Optical switches research based on Cr-doped Bi2S3 nanowire

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Abstract

Cr-doped Bi2S3 nanowires with the length up to 20 μm were synthesized via the composite molten salt solvent method. Single nanowire based device was fabricated by Cr-doped nanowires with a contact of metal-semiconductor-metal, and they formed two back to back Schottky diodes. The photocurrent response based on Cr-doped Bi2S3 nanowire device showed distinct optical switch property under the intermittent illumination of white light. The rise and decay time were less than 0.03s. The device can stay stable and reversible during a long time experiment, exhibiting a good property of optical switch.

Keywords: Cr-doped Bi2S3 nanowire; optical switch; Nanodevice

1. Introduction

Nanodevice unites made from single one-dimensional nanostructures, such as nanowires, nanobelts and nanotubes have attracted extensive attention due to their novel properties of electronic, optoelectronic and electrochemical in the past few decades [1-2]. Additionally, the integration of one-dimensional nanoscale building blocks into two- and three-dimensional ordered superstructures or complex functional architectures, which not only offers possibilities for advanced nanodevices but also offers opportunities to explore their novel collective properties. Among them, photo detectors or so-called optical switches are essential elements in optical gating devices. In this context, several semiconducting materials, such as GaN, ZnO [3-4], have been fabricated into nanoscale electronic or photoelectric devices with high sensitivity and fast response due to their high surface-to-volume ratio. But they were limited to UV detection because of their wide band gaps.
Among these numerous electronic and photoelectric materials, bismuth sulfide (Bi$_2$S$_3$) is one of the most important V-VI semiconductors and has potential application in various fields, such as thermoelectric, electronic and optoelectronic devices, etc [5-6]. With the direct gap energy ranging from 1.3 to 1.7 eV, Bi$_2$S$_3$ exhibits pronounced positive photoconductivity upon visible light exposure, and is a good candidate for optical switches. Because the electron transport in crystalline wires is several orders of magnitude faster than percolation through a polycrystalline structure and the surface-to-volume ratio is relatively high in nanoscale, the photoelectric properties of 1D single crystalline Bi$_2$S$_3$ nanostructures have been widely studied. However, most of the devices are based on films made from 1D Bi$_2$S$_3$ nanostructures. Little research was studied on electric and photoelectric properties of individual 1D Bi$_2$S$_3$ especially for Cr-doped Bi$_2$S$_3$ nanostructures. In this work, we have successfully synthesized Cr-doped Bi$_2$S$_3$ nanowires and investigated the electric and photoelectric properties of the nanowires by fabricating simple photoelectric devices made of individual Cr-doped nanowire.

2. Experiments

All the analytically-pure chemical reagents including bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O), potassium nitrate (KNO$_3$), lithium nitrate (LiNO$_3$), sodium sulfide (Na$_2$S·9H$_2$O) and potassium dichromate (K$_2$Cr$_2$O$_7$) were purchased from Chengdu chemical company, and they were used as received without further purification. Cr-doped Bi$_2$S$_3$ nanowires were obtained via the composite molten salt solvent method. Briefly, 9 g mixed nitrate (LiNO$_3$/KNO$_3$=1:2) was put in a Teflon vessel, and 1 mmol Bi(NO$_3$)$_3$·5H$_2$O and 4 mmol Na$_2$S·9H$_2$O were added into the mixed nitrates, about 2% molar percentage of potassium dichromate (K$_2$Cr$_2$O$_7$) was mixed with Bi(NO$_3$)$_3$·5H$_2$O and Na$_2$S·9H$_2$O before heated.

The products were characterized by X-ray diffraction measurement (XRD-6000, Shimadzu) with the use of Cu Kα radiation (λ=1.5418Å) at a 2°/min scanning speed in the range from 10°-70°, field emission scanning electron microscopy (FESEM, Nova 400 Nano SEM), transmission electron microscopy (TEM, TECNAI20, Philips) and optical microscope (OLYMPUS, MX61). Quartz spectral filters were used to generate the excitation wavelength of 365, 436, 546, 577 nm, respectively. The conduction property and the photosensitivity of a single nanowire were measured by using a CHI660D workstation (CHI Co.) under the radiation of a simulated sunlight (CHF-XM-500W). The light intensity was calibrated by a photometer (FZ-A). All the experiments were carried out at a dark room and in the open air condition.
3. Result and discussion

![典型的XRD光谱（a）和EDX（b）的Cr掺杂Bi₂S₃样品](image)

Figure 1a shows the typical XRD spectrum of the Cr-doped Bi₂S₃ sample. It is found that no peak from impurities can be observed in the XRD spectrum of the Cr-doped sample, proving that none of the other different crystalline phases was formed. Thus we can conjecture that the obtained sample is Bi₂S₃. In order to make a further study of the composition, EDX was taken to explore chemical composition of the Cr-doped nanowires, and the representative spectrum is displayed in Fig. 1b. We measured several nanowires and several parts of one nanowire, and all the results indicate the existence of C, Cu, Bi, Cr and S in the samples, where C and Cu peaks are from the carbon film and the copper grid. In a word, the result of both of the XRD spectrum and EDX proves that Cr element is diffused into the Bi₂S₃ crystal lattice.

SEM, TEM and HRTEM were employed to characterize the morphology, size and crystal structure of the Cr-doped Bi₂S₃ nanowires. The images were shown in Fig. 2a-c. The diameter of nanowires is ranging from 50 to 200 nm and the length is up to 20 μm. We found that little Cr element diffused into the Bi₂S₃ crystal lattice has small influence on the growth of morphology compared with the pure Bi₂S₃ nanowires. The nanowire has the lattice spacing of about 0.38 and 0.57 nm, which can correspond to the (101) and (200) planes of the orthorhombic Bi₂S₃, respectively. This growth direction coincides with that reported for Bi₂S₃ nanowire network [8].

The corresponding FFT pattern was shown as an insert in Fig. 2c, showing strongly ordered electron diffraction spots. The (200) plane is parallel to the growth direction, suggesting that the nanowire prefers to grow along the [001] direction. Fig. 2d shows the photograph of Cr-doped Bi₂S₃ nanowire device.
Fig. 2 The SEM(a),TEM(b) and HRTEM(c) of Cr-doped Bi$_2$S$_3$ nanowires and the photograph of Cr-doped Bi$_2$S$_3$ nanowire device(d).

The photocurrent response of the Cr-doped Bi$_2$S$_3$ nanowire device was investigated at a dark room. The typical I-V curves measured in the dark, 53(1), 75(2), 100(3), 130(4), 158(5)mW/cm$^2$ were shown in Fig. 3a respectively, and the bias sweeps from -1 V to 1 V. The Cr-doped Bi$_2$S$_3$ nanowire device has a clear increase in conductance upon exposure to visible light with different current. The typical I-V curves of both dark current and photo current exhibit the nonlinear characteristic, and the phenomenon is similar to the I-V characteristic of the metal-semiconductor-metal structure, which can be explained as Cr-doped Bi$_2$S$_3$ nanowire lying across two Au electrodes, forming two metal-semiconductor-metal back to back Schottky diodes [7].

Figure 3b shows the photo-response with the light was switched on and off at a time interval of 10 s. The bias applied was 1 V and the light was the white light. From the experiment, it was found that a pronounced increase in current with the increase of white light intensity and a reversible photocurrent switching effect of the device is obviously displayed. The response speed is an important parameter to determine the capability of an optical switch to follow a quickly varying optical signal.
To find out the rise and decay time, one response cycle of the curve are magnified as shown in figure 3c and d. It is clear that both the response and recovery time of the current for the Cr-doped Bi$_2$S$_3$ nanowire are less than 0.03 s when we switch the light on and off. No significant variations in the current under a constant bias voltage were observed during the more than one hour of continuous operation, indicating that the device made by Cr-doped Bi$_2$S$_3$ nanowire is stable over a wide frequency range.

4. Summary

Cr-doped Bi$_2$S$_3$ nanowires were successfully synthesized via the composite molten salt solvent method. The conductance of Cr-doped Bi$_2$S$_3$ nanowire exhibits a pronounced positive photoconductivity and a fast response under visible light illumination, and also keeps stable and reversible at the room temperature in an open air condition. It indicating that Cr-doped Bi$_2$S$_3$ nanowire is a good candidate for optoelectronic switches.

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References