



# Optical switches based on $\text{Bi}_2\text{S}_3$ nanowires synthesized by molten salt solvent method

Yi Xi<sup>a,b</sup>, Chenguo Hu<sup>a,\*</sup>, Xiaomei Zhang<sup>b</sup>, Yan Zhang<sup>a</sup>, Zhong Lin Wang<sup>b,\*</sup>

<sup>a</sup> Department of Applied Physics, Chongqing University, Chongqing 400044, PR China

<sup>b</sup> School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

## ARTICLE INFO

### Article history:

Received 15 July 2009

Accepted 2 August 2009 by A.H. MacDonald

Available online 8 August 2009

### PACS:

42.79.Pw

61.46.Km

### Keywords:

A.  $\text{Bi}_2\text{S}_3$  nanowire

B. Molten salt solvent method

D. Photoelectric property

## ABSTRACT

Bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) nanowires have been synthesized for the first time by a one-step, low temperature, ambient pressure, environment friendly molten salt solvent method. The photoelectric response of  $\text{Bi}_2\text{S}_3$  nanowire films has been characterized in the visible light of different wavelengths and ultraviolet, and the results indicated its great potential applications as optical sensors/switches and optoelectronic nanodevices with a response time in  $\sim$ ms range.

© 2009 Elsevier Ltd. All rights reserved.

## 1. Introduction

Semiconductive nanomaterials have drawn intensive and wide attention in both academic and industrial research because of their novel electronic and optical properties for the construction of advanced functional nanodevices, such as field effect transistors [1,2], laser devices [3], sensors [3–5], nanogenerators [6–8] and photodetectors [9,10]. The synthesis of nanostructured materials with controlled structures and novel properties has been widely studied for their novel physical and chemical properties [11]. The shape and the size of nanostructures are two critical factors for determining their properties.

Metallic sulfides have photoelectric property, and are widely used as biomarkers for the fabrication of nanoelectronic devices and photoelectric devices. Among the numerous metallic sulfides, bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) is one of the most important V–VI semiconductors, and has attracted great attention for its technological applications. It is a semiconductor with a direct band gap ( $E_g$ ) of 1.3 eV [12], and can be applied as a photovoltaic material, photodiode array, sensor and in IR spectroscopy [13,14]. It was also noted that, bismuth sulfide is a family of solid-state materials with potential applications in thermometric cooling technology due to the Peltier effect [15]. In recent years,  $\text{Bi}_2\text{S}_3$  has been synthesized

through various solution-based synthetic schemes including the most popular solvothermal/hydrothermal processes [16–19] and template growth [20]. However, rigorous conditions are normally required such as reactions in organic solvents with high pressure or chemical vapor deposition at high temperatures. In this study, we demonstrate for the first time a new molten salt solvent strategy that provides a one-step, convenient, low temperature, ambient pressure, low cost, environment friendly and possibly mass-production route for synthesizing  $\text{Bi}_2\text{S}_3$  nanowires and other sulfide nanostructures. The optoelectronic response and surface chemical properties of the nanomaterials have been studied with the successful demonstration of wide wavelength optical detector/switch and sensors. It is expected that the present research may offer useful guidelines to the design and application of  $\text{Bi}_2\text{S}_3$ .

## 2. Experiments

All of the analytically-pure chemical reagents including  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{LiNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , were purchased from Chongqing Chemical Company and used as received without further purification. 9 g of mixed nitrate ( $\text{LiNO}_3/\text{KNO}_3 = 1 : 2$ ) was put in a 25 ml Teflon vessel, and 0.1 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 0.15 mmol  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  were added into the mixed hydroxides. The Teflon vessel was heated to 120 °C and kept at 120 °C for 24 h before it cooled down naturally. The products were washed with deionized water, and then dried at 60 °C for 3 h. The products were characterized by XRD (BDX3200, China), FE-SEM (Nova 400 Nano SEM), TEM (TEM, JEOL4000EX) and HRTEM (HRTEM 400 kV,

\* Corresponding author.

E-mail addresses: [hucg@cqu.edu.cn](mailto:hucg@cqu.edu.cn) (C. Hu), [zlwang@gatech.edu](mailto:zlwang@gatech.edu) (Z.L. Wang).

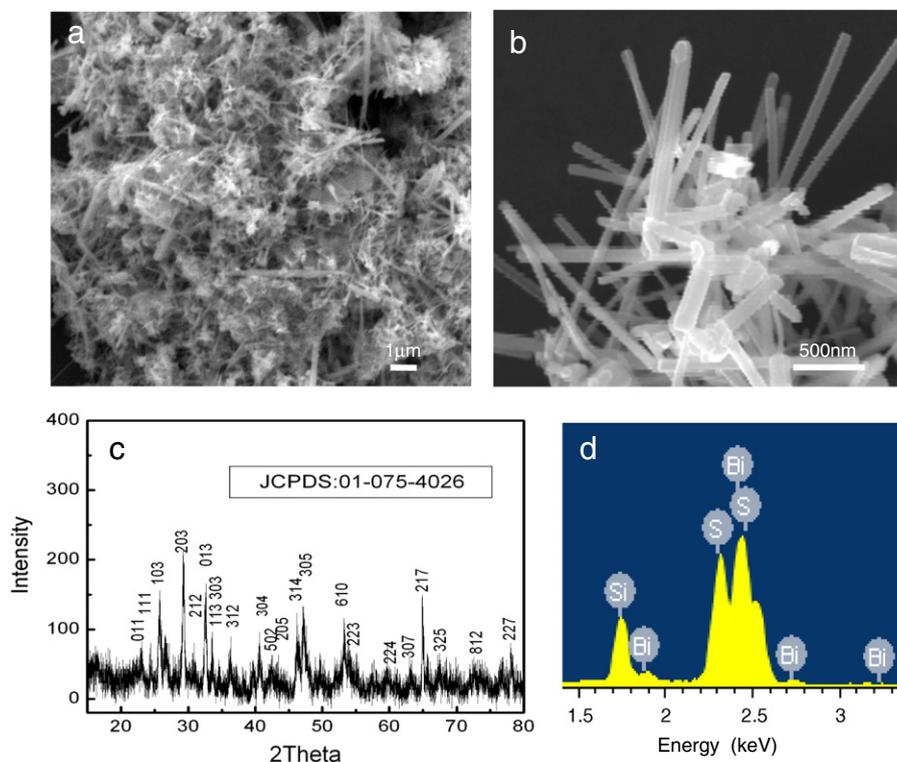


Fig. 1. SEM image (a,b), XRD images (c) and the energy dispersive spectrum (d) of  $\text{Bi}_2\text{S}_3$  nanowires.

JEOL4000EX). The photoelectric property of the sample was measured by Keithley 4200 and PL system.

### 3. Results and discussion

SEM is employed to analyze the morphology of the nanowires, as shown in Fig. 1a, b. The SEM images show that the nanowires are around 100 nm in diameter and 1–3  $\mu\text{m}$  in length. Fig. 1c is the XRD pattern of the  $\text{Bi}_2\text{S}_3$  prepared without any surfactant in the molten salt solvent, which is indexed as an orthorhombic structure of  $\text{Bi}_2\text{S}_3$  with the lattice parameters of  $a = 11.193 \text{ \AA}$ ,  $b = 11.345 \text{ \AA}$ ,  $c = 3.994 \text{ \AA}$ , space group  $P_{nma}(62)$  [JCPDS 01-075-4026]. The energy dispersive x-ray spectroscopy (EDS) in Fig. 1d confirmed that the samples are only composed of elements Bi and S. The C and Si signals came from the unavoidable organic contaminants and the substrate used, respectively.

The nanowires were also examined by transmission electron microscopy (TEM). Selected-area electron diffraction (SAED) pattern and high-resolution TEM (HRTEM) are shown in Fig. 2. Fig. 2a shows a typical TEM image of the  $\text{Bi}_2\text{S}_3$  nanowires. Fig. 2b and c are dark field image and bright field image of a single nanowire, respectively. Fig. 2d is a typical HRTEM image taken from a single  $\text{Bi}_2\text{S}_3$  nanowire, indicating that the nanowire has lattice planes with spacing of 0.35 and 0.48 nm, corresponding to the spacing of the {201} and {1–11} planes of orthorhombic phase  $\text{Bi}_2\text{S}_3$ , respectively. The inset in Fig. 2d is a corresponding SAED taken from a single nanowire along [121], indicating that the single  $\text{Bi}_2\text{S}_3$  nanowire is single crystalline.

The possible reaction mechanism in the molten salt solvent could be expressed by the following three equations.

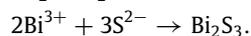
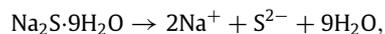
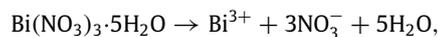


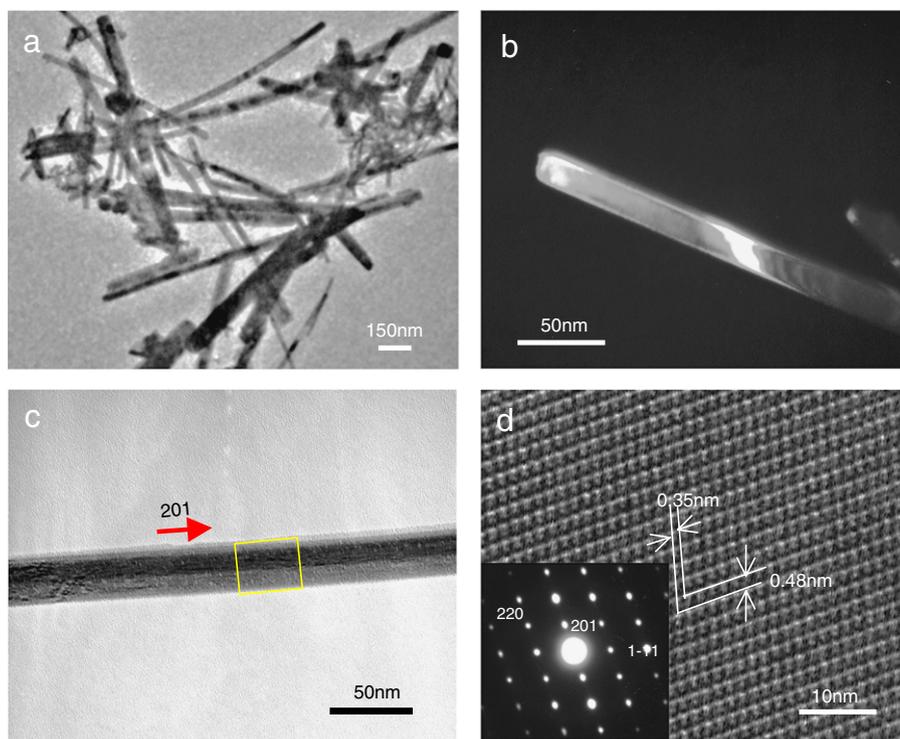
Fig. 3a shows the typical  $I$ – $V$  curves of  $\text{Bi}_2\text{S}_3$  nanowire film measured in dark, under illuminations of UV (300 nm), blue

(440 nm), green (550 nm) and red (650 nm) light, respectively. The bias sweeps from  $-30 \text{ V}$  to  $30 \text{ V}$  at the room temperature in open air condition. The data presented here were normalized in reference to the intensities in corresponding to the incident light at the specific wavelength. The  $\text{Bi}_2\text{S}_3$  nanowire film has a clear increase in conductance upon exposure to visible light with different wavelengths. This behavior is consistent with the report of  $\text{Bi}_2\text{S}_3$  nanowire network film [21]. When the light irradiation has photon energy higher than its band gap, it excites the electrons from the valence band into conduction band, thus increasing the charge carrier concentration via direct electron–hole pair creation [21]. The  $I$ – $V$  measurements exhibit the nonlinear characteristic under the different wavelengths of light, which display weak rectifying characteristics. The phenomenon is similar to the  $I$ – $V$  characteristic of the metal–semiconductor–metal structure, which can be explained as  $\text{Bi}_2\text{S}_3$  nanowire film lying across two Ag electrodes, forming two metal/semiconductor/metal back-to-back Schottky diodes [22].

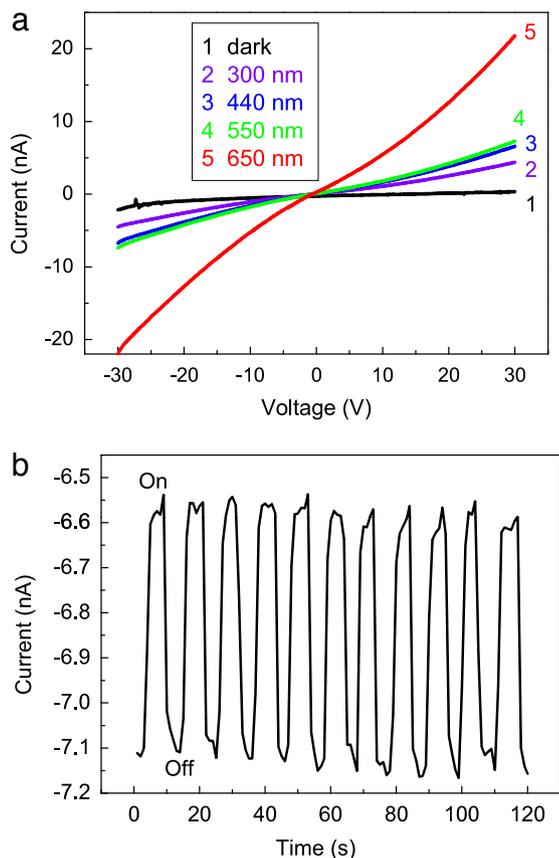
Fig. 3b shows the photo-response as a function of time when the light was switched on and off at a time interval of 2 s. The bias applied was also 30 V. The light was the white light. From the experiment, it was found that the response and recovery time of the current for the  $\text{Bi}_2\text{S}_3$  nanowire is less than 0.1 s under switching light on and off, indicating a much faster optical response than the results reported before [23]. All of the measurements were carried out under ambient environment, indicating that the  $\text{Bi}_2\text{S}_3$  nanowire films have much better stability and adaptability than that of the report  $\text{Bi}_2\text{S}_3$  nanowires performed under vacuum or nitrogen environment [23,24].

### 4. Conclusion

In summary, we report the molten salt solvent strategy that provides a one-step, convenient, low temperature, ambient pressure, low cost, environment friendly and possibly mass-production route for synthesizing  $\text{Bi}_2\text{S}_3$  nanowires. This approach



**Fig. 2.** TEM and HRTEM images of the sample. (a) TEM image of a typical  $\text{Bi}_2\text{S}_3$ . (b) The single nanowire of TEM in the dark field model. (d) Typical HRTEM image taken on a single nanowire. (Inset) Corresponding electron diffraction pattern (SAED) taken on the single nanowire.



**Fig. 3.** (a) The optical properties of  $\text{Bi}_2\text{S}_3$  vs different wavelengths of light, (b) the incident white light vs the shining time (2 s).

does not need any templates or surfactants to control morphology, which opens up a new field of research for the synthesis of

metallic sulfide nanowires. The photo-switchable conductivity of  $\text{Bi}_2\text{S}_3$  nanowire films showed great potential applications in optoelectronic nanodevices.

### Acknowledgments

This work is financially supported by the NSFC (20741006), Postgraduates' Science and Innovation Fund ((200801CIA0080267) and Innovative Talent Training Project (S-09109) of the 3rd-211 Project of Chongqing University. NSF and BES DOE. Thanks go to Dr. Yong Ding for his assistance in TEM analysis.

### References

- [1] W.Y. Fu, Z. Xu, X.D. Bai, C.Z. Gu, E.G. Wang, *Nano Lett.* 9 (2009) 921.
- [2] B.P. Timko, T. Cohen-Karni, G.H. Yu, Q. Qing, B.Z. Tian, C.M. Lieber, *Nano Lett.* 9 (2009) 914.
- [3] X.F. Duan, Y. Huang, Y. Cui, J.F. Wang, C.M. Lieber, *Nature* 409 (2001) 66.
- [4] Y. Cui, Q.Q. Wei, H.K. Park, C.M. Lieber, *Science* 293 (2001) 1289.
- [5] S.J. Guo, D. Wen, S.J. Dong, E.K. Wang, *Talanta* 77 (2009) 1510.
- [6] M.P. Lu, J.H. Song, M.Y. Lu, M.T. Chen, Y.F. Gao, L.J. Chen, Z.L. Wang, *Nano Lett.* 9 (2009) 1223.
- [7] Z.L. Wang, X.D. Wang, J.H. Song, J. Liu, Y.F. Gao, *IEEE Perv. Comp.* 7 (2008) 49.
- [8] X.D. Wang, J.H. Song, J. Liu, Z.L. Wang, *Science* 316 (2007) 102.
- [9] B.Z. Tian, T.J. Kempa, C.M. Lieber, *Chem. Soc. Rev.* 38 (2009) 16.
- [10] T.J. Kempa, B. Tian, D.R. Kim, J. Hu, X. Zheng, C.M. Lieber, *Nano Lett.* 8 (2008) 3456.
- [11] F. Caruso, *Adv. Mater.* 13 (2001) 11.
- [12] J.D. Klein, R.D. Herrick, D. Palmer, M.J. Sailor, *Chem. Mater.* 5 (1993) 902.
- [13] C.R. Martin, *Science* 266 (1994) 1961.
- [14] D. Routkevitch, T. Bigioni, M. Moskovits, J.M. Xu, *J. Phys. Chem.* 100 (1995) 14037.
- [15] P. Boudjouk, D.G. Grier, B.R. Jarabek, G.J. McCarthy, *Inorg. Chem.* 37 (1998) 3538.
- [16] Y. Zhao, X. Zhu, Y.Y. Huang, S.X. Wang, J.L. Yang, Y.J. Xie, *J. Phys. Chem. C* 111 (2007) 12145.
- [17] D.L. Chai, X.S. Yuan, B.J. Yang, Y.T. Qian, *Solid State Commun.* 148 (2008) 444.
- [18] X.P. Shen, G. Yin, W.L. Zhang, Z. Xu, *Solid State Commun.* 140 (2006) 116.
- [19] X.L. Yu, C.B. Cao, H.S. Zhu, *Solid State Commun.* 134 (2005) 239.
- [20] J. Jiang, S.H. Yu, W.T. Yao, H. Ge, G.Z. Zhang, *Chem. Mater.* 17 (2005) 6094.
- [21] H.F. Bao, C.M. Li, X.Q. Cui, Q.L. Song, H.B. Yang, J. Guo, *Nanotechnology* 19 (2008) 335302(5pp).
- [22] H.F. Bao, X.Q. Cui, C.M. Li, Y. Gan, J. Zhang, J. Guo, *J. Phys. Chem. C* 111 (2007) 12279.
- [23] A.D. Schriber, M.B. Sigman, B.A. Korgel, *Nanotechnology* 16 (2005) S508.
- [24] Y. Yu, C.H. Jin, R.H. Wang, Q. Chen, L.M. Peng, *J. Phys. Chem. B* 109 (2005) 18772.