotubes is lower than that of ZnO nanowires. This ZnO nanowire anode ionization device is used to detect the identity of several gas species, such as He, NO₂, CO, H₂, air and O₂. Figure 3(b) shows the breakdown voltages of several gases at room temperature and at a chamber pressure of 10³ Pa. For all the tests, the anode–cathode separation is maintained at 100 μm. Note that each gas exhibits a distinct breakdown behavior: helium displays the lowest breakdown voltage (175 V) and O₂ shows the highest one (524 V). Obviously, this is a fingerprinting property. Each breakdown voltage is associated with one kind of gas. Table 1 shows the working voltage of different types of field ionization gas sensor.

To study the effect of pressure-dependent field ionization, tests were conducted at reduced pressures (shown in figures 4(a) and (b)). Figure 4(a) shows the effect of pressure on the breakdown voltages of air, H₂, CO and He from.

**Figure 4.** Effect of gas concentration on electrical breakdown. (a) Breakdown voltage as a function of concentration. (b) Discharge current at breakdown as a function of gas concentration.

In this work, the pressure decreased from 10⁵ to 1 Pa. As shown, the initial breakdown voltages of the four gases increase with decreasing pressure in the chamber. This could result from the current multiplication being proportional to the density of neutral gas molecules as predicted by Paschen's law for uniform electric field [20]. This phenomenon also indicates a certain concentration threshold might be needed for the discharge to be self-sustaining. It is also noted that the breakdown voltages do not increase very significantly with gas pressure because breakdown behavior in this case is dominated by the highly nonlinear electric field near the nanowire tips, resulting in a pre-breakdown plasma that helps assist in bridging the electrode gap and reduces the sensitivity of the breakdown voltage to gas pressure.

Figure 4(b) shows the self-sustaining current discharge at breakdown for air, H₂, CO and He. The discharge current varies logarithmically with pressure. This trend is valid over a wide range of gas pressure, ranging from 10⁵ downwards to 1 Pa. This shows that the self-sustaining discharge current

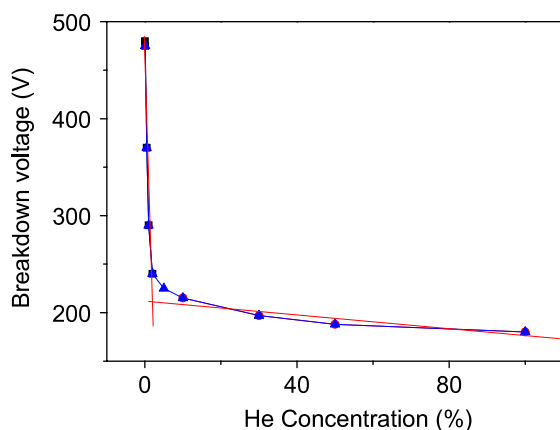


Figure 5. Breakdown voltage of He gas in a mixture with air as a function of concentration.

generated at breakdown is a characteristic property of the number of gas molecules per unit volume that may contribute to the conduction. For example, figure 4(b) indicates that for air a current discharge of $73 \mu\text{A}$ corresponds to a concentration with pressure of 1 Pa, while the discharge current increases logarithmically to about $198 \mu\text{A}$ as the air pressure is increased to 10^5 Pa. Therefore the discharge current may offer a convenient mean to quantify the gas pressure of the species being detected.

Ionization sensors such as photo-ionization detectors (PIDs), flame-ionization detectors (FIDs) or electron-capture detectors (ECDs) are not suitable for directly sensing gas mixtures. The carbon nanotube ionization sensor has been used to monitor gas mixtures without the direct use of a chromatography arrangement. Therefore, the ZnO nanowire ionization sensor is expected to show the same ability. Figure 5 shows the results for a He–air mixture with several different relative concentrations of the component gases. For the mixture containing over 50% He, the breakdown voltage is nearly the same as that of pure He. However, as the relative concentration of He gas in the mixture is reduced, the breakdown voltage increases, for example from about 185 V (for 50% He) to about 240 V (for 2% He). This is because air gas has a higher breakdown voltage than He gas (figure 4(a)), so the presence of air molecules tends to impede the breakdown of He. Below 1.7% He concentration (after linearly fitting) [9], the breakdown of He ceases and the breakdown voltage rises sharply to the value for pure air (480 V). Similar results were also obtained in the detection of CO and NO₂ in a mixture with air. These tests indicate that the nanowire ionization sensor shows promise for room-temperature detection of gases at a low percentage level in mixtures with air. According to our results, the detection limit of the gas sensor is about 5% concentration.

The breakdown voltage was found to become lower as the inter-electrode spacing was reduced. This is expected, as reducing the electrode separation increases the electric field in the gap. Figure 6 shows breakdown voltages as a function of electrode separation when ZnO nanowires and CNTs film are used as the anode, respectively. For the carbon nanotubes, the breakdown voltages decrease from 367 V at $150 \mu\text{m}$ separation

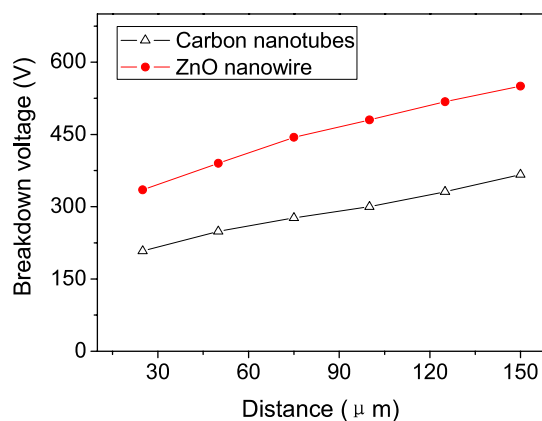


Figure 6. Breakdown voltage of air versus inter-electrode separation.

to 208 V at $25 \mu\text{m}$ separation; for the ZnO nanowires anode, the breakdown voltages decrease from 550 V (at $150 \mu\text{m}$ separation) to 335 V (at $25 \mu\text{m}$ separation). Generally, though the breakdown voltage of ZnO nanowires is larger than that of CNTs, comparing with the higher breakdown voltage of metal anode it is acceptable to employ ZnO nanowires as an alternative anode to CNTs.

The stability of ZnO nanowire gas sensors was tested. The working voltage is higher than the breakdown voltage, which is driven by a 2 Hz square wave from a function generator to provide pulsed ionization. The breakdown phenomena were generated continuously 1000 times in air at 1000 Pa as shown in figure 7(a). It can be clearly seen that the breakdown stability of ZnO nanowires is much better than that of CNTs. The voltage fluctuation of ZnO nanowires is less than 5%, while the breakdown voltage of carbon nanotubes increases with the increase of time and ends up at more than 200% of the initial value (in this work). To find the reason for this phenomenon, the morphologies of the samples after continuous breakdown were characterized by SEM, as shown in figures 7(c) and (d). Obviously, after measurements, the ZnO nanowire array appears unchanged compared to the unused one. The entire CNTs arrays collapsed, entangled each other and maybe burned away. All these could significantly decrease the effective working area.

It is very important to explore the reason that offers ZnO nanowires an even more promising stability than that of CNTs. Firstly, during the process of the breakdown, a strong electric field could induce structural deformation of nanotubes and large emission current could cause emitting tip evaporation [21, 22]. Secondly, the carbon nanotubes could be crashed by large electrical current so that the ability of field ionization should drop [23]. However, ZnO nanowires show chemical stability, high melting point and rigidity. Though the breakdown voltage is higher than that of carbon nanotubes, considering the practical application, the better performance on stability recommends that ZnO nanowires could be a better candidate for a field ionization gas sensor than CNTs.

4. Conclusion

In summary, we demonstrate a gas sensor using ZnO nanowires as the field ionization anode. The sensor has the merits of low

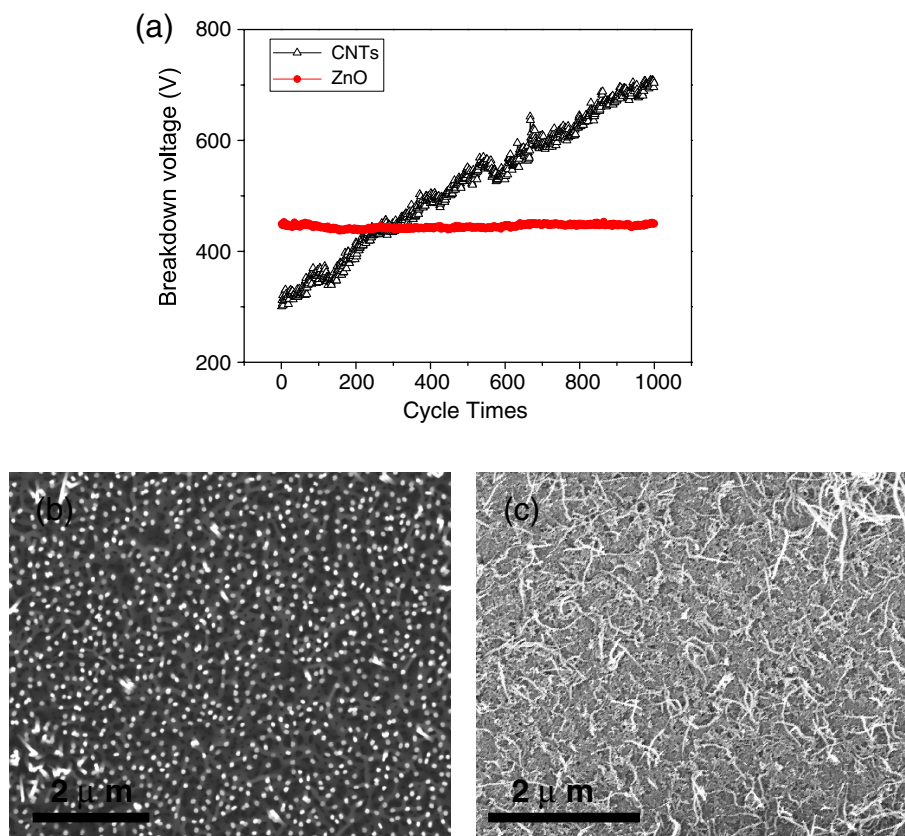


Figure 7. (a) The stability tests of gas sensors with ZnO nanowires and carbon nanotubes as the anodes. The SEM images after stability tests: (b) ZnO nanowires and (c) carbon nanotubes.

cost and low voltage. The sharp tips of the nanowires generate very high electric fields at relatively low voltages, though the breakdown voltages of ZnO nanowires are appreciably higher in comparison to that of CNT electrodes. Sensors with ZnO nanowires as the anode show good sensitivity and selectivity; furthermore, the detection limitation of the field ionization based ZnO nanowire gas sensors is about 5%. More importantly, the stability and anti-oxidation of ZnO nanowires are significantly better than CNTs as electrodes. Therefore, the simple, low-cost, sensors described here could be deployed for a variety of applications, such as environmental monitoring and sensing in chemical processing plants.

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