Fabrication Process of Single CuO Nanowire Devices

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One-dimensional nanostructures such as nanowires have been extensively investigated as a promising type of material for applications of nanoscale technology. The fabrication of single-nanowire devices are consequently important and interesting. This study introduced a feasible method for growing CuO nanowires on Cu foils. The nanowires had diameters of 10~150 nm and lengths of more than 7 μm and were grown by means of thermal oxidation in a vacuum. They were entirely and uniformly grown over the Cu foil surfaces and could be extracted and dispersed in an ethanol solution for further purposes. In addition, a simple fabrication method for realizing device functionality from a single CuO nanowire was reported. Fabricated devices were carefully checked by field-emission scanning electron microscopy (SEM). The probability of the realization of a single-CuO-nanowire device relative to that of all other types was estimated to be around 25%. Finally, the I-V characteristics of the devices were analyzed.

Keywords : Nanowire FET, CuO, Growth, Semiconductor device

1. Introduction

Single-nanowire-based devices have been widely studied nowadays to investigate the natural properties of materials in the one-dimensional (1D) nanoscale structures. Many studies have been carried out to assess the use of these devices for energy storage, detector and low-power thin-film transistor (TFT) applications [1–4], etc. Up to this moment, there are two typical approaches to fabricate the devices. For the first method, nanowires are dispersed in an aqueous solution (typically ethanol) and a droplet of the solution is transferred to an electrode deposited substrate by a coating technique. Although this method is very simple to process, the contact between the wire and the electrode is frequently

contaminated by many factors, including contamination of the aqueous solution by non-nanowire species. The second approach is based on a photolithography process in which nanowires are initially transferred onto a substrate, after which electrodes are patterned and deposited onto the wires by photolithography. When using this method, single-nanowire devices can be fabricated by modulating the transfer process.

In recent years, cupric oxide (CuO), a narrow-bandgap metal oxide semiconductor, has attracted much attention. Nanometer-scale CuO is a material which has potential for use in heterogeneous catalyst [5], photocatalyst [6], gas-sensing [7], and bio-sensing [8] applications. It can also serve as a cathode material in lithium ion batteries [9] and as a photoconductive material [10]. Numerous

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nanostructures of CuO, e.g., nanoparticles [8], nanowires [4], nanobelts [11] and nanoflowers [12], among others, have been synthesized via many physical as well as chemical methods. Interestingly, CuO nanowires can be grown easily by oxidizing Cu foil at elevated temperatures [4,13]. Thus far, the thermal oxidation of Cu foil in the presence of oxygen appears to be the most effective route to obtain high-quality CuO nanowires.

In this paper, CuO nanowires were synthesized by thermal oxidation method. In addition, a simple fabrication method of a single CuO nanowire field-effect transistor (FET) was reported.

II. Experimental Section

For the CuO growth, a $1 \times 1 \text{ cm}^2$ Cu foil sample (purity: 99.9% Cu, $100 \mu\text{m}$ thickness) was cleaned sequentially in a solution of HF:DI-water (1:2), DI water, and ethanol for 3 minutes each before drying with compressed N_2 . The foil was then fixed at the center of a CVD system. During the treatment, the temperature and pressure were controlled at 450°C and 0.1 Torr, respectively. A mixture of oxygen and nitrogen with oxygen partial pressure (O_{pp}) levels of 10%, 20% and 50% was subsequently introduced for the treatment. The total gas flow rate was 50 sccm. After a 12-h treatment, the samples were cooled naturally. The shapes and structures of the wires were characterized by field-emission scanning electron microscopy (FESEM, JSM-6701F). In addition, the nanowires were dispersed on a molybdenum grid for transmission electron microscopy (TEM—Tecnai G2F20 S-TWIN, Philips) observations.

The fabrication steps of the bottom-gate structure field-effect transistor using a single nanowire as a channel are illustrated in Fig. 1. First, the black crust on the Cu foil surface was scratched and dispersed in 10 ml ethanol. The solution was then treated in an ultrasonic bath for 10 min. After holding it for 24 h, 1 ml of the as-dispersed solution was transferred to another 10 ml of ethanol and the new solution was sonicated for 10 min.

Figure 1. Fabrication steps of the single nanowire device.

Second, the final solution was dropped and spin-coated onto a $2 \times 2 \text{ cm}^2$ p-type silicon substrate (a 100-nm SiO_2 layer was created on the Si substrate by thermal oxidation, which was employed as a gate dielectric oxide) at a speed of 1000 rpm for 2 min (Fig. 1(a, b)). The substrate was subsequently sonicated in an ethanol solution for 30 min to remove the bulk CuO and contaminates. Third, bi-layer photoresist (PR) / lift-off resist (LOR) photolithography was used to patterned the electrodes (Fig. 1(c, d)). The substrate was then exposed to oxygen plasma for 1 min to remove any residual PR on the nanowires. After depositing Ni/Au (40/60 nm) for a source/drain electrode by e-beam deposition, the bi-layer was lifted off by Remover PG (Fig. 1e). All devices were then checked by an optical microscope and by SEM. The good single nanowire devices (Fig. 1f) were marked for further measurements. The current-voltage (I-V) characteristics were assessed in the dark at room temperature by an Agilent 4156C semiconductor parameter analyzer.

III. Results and Discussion

1. Synthesis of CuO nanowires

The influence of the oxygen partial pressure on the growth of CuO nanowires is shown in Fig. 2. This figure clearly shows that the nanowires are denser and longer under a higher oxygen partial pressure. The diameters and lengths of the observed wires were approximately

Figure 2. Influence of oxygen partial pressure on the growth of CuO nanowires. (a): $O_{pp} = 10\%$, (b): $O_{pp} = 20\%$, (c): $O_{pp} = 50\%$.

10~150 nm and $\geq 7 \mu\text{m}$, respectively. In addition, the nanowires resembled a bamboo tree in which bunches of wires were formed simultaneously. Interestingly, the nanowires were grown uniformly on the entire foil surface. Therefore, a large number of wires could be extracted and obtained.

TEM, high-resolution TEM (HRTEM) and fast Fourier transform (FFT) images of the extracted nanowire are shown in Fig. 3. The single-crystal structure of the nanowire was detected in the HRTEM images (Fig. 3(b,c)), in which the interplanar spacing of the structure was 0.23nm, corresponding to the calculated spacing of the (200) plane of monoclinic CuO ($a = 4.69\text{\AA}$, $b = 3.42\text{\AA}$, $c = 5.13\text{\AA}$ and $\beta = 99.65^\circ$). Three bright dots representing CuO (200), (110) and (020) in the FFT dark-field image (Fig. 3(d)), as calculated from the HRTEM imagery (Fig. 3(c)) by Gatan Microscopy Suite (ver. 1.7.1), confirmed the CuO phase of the wire. Moreover, the data indicated that the growth of the nanowires was along the [100] direction.

The formation of the CuO nanowires can be summarized as follows: first, under a heat treatment,

Figure 3. TEM (a), HRTEM (b, c) and FFT (d) images of the single CuO nanowire.

the atoms of Cu move and collide with each other randomly on the foil surface. By reacting with adsorbed oxygen from outside, an oxide layer is formed on the surface, which leads to the introduction of CuO nuclei and seeds. Second, the CuO seeds can easily become

attractive sites for nearby atoms, molecules or nuclei. Thus, the seeds can be expanded in size or merged with several secondary seeds nearby. This explains why bunches of wires were formed. Third, crystallization was carried out with different priorities toward different faces depending on the preferred growth direction or preferred bonding direction.

2. Field-effect properties of the device

FESEM images of the single CuO nanowire devices are shown in Fig. 4. For a good device, only one wire was found to connect the two electrode terminals, and there were no impurities around the wire. Figs. 4(a) and 4(b) show devices with long and short single CuO nanowires, respectively. Occasionally, a short wire was found to have overlapped the main wire, as shown in Fig. 4(b). With regard to our observation, the probability of the appearance of a single CuO nanowire device relative to that of all other types was estimated to be around 25%.

The current of the drain source (I_{DS}) versus the gate (V_G) and the drain-source (V_{DS}) curves of a typical single CuO nanowire FET are shown in Fig. 5. In Fig. 5(b), the absolute conductance levels of the nanowire obtained under gate voltages (V_G) of -70 , -60 , -50 , -40 , and -30 V are shown to decrease monotonically as the gate potential is increased. This suggests that the device exhibited p-type semiconducting characteristics. This

result is comparable to the findings of Liao et al. [4]. In our data, a high carrier concentration along with surface adsorption of the CuO nanowire may cause I_{DS} to be unsaturated. Usually, nanowire FETs show field-effect characteristics which are weaker than those of thin films. Nevertheless, the successful operation of the device demonstrates the great potential of fabricating sensors and optical devices based on single-metal oxide nanowires.

Figure 4. FESEM images of the single CuO nanowire devices.

Figure 5. I-V characteristics of a single CuO nanowire FET.

IV. Conclusion

In conclusion, CuO nanowires with diameters of 10~150 nm and lengths of $\geq 7 \mu\text{m}$ were synthesized by means of thermal oxidation. A feasible process of fabricating single-nanowire devices was introduced and used to make a single CuO nanowire field-effect transistor. The I-V characteristics of the devices confirm the p-channel mode controlled by the gate and drain bias.

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