Optoelectronic characteristics of CuO nanorods*

Xie De-Hua(谢德华), Wang Fei-Fei(王菲菲)†, Lü Hao(吕 浩), Du Min-Yong(杜敏永), and Xu Wen-Jie(徐文杰)

School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, *China*

(Received 20 September 2012; revised manuscript received 24 October 2012)

Optoelectronic characteristics of p-type CuO nanorods, synthesized by a simple hydrothermal method, were investigated at different atmospheres and oxygen pressures. The CuO nanorods have lower resistance in air than in a vacuum, unlike the n-type semiconductors. This is explained in terms of the surface accumulation conduction. Measurements at different oxygen pressures indicate that oxygen has an important effect on the optoelectronic properties of p-type nanomaterials.

Keywords: CuO nanorod, optoelectronic characteristics

PACS: 81.07.Gf, 68.43.–h **DOI:** 10.1088/1674-1056/22/5/058103

1. Introduction

Presently, the low-dimensional nanostructures are the fundamental materials for building nanodevices and nanosystems[1–4] with superior characteristics. The Photodetector is one of the most important applications of low-dimensional semiconductor materials. The optoelectronic characteristics of semi-conducting nanostructures have been investigated intensively, and some one-dimensional nanomaterials, such as nanowires and nanobelts, have shown a high sensitivity to illumination.[5–12] So far, most optoelectronic studies have focused on n-type-semiconductor nanostructures. The transport mechanisms of n-type semiconductors at different atmospheres and the illumination have been well analyzed and discussed. However, the optoelectronic properties of quasi-one-dimensional p-type materials have rarely been investigated.

Cupric oxide (CuO), one of the most popular p-type semiconductor oxides, has attracted much attention for its potential applications in many fields, such as gas sensors,[13] heterogeneous catalysts,[14] lithium copper oxide electrochemical cells,[15] dye-sensitized solar cells,[16] and field emission emitters.[17] CuO nanostructures can be synthesized through the soft solution method,[18] the self-catalytic method, and the electrochemical method.[19–22]

In the present work, the p-type CuO nanorods were synthesized and the optoelectronic characteristics of CuO nanorods were investigated at different atmospheres and oxygen pressures. The resistance of p-type CuO nanorods increases with the decrease of the oxygen pressure, unlike n-type semiconductors. A surface accumulation conduction model is given to explain the sensing mechanism of the p-type CuO nanorods.

2. Experiment

The CuO nanorods were fabricated by a typical hydrothermal method as described in our previous work.[23] We dissolved 0.22 g $Cu(OAc)_2$ and 0.6 g CTAB into a 50-ml mixture of distilled water and ethanol, and an NaOH solution was added drop by drop under continuous stirring. After about 10 min, dark green precursors appeared in the solution. Then the solution was transferred into a Teflon-lined stainless steel autoclave and placed in an oven at 120 °C–150 °C for 12 h. Afterwards, the autoclave was allowed to cool to room temperature naturally. The black product was washed with distilled water and ethanol several times to remove remaining ions.

The morphology of the as-synthesized sample was characterized by scanning electron microscopy (SEM, Hitachi, S-4200). The crystal structure was analyzed by X-ray diffraction (XRD, Japan, Rigaku, D/MAX-2400) with graphite-monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The device for the electrical measurement was fabricated by conventional photolithography. The CuO nanorods were dispersed in ethanol by ultrasonication and then dropped on a ceramic substrate with pre-patterned Pt interdigital electrodes. The separation between the interdigital electrodes was about 100 μm, and the width of the electrodes was about 200 μm. A uniform thin film of CuO nanorods formed on the electrodes after drying. Measurements were carried out in a vacuum and in air with a UV lamp illumination. The UV lamp can be switched on and off manually with a power of 8 W and a wavelength of 254 nm (about 4.9 eV in photon energy).

3. Results and discussion

The morphology of the as-prepared CuO was characterized by SEM. Figure 1(a) shows a typical SEM image of the

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11144010, 11004169, and 11074105), the Research Award Fund for Outstanding Middle-aged and Young Scientist of Shandong Province, China (Grant No. BS2011ZZ004), and the University Student's Science and Technology Innovation Fund of Ludong University, China (Grant No. 12cg030).

†Corresponding author. E-mail: ffwang@ldu.edu.cn

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CuO nanorods. The synthesized nanorods are about 80 nm in diameter and 700 nm in length. The crystal structure and phase of the products are determined from the XRD patterns. Figure 1(b) shows the XRD pattern of the as-prepared products. All the diffraction peaks are indexed to the tenorite structure of CuO with lattice constants $a = 4.96$ Å, $b = 3.43$ Å, and $c = 5.13$ Å (JCPDS: 41-0254).

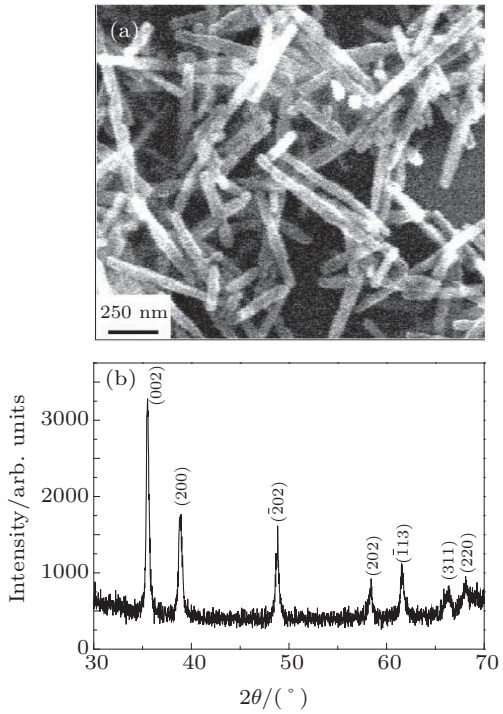


Fig. 1. (a) SEM image of the CuO nanorods. (b) X-ray diffraction patterns of the sample.

The typical photoresponse of the CuO nanorods to UV illumination in air is shown in Fig. 2 (a) as a function of time at the bias of 5 V. Upon UV exposure the current first increases rapidly from 1.2 nA to 4.0 nA and then at a slower rate. The light is turned off after 860 s of exposure. After that, the current decreases slowly. It takes more than 710 s for the current to return to the original dark level. Figure 2(b) shows the photoresponse of CuO nanorods to UV illumination under a vacuum at a bias of 5 V. Comparing Fig. 2(a) with Fig. 2(b), we can see that the dark conductivity is much higher in air than in a vacuum. The photosensitivity S is defined as $S = S_{\rm ph}/S_{\rm d}$, in which $S_{\rm d}$ is the dark conductivity and $S_{\rm ph}$ the photoconductivity under illumination. The photosensitivity is considerably higher in a vacuum than in air, which is related to the lower conductivity of the sample under a vacuum. It takes a shorter time for the adsorbed oxygen to desorb under a vacuum than in air. Thus, the rise time for CuO nanorods is longer in air than in a vacuum.

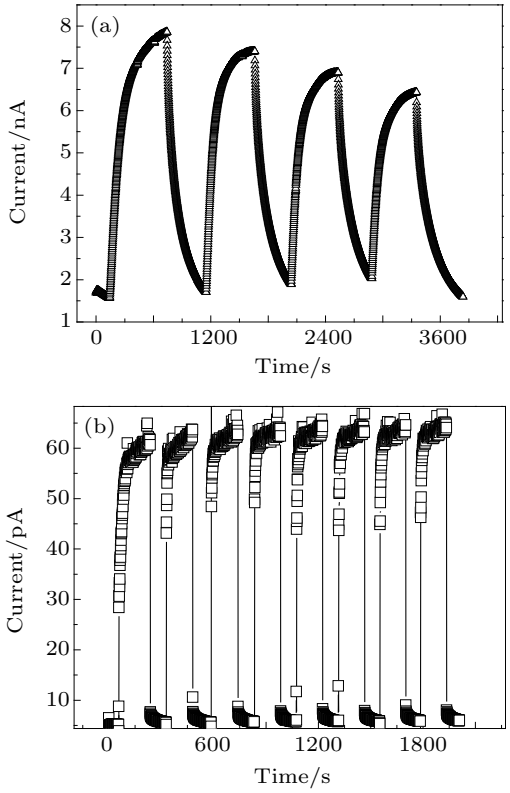


Fig. 2. Reversible switching of CuO nanorod photoconductor between low and high conductance states when the UV light is turned on and off (a) in air and (b) under a vacuum. The bias on the nanorods is 5 V.

Usually, the gas molecules adsorbed on a nanomaterial surface have significant tuning effects on the material's electrical properties due to their high surface-to-volume ratio. On exposure to ambient air, the oxygen molecules adsorbed on the surface of a nanomaterial will affect the carrier density, so the resistance changes as the device is moved from air to a vacuum. For n-type semiconductors, such as ZnO and CdS, electrons are the majority carriers. When a sample is exposed to air, oxygen traps electrons from the sample surface, which leads to the formation of a depletion layer at the surface.[24,25] The exhaustion of carriers near the surface by oxygen adsorption leads to the increase of device resistance. Furthermore, the intrinsic Fermi level is raised by the trapped electrons at the surface, which results in a built-in electrical field and leads to the formation of barriers for electrons. For p-type semiconductors, however, the situation is quite different. The bottom of the conduction band of CuO is about 4.07 eV below the vacuum energy, and its band gap is 1.36 eV.[26] Adsorbed oxygen with chemical potential of about 5.7 eV[27] below the vacuum energy will form acceptor levels near the valence band at the surface. The electrons are trapped by the adsorbed oxygen and the energy band also bends upward at the surface, which leads to the formation of an accumulation layer for CuO with holes as majority carriers. Trapping electrons leaves more holes available near the surface. Such a process is described by

$$O_2 \longleftrightarrow O^{2-} + \text{Vacancy}_{Cu^{2+}} + 2\text{hole}.$$

At the surface, the bending band blocks the transport of electrons as a potential barrier, but contributes to the transport of holes, the majority carriers of p-type CuO. So the resistance of CuO in air is lower than that under a vacuum because of the surface accumulation.

A further experiment was carried out to investigate the effects of oxygen adsorption on the electrical properties. Figure 3 shows the response under the same UV radiation at three values of oxygen pressure: 1.0×10^5 Pa, 3.6×10^2 Pa, and 7.0×10^3 Pa. It can be seen from Fig. 3 that the decay rate becomes faster with decreasing oxygen concentration. It takes less time for the adsorbed oxygen to desorb under a vacuum than in air. Thus, the rise time for CuO nanorods is longer in air than under a vacuum. It can also be seen from Fig. 3 that the photoconductance of the device decreases as chamber pressure decreases from atmospheric pressure to several hundred pascals. This is also attributed to the effects of oxygen desorption. Some of the adsorbed oxygen will desorb from the surface as the partial pressure of oxygen decreases. Hence, the surface accumulation layer becomes thinner as the partial pressure of oxygen decreases, which results in a higher sensor resistance. The photoresponse phenomenon at different oxygen pressures further indicates that oxygen molecules adsorbed on the surface have significant tuning effects on the electrical properties of the nanorods. This gives further evidence of accumulation conduction, which was revealed earlier by ethanol sensing experiments on CuO nanorods.[23]

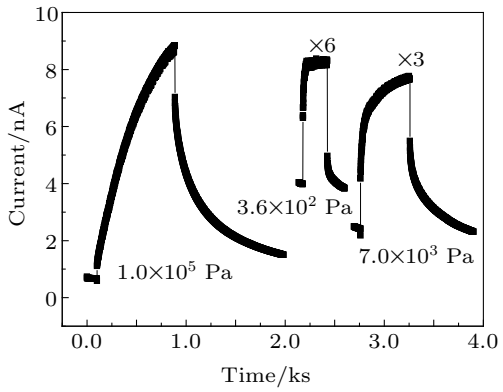


Fig. 3. Photoresponse of the nanorods film to UV illumination at various oxygen pressures: 1.0×10^5 Pa, 3.6×10^2 Pa, and 7.0×10^3 Pa from left to right.

The experiments indicate that the sensor resistance decreases with increasing oxygen adsorption and increases with decreasing oxygen adsorption. The change of sensor resistance can be derived from an analysis of the gas adsorption and the change of carriers. Consequently, the sensing behavior of p-type CuO nanorods can be explained by the surface accumulation conduction model proposed here.

4. Conclusion

In summary, CuO nanorods were synthesized via a hydrothermal method. The sensing properties in air and under a vacuum, and at different oxygen pressures were investigated and analyzed. The experiments indicate that the p-type CuO nanorods have lower resistance and a slower desorption rate with the increase of the oxygen adsorption. Oxygen molecules adsorbed on the surface of CuO nanorods have significant tuning effects on the electrical properties of the nanorods. A model based on surface accumulation conduction is given to explain the sensing mechanism of the p-type CuO nanorods. Our findings imply a potential application of CuO nanorods to room-temperature sensors.

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