Fabrication of a Single CuO Nanowire-based Gas Sensor Working at Room Temperature

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Abstract—CuO is an important p-type metal oxide semiconductor material and it has been used in many fields for its excellent physical and chemical properties, such as field effect transistors, photovoltaic cells, field emission nanodevices, and chemical and gas sensors. In this paper, CuO nanowires are synthesized by thermal oxidation of copper foil and suitable DEP parameters are chosen to assemble a single CuO nanowire on microelectrodes to fabricate a single CuO nanowire-based device. Experiments in this paper show that the single CuO nanowire-based device can work as field effect transistor and gas sensor. The single CuO nanowire device has a significant respond to the atmosphere with alcohol at room temperature, so it has potential to work as an alcohol gas sensor at room temperature. The single CuO nanowire device also has quick and significant respond to the humidity at room temperature and a novel liner relationship between conductivity and the relative humidity from 30% to 100%.

Keywords—CuO nanowire; assembly; dielectrophoresis; DEP; field effect transistor; FET; alcohol gas sensor; humidity sensor

I. INTRODUCTION

Metal oxides are important semiconductor materials and they have been used in field effect transistors, photovoltaic cells, field emission nanodevices, and chemical and gas sensors. Metal-oxide-based sensor can detect many things, such as CO, CO\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{5}OH, CH\textsubscript{3}H\textsubscript{2}O, H\textsubscript{2}, H\textsubscript{2}S, NH\textsubscript{3}, NO, NO\textsubscript{2}, O\textsubscript{2}, O\textsubscript{3}, SO\textsubscript{2}, acetone, dimethylamine (DMA), humidity, liquid petroleum gas (LPG), petrol, trimethylamine (TMA), smoke, and many others[1, 2].

In recent two decades, researching in nanoscale structure materials have explosively grown for their small size and excellent physical properties. One-dimensional nanostructures, such as whiskers and nanowires, have attracted increasing interest due to their novel performances in field effect transistors (FETs) and sensors. For nanometer scale of nanowires, metal oxide nanowire FETs potentially lead to tera-level ultrahigh-density nanoscale electronic devices[3]. Nanowire-based sensors with high surface area/volume ratio and less agglomerated configuration are advantageous to accomplish high gas sensitivity and rapid response speed[4].

As Nanowire-based metal oxide sensors with high surface area/volume ratio and less agglomerated configuration, metal oxide sensors with nanostructure have a better performance than the traditional metal oxide gas sensors. The surfaces of metal oxide nanowire sensors can be functionalized with molecule-selective receptors increasing the sensitivity and selectivity[5]. As the functionalized surfaces of nanowires extend sensing range of the metal oxide nanowire sensors, the metal oxide nanowires not only used in gas sensors, but also used in biological sensors and many other sensors.

CuO is an important p-type semiconductor with a direct bandgap of about 1.2 to 2.0 eV and exhibits many excellent physical and chemical properties[6-9]. CuO nanowires have been applied in FETs, photovoltaic cells, field emission nanodevices, and chemical and gas sensors[9-12]. The CuO sensors can be utilized to detect many things, such as CO[13, 14], H\textsubscript{2}S[15-17], NO\textsubscript{2}[11, 18], H\textsubscript{2}[19], H\textsubscript{2}O[20], glucose[21, 22], pH[23], air quality control in automotive[11]. The sensors or devices with CuO nanowires are almost all nanowires arrays grown on the Cu substrate or other substrate[10, 24]. In this paper, we fabricate a single CuO nanowire device as a gas sensor. This device can contribute to researching in single CuO nanowire and work as a novel CuO-based gas sensor at room temperature.

To fabricate a single CuO nanowire device, there are different methods. Using focused ions beam (FIB) system to deposit line-shaped Pt wirings connecting the CuO nanowire and microelectrodes[25] or directly depositing lots of CuO nanowires on an electrode array surface to bridge two electrodes by chance[18] are all be utilized. Both of those two methods cannot fabricate CuO nanowire devices quickly and efficiently. In this paper, single CuO nanowire is driven to gap of two microelectrodes by dielectrophoresis (DEP) to fabricate single CuO nanowire gas sensor.

DEP technology is a simple and effective method to operate and assemble micro-nano objects, and also it can be used to massively fabricate nano-scale devices from bottom-up. Since it is invented, it is widely used in many research fields, such as separation of biological particles and cells[26], fabrication of nanowire/carbon nanotube devices[27-29], assembly of nanoparticles and etc.[30]. Here single CuO nanowire is actuated and assembled to the microelectrodes by DEP technology and single CuO nanowire FET is fabricated, and then its sensitivity to alcohol and humid air is measured with a home-made test system, thus single CuO nanowire gas-sensor is firstly fabricated by the method. Our experiments show that the new gas sensor with single CuO nanowire can...
work at room temperature, which differs from previous CuO nanowires sensor only working at high temperature.

II. MATERIALS AND METHOD

A. preparation of CuO nanowires

CuO nanowires can be synthesized by heating copper substrates in air within the temperature range from 400 to 700 °C[31]. The nanowires were prepared by thermally oxidizing a commercial copper foil (purity 99.9%) in air at 500 °C. The copper foil was cut into pieces at size of 0.5mmX0.5mm. Before heating the copper foil, the copper foil need a pretreatment. At first, put the pieces of copper foil into acetone solution sonicated for 5-10 min to clean grease, and then rinse the copper foil with deionized water; second, put the copper foil into dilute hydrochloric acid for 1min to clean oxide of the surface, and then rinse the copper foil with deionized water; third, dry the copper foil by a flux of nitrogen, and then put the copper foil into a dry sealed box. The copper foils are heated in a heating furnace at 500 °C for 10 h. The CuO nanowires will grow on the copper substrates which show in Fig. 1.

![Fig. 1](image1.png)

Fig. 1. The CuO nanowire arrays on the copper substrates; scale bar is 50μm; the inset is clean copper foil; scale bar is 100μm

The CuO nanowire arrays on the copper substrates can be transported and dispersed in ethanol by ultrasonic treatment. For the CuO nanowires are brittle, the CuO nanowires will be separated from copper substrate and dispersed in ethanol after only 3-5s ultrasonic treatment. Dropped on surface of silicon, the dispersed CuO nanowires can be imaged as Fig. 2(a) by atomic force microscope (AFM) after the solution was evaporated. The AFM image show that diameter of CuO nanowire is at about 100 nm.

![Fig. 2](image2.png)

Fig. 2. (a) An AFM image of the dispersed CuO nanowires; (b) Solution of CuO nanowires; (c) Height of CuO nanowire

B. fabrication of microelectrodes

The microelectrodes are manufactured by lithography whose structure is shown in Fig. 3. The microelectrodes are made of Au. Width of the microelectrode is at 30μm and thickness is at 30nm. The substrate is made up SiO₂ layer and Si layer, and thickness of SiO₂ layer is at 300nm.

![Fig. 3](image3.png)

Fig. 3. Schematic diagram of the microelectrodes

C. Dielectrophoresis method

The DEP force arises from an induced dipole moment caused by non-uniform electric field, and it is widely used to manipulate micro or nano-scale particles and nanowires.

The DEP force of CuO nanowire in liquid can be calculated with classic equation (1)[32]

\[ F_{DEP} = \frac{\pi r^2 l}{2} \varepsilon K(\omega) \sqrt{\varepsilon_l^2} \]

(1)

\[ K(\omega) = \text{Re} \left[ \frac{\varepsilon_- - \varepsilon_+}{\varepsilon_0^2} \right] \]

(2)

\[ \varepsilon^* = \varepsilon - \frac{i \sigma}{\omega} \]

(3)

\[ \omega = 2\pi f \]

(4)

In those equations, \( r \) is the diameter of the CuO nanowire; \( l \) is the length the CuO nanowire; \( \varepsilon_{lm} \) is relative permittivity of the liquid; \( \varepsilon_n \) is relative permittivity of the CuO nanowire; \( \sigma \) is conductivity; \( f \) is frequency of the applied AC voltage.

When the CuO nanowires solution is dropped on the microelectrode gap and the AC voltage is applied on the
microelectrodes, the DEP force will drive the CuO nanowires to the microelectrode gap and one or more CuO nanowires will bridge the microelectrodes.

To guide the experiments, theoretic analysis and simulation of assembling CuO nanowires is performed. Here, COMSOL Multiphysics is used to compute the electric field and DEP force around the microelectrodes. Result is shown in Fig. 5 and it predicts that the DEP force will drive the CuO nanowires to the gap of the microelectrodes.

Fig. 4. Result of simulation; the arrows are directions of DEP force

III. EXPERIMENT

A. assembly of single CuO nanowire

Put a piece of heated copper foil into 5ml ethanol solution and sonicate them for 3-5 s, and the CuO nanowires are dispersed in the solution. When the CuO nanowires solution dropped on the microelectrodes gap and the AC voltage applied on the microelectrodes by the function generator, there will be a non-uniform electric field around the microelectrodes which brings DEP force by dipole moment. The AC voltage is at 6-9V and 0.5-1 MHz. Electric circuit of DEP show in Fig. 5.

Fig. 5. Electric circuit of DEP, F_{DEP} drive the CuO nanowire to the gap

The AC voltage applied on the microelectrodes hold for 2-3s. Waiting the solution evaporated, utilize atomic force microscopy (AFM) or scanning electron microscopy (SEM) to inspect assembly of CuO nanowire. Assembly of single CuO nanowire show in Fig. 6. In experiment, to assemble a single CuO nanowire to the microelectrodes gap, it is very important that choosing concentration of the CuO nanowire solution and time of DEP duration. Suitable parameters of AC voltage and frequency course DEP force which can drive CuO nanowire to the microelectrode gap, but they cannot control how many CuO nanowires assembled on the gap. After many times experiments, parameters used in this paper are appropriate to assemble a single CuO nanowire nanodevice.

Fig. 6. Assembly of a single CuO nanowire imaged by AFM (a) and SEM (b)

B. FET testing of single CuO nanowire nanodevice

Using DEP assembled single CuO nanowire nanodevice to work as a FET in which the CuO nanowire is utilized to as the conductive channel, FET effect is measured by semiconductor parameter analyzer (Agilent 4155C). The experimental electric circuit show in Fig. 7.

Fig. 7. The experimental electric circuit of FET

In the electric circuit, the microelectrodes are source and drain, and the n-Si play role of gate in FET. The semiconductor parameter analyzer apply a sweeping voltage from -5V to 5V in every 100mV on the source and the drain, namely V_{S,D}, and it also can get current between the source and the drain, namely I_{S,D}, at same time. For the single CuO nanowire is the conductive channel, the current I_{S,D} is the current pass through the single CuO nanowire. When the gate voltage apply on the n-Si, electric field caused by gate voltage will effect conductance by changing concentration of carriers in the CuO nanowire. As the CuO is p-type semiconductor, the carriers are holds with positive charge. When a positive gate voltage is applied, the electric field will reduce concentration of holds and increase resistance of the CuO nanowire. When the gate voltage is negative, there will be an opposite conclusion. The results show in Fig. 8.

Fig. 8.
In this paper, a single CuO nanowire-based gas sensor has been fabricated working at room temperature. There are several groups have study on CuO nanowires-based gas sensors, such as H$_2$S sensor[15-17], humidity sensor[10, 24], but their sensor device use CuO nanowire arrays working at more than 200 °C. The single CuO nanowire-based sensor device is fabricated by DEP, and the single CuO nanowire bridge two microelectrodes exposing in the air, as shown in Fig. 6. The single CuO nanowire is conducting channel of the two microelectrodes. When the sensor device is exposed in a reducing gas, the resistance between the two microelectrodes will increase. For the CuO nanowire is a p-type semiconductor and it can get some electrons from the reducing gas adsorbed on the surface of the CuO nanowire, the resistance of the conducting channel of the two microelectrodes is increasing. When the sensor is exposed in an oxidizing gas, there will be an opponent conclusion.

The results prove the single CuO nanowire have potential to work as an alcohol gas sensor at room temperature. For the nano-structure and small size of the CuO nanowire, the CuO nanowire is easier to adsorb gas molecules and the total of gas molecules is very little. This imply the single CuO nanowire-based gas sensor may have ability to detect alcohol gas at a very low concentration.

The CuO-based sensor also have ability to detect humidity of environment at more than 200 °C[10, 24].
show that the single CuO nanowire-based sensor also can work as a humidity sensor at room temperature. The alcohol test system is transformed to test humidity sensitivity of single CuO nanowire which is shown in Fig. 11.

When the first chamber is fill water, using the SourceMeter to apply a 5 volt voltage on the microelectrodes and detecting the current through the CuO nanowire at same time, results show that water molecule can change conductivity of the CuO nanowire which is shown in Fig. 12.

When the first chamber is with saturated saline solution, it can provide an atmosphere with constant humidity. Different kinds of saturated saline solution can provide different values relative humidity (RH), such as saturated MgCl₂ solution is with 33% RH, saturated K₂CO₃ solution is with 43% RH at room temperature. By using the saturated saline solution and apply a 5 volt voltage on the microelectrodes, the current respond of the single CuO nanowire exposed in different RH atmosphere can be detected which is shown in Fig. 13.

When the single CuO is exposed in wet air, the conductivity of the CuO nanowire is with the current growth. The result show that the relationship between RH and the current is liner. This conclusion is great useful to design a humidity sensor.

The experiment and conclusion all support the single CuO nanowire device working as a humidity sensor at room temperature, and it has quick and significant respond to the humidity. For more important, the conductivity of the single CuO nanowire device has a novel liner relationship with the relative humidity from 30% to 100%. Those conclusions indicate that the single CuO nanowire device has a very wonderful application prospects working as a sensor for humidity.

IV. CONCLUSION

In this paper, CuO nanowires are synthesized by thermal oxidation of copper foil, and using the CuO nanowires, a single CuO nanowire device is fabricated by DEP method. To assemble a single CuO nanowire on the microelectrodes, concentration of the CuO nanowire solution, applied voltage and frequency on the microelectrodes, voltage holding time all need to choose suitable value in the DEP experiment. Perfect assembly of single CuO nanowire on the microelectrodes certify that the DEP parameters in this paper are suitable. Experimental results show that the single CuO nanowire device can work as a FET, and it has potential application in very large scale integration (VLSI) to replace silicon-based semiconductor materials. The single CuO nanowire device also has sensitivity to alcohol gas and humidity. As the alcohol gas is a reducing gas, the alcohol gas can lower conductivity of CuO nanowire which adsorbed alcohol molecule on its surface. The single CuO nanowire device has a significant respond to the atmosphere with alcohol at room temperature, and it has potential to work as an alcohol gas sensor at room temperature. The experiments also show that the conductivity of CuO nanowire grow with relative humidity increasing and the single CUO nanowire device has quick and significant respond to the humidity at room temperature. The novel liner relationship between conductivity of the single CuO nanowire and the relative humidity from 30% to 100% is very important to design a single CuO nanowire-based humidity sensor. Experimental results indicate that the single CuO nanowire device has a very wonderful application prospects working as a sensor for humidity at room temperature.

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