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Synthesis of 2D semiconducting single crystalline Bi_2S_3 for high performance electronics

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2-Dimensional (2D) semiconducting materials are attractive candidates for future electronic device applications due to the tunable bandgap, transparency, flexibility, and downscaling to the atomic level in material size and thickness. However, 2D materials have critical issues regarding van der Waals contact, interface instability and power consumption. In particular, the development of semiconducting electronics based on 2D materials is significantly hindered by a low charge-carrier mobility. In order to improve the critical shortcoming, diverse efforts have been made in synthesis and device engineering. Here, we propose a synthesis method of single crystalline 2D Bi_2S_3 by chemical vapor deposition for high performance electronic device applications. The ion-gel gated field effect transistor with the as-grown Bi_2S_3 on the SiO_2 substrate exhibits a high mobility of $100.4 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and an on-off current ratio of 104 under a low gate voltage below 4 V at room temperature without chemical doping and surface engineering. The superior performance is attributed to the high crystal quality of Bi_2S_3 that shows low sulfur vacancies and atomic ratio close to the ideal value (2:3) under a rich sulfur growth process using H_2S gas instead of sulfur powder. The synthesis method will provide a platform to realize high performance electronics and optoelectronics based on 2D semiconductors.

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1. Introduction

Field effect transistors (FETs) based on silicon are one of the main components of modern electronic integrated circuit and high-speed electronic devices due to their high charge-carrier mobility and low power consumption. Silicon-based FETs have been steadily improved and dramatically developed in fabrication processes for decrease of cost and improvement of electronic performance to date. Recently, the channel size of FETs has reached its theoretical limitation of scaling of less than 10 nm. The short channel of FETs results in critical issues such as high-power consumption, heat dissipation, high contact resistance and leakage current. Alternative materials are required to overcome the limitations and problems in conventional silicon-based transistors.

Two-dimensional (2D) materials such as graphene, BN, and MoS_2 have been attracting great attention due to their unique physical and chemical properties.^{1–5} Among these materials, 2D semiconducting materials such as MoS_2 , WSe_2 and phosphorene have high potential in future electronic device

development because of their atomic-scale thickness, high flexibility, and controllable band gap.^{5–10}

However, common 2D semiconducting materials have critical issues such as high contact resistance, interface instability and high power consumption.^{11–15} In particular, they exhibit low intrinsic charge-carrier mobilities ($0.1\text{--}10 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$) at room temperature that critically impedes their application in electronic devices.^{16–18,29} Although phosphorene exhibits outstanding electrical mobility ($1000 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$), it is not an appropriate candidate for next-generation electronic devices due to significant instability in the air.^{19,20}

Bi_2S_3 (bismuth sulfide) is an anisotropic orthorhombic structured 2D semiconducting material.^{21,22} It exhibits superior optoelectronic properties due to unique physical properties such as strong spin-orbit coupling and a band gap of 1.3 eV.^{23–25} It also possesses excellent thermoelectric properties because of small effective carrier masses, a high Seebeck coefficient and low thermal conductivity.^{21,26} Above all, Bi_2S_3 presents theoretically a high electron mobility of $200 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and a hole mobility of $1100 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ that can be applied in high performance electronic devices.²⁷ However, electronic devices based on synthesized Bi_2S_3 have shown a relatively low mobility like other 2D semiconducting materials owing to low crystal quality and unintentional impurities and vacancy defects.^{28,29}

We have developed a synthesis method for single crystalline Bi_2S_3 by chemical vapor deposition (CVD). Bi_2S_3 was grown

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Table 1 Comparisons of mobility and current on/off ratio between the synthesized Bi_2S_3 with other conventional 2D materials using the chemical vapor deposition (CVD) method

2D materials (CVD)	Progress	Layer	Mobilities ($\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$)	On/off ratio	Ref.
MoS_2	$\text{MoO}_3 + \text{S}$ (powder)	Monolayer	~ 4	$\sim 10^7$	Van Der Zande <i>et al.</i> , Nature materials, (2013) ⁴¹
WS_2	$\text{H}_2\text{WO}_4 + \text{NaCl} + \text{S}$ (powder)	Monolayer	~ 28	—	F. Reale <i>et al.</i> , Scientific reports, (2017) ⁴²
ReS_2	$\text{Re} + \text{S}$ (powder) $\text{NH}_4\text{ReO}_4 + \text{S}$ (powder)	Monolayer bilayer	~ 9 $\sim 7.2 \times 10^{-2}$	$\sim 10^6$ $\sim 10^3$	X. He <i>et al.</i> , Small, (2015) ⁴³ K. Keyshar <i>et al.</i> , Advanced Materials, (2015) ⁴⁴
Bi_2S_3 (nano wire)	$\text{Bi}_2\text{O}_3 + \text{S}$ (powder)	—	~ 0.563	$\sim 10^3$	F. Lu <i>et al.</i> , ChemPhysChem, (2015) ⁴⁵
Bi_2S_3 (nano sheet)	$\text{Bi} + \text{S}$ (powder)	—	~ 28	$\sim 10^3$	K. A. Messalea <i>et al.</i> , Advanced Materials Interfaces, (2020) ⁴⁶
Bi_2S_3 (single crystal)	$\text{Bi}_2\text{O}_3 + \text{H}_2\text{S}$ (gas)	Few layer	~ 100.4	$\sim 10^4$	This work

directly on a SiO_2 substrate using Bi_2O_3 powder and H_2S gas instead of conventional sulfur powder. Sulfur powder is broadly used to synthesize 2D materials such as MoS_2 , WS_2 and ReS_2 (Table 1). However, it is difficult to provide a steady density of sulfur during the growth process due to a solid state material. Moreover, the CVD method using sulfur powder can result in high sulfur vacancies which is the main reason for the low crystallinity of 2D materials such as MoS_2 , WS_2 and ReS_2 .

Previous reports have demonstrated that an annealing process under sulfur supply can improve the quality of crystals by lowering the ratio of sulfur vacancies in the crystal structures.^{30,31} H_2S is the ideal precursor for the CVD method because of the gas phase material that can exactly control the density and supply duration of the precursor. H_2S was used to improve the crystallinity and solve the critical problem of sulfur vacancies of 2D materials such as MoS_2 and WS_2 , because it can provide a steady and rich supply of sulfur during the process of growth. X-ray photoelectron spectroscopy (XPS) proved an atomic ratio of ideal value (2:3) that suggests high crystal quality with few sulfur defects. The single crystallinity and high crystal quality of Bi_2S_3 were confirmed by high-resolution

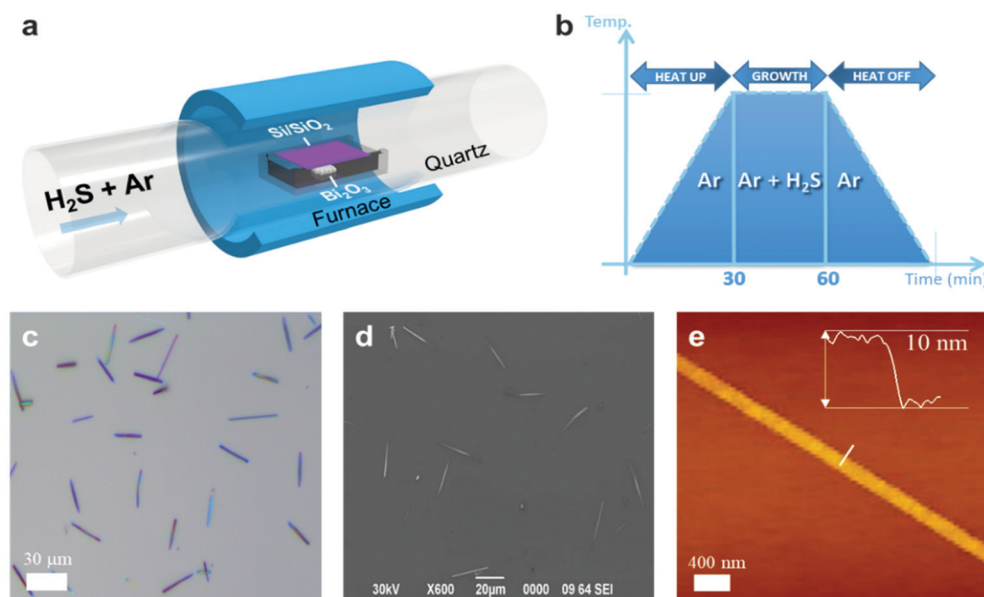
transmission microscopy (HR-TEM). The smooth surface properties without impurities were revealed by atomic force microscopy (AFM). Above all, an ion-gel gated transistor based on as-grown Bi_2S_3 exhibited a high charge-carrier mobility of $100.4 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ and an on-off ratio of 104 under a low gate voltage below 4 V at room temperature without chemical treatments and surface engineering that demonstrate high crystal quality of Bi_2S_3 . These results demonstrate the feasibility of application of synthesized Bi_2S_3 in high performance and low voltage electronics and optoelectronics.

2. Results and discussion

2.1. Synthesis and improvement of the crystallinity of Bi_2S_3 using the LPCVD system

Fig. 1(a) shows a schematic diagram of the experimental set-up for synthesis.

As depicted in the figure, 2D Bi_2S_3 multilayer flakes were synthesized in a vacuum quartz tube in a furnace chamber under low pressure ($\sim 10^{-3}$ torr). CVD method was carried out

**Fig. 1** The synthesis method of Bi_2S_3 and its characterization. (a) Schematic illustration of experimental set-up of Bi_2S_3 , (b) diagram of synthesis process of Bi_2S_3 , (c) OM image of as-grown Bi_2S_3 , (d) SEM image of as-grown Bi_2S_3 , and (e) AFM image and height profile of as-grown Bi_2S_3 .

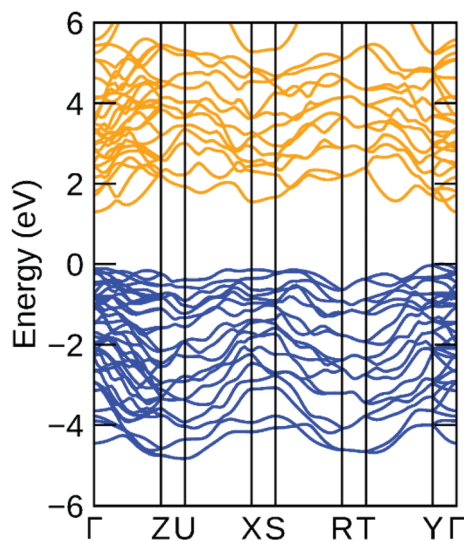


Fig. 3 Electronic band structure of bulk Bi_2S_3 . Blue/orange lines for valence/conduction band. The VBM is set to be $E = 0$.

grid. Fig. 4(b) and (c) show the selected area electron diffraction (SAED) pattern and the HR-TEM image of the Bi_2S_3 flake, respectively. The SAED pattern in Fig. 4(b) presents a periodic orthogonal feature that is associated with a classical anisotropic orthorhombic structure of Bi_2S_3 .

HR-TEM image shows no impurities and defects in the Bi_2S_3 crystal. Above all, the SAED pattern reveals a high-quality and perfect single crystal of a synthesized Bi_2S_3 flake. The diffraction points indicate the lattice planes in the SAED pattern and the (001) plane is perpendicular to the (020) plane.³⁸ This result is in good agreement with the lattice structure of Bi_2S_3 which is the orthorhombic crystal system with the lattice parameters of

$a = 0.112 \text{ nm}$, $b = 1.125 \text{ nm}$, $c = 0.397 \text{ nm}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ as shown in Fig. 4(d).^{39,40} Also, the low magnification image of HR-TEM in Fig. 4(C) demonstrates the anisotropic growth of Bi_2S_3 along a main axis of the [001] direction which is perpendicular to the [010] direction due to the anisotropic orthorhombic structure of Bi_2S_3 (Fig. 4(d)).

2.3. Electrical performance of a Bi_2S_3 FET

A FET was fabricated to evaluate the electronic properties of the synthesized Bi_2S_3 sample.

In this work, an as-grown multilayer Bi_2S_3 flake was used for fabrication as shown in Fig. 5(a) and (b). As shown in Fig. 5(a), 5 nm Cr and 50 nm Au as the electrode were deposited using an e-beam evaporator. The gate insulator was made by drop-casting an ionic liquid onto the Bi_2S_3 flake (Fig. 5(b) and (c)). The ion-gel solution consists of a poly(ethylene glycol) diacrylate (PEG-DA) monomer, a 2-hydroxy-2-methylpropiophenone (HOMPP) initiator, and a 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonfyl)imide (EMIM: TFSI) ionic liquid with a weight ratio of 2 : 1 : 22. In Fig. 5(d), the transfer characteristics of the ion-gel gated FETs exhibited n-type behavior, which is consistent with previous reports. The field effect mobility can be calculated using the equation $\mu = (L/WV_{\text{D}}C_{\text{ion-gel}})(\Delta I_{\text{D}}/\Delta V_{\text{G}})$, where L , W , and $C_{\text{ion-gel}}$ are the channel length, the channel width, and capacitance of the ion-gel gate dielectric.

The value of $\Delta I_{\text{D}}/\Delta V_{\text{G}}$ was obtained from the slope of the transfer characteristic curve plotted in Fig. 5(d). The FET exhibited a high electron mobility of $100.4 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, and a high current on/off ratio of $\sim 10^4$ at $V_{\text{D}} = 1 \text{ V}$, which are superior to those of other conventional 2D materials such as

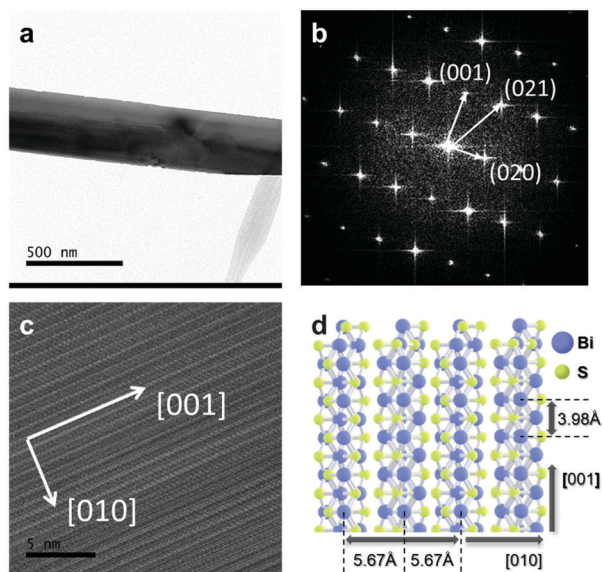


Fig. 4 Structure analysis of Bi_2S_3 . (a) TEM image of Bi_2S_3 on a TEM grid, (b) SAED patterns of single crystalline Bi_2S_3 , (c) HRTEM image of anisotropic Bi_2S_3 structure, and (d) schematic illustration of Bi_2S_3 crystal structure.

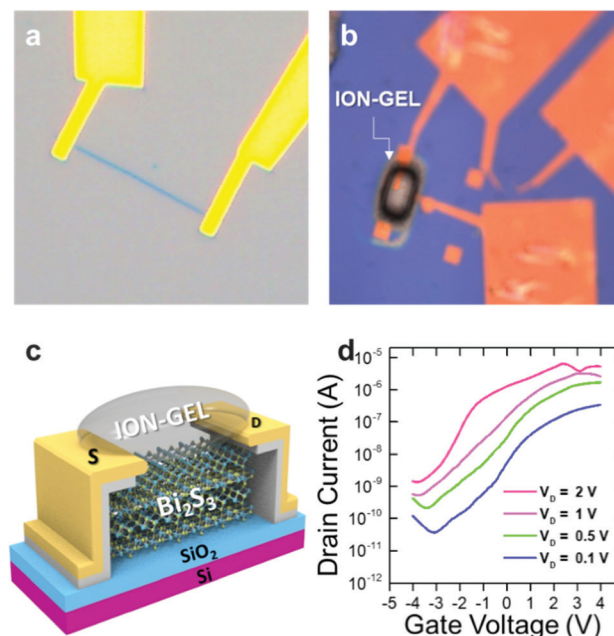


Fig. 5 Electronic properties of Bi_2S_3 : (a) OM image of FET based on as-grown Bi_2S_3 , (b) OM image of the ion-gel gated transistor of Bi_2S_3 , (c) schematic diagram of ion-gel gated Bi_2S_3 FET, (d) transfer characteristics of Bi_2S_3 transistor.

MoS₂, WS₂ and ReS₂ as well as those of the previously reported Bi₂S₃ (Table 1). The excellent electronic device performance again proves the high crystallinity of the synthesized flakes and demonstrates the feasibility of practical and high-performance electronic device applications.

3. Experimental

3.1. Synthesis of Bi₂S₃

Bi₂O₃ powder (99.9%, Sigma Aldrich) was used as the precursor for the synthesis of Bi₂S₃. Bi₂S₃ was grown in a vacuum quartz tube in a furnace under low pressure (~103 torr). Before synthesis, SiO₂/Si (300 nm SiO₂) wafer was cleaned in acetone and isopropyl alcohol (IPA) and then rinsed in DIW several times. A mass of Bi₂O₃ 5 mg powder in a quartz boat was put onto the edge of the furnace and covered by SiO₂/Si wafer. The furnace was heated up to 550 °C for 30 min and then H₂S gas was injected for sulfurization of Bi₂O₃ for 30 min. The furnace chamber was cooled down to room temperature. Ar gas was injected over the whole process.

3.2. Characterization of synthesized Bi₂S₃

Raman and PL spectroscopy was carried out at 532 nm laser wavelength, and 1 mW laser power, which avoids thermal damage to samples. The Raman instrument (NTMDT AFM-Raman spectroscope) was calibrated using a Si peak of 520 cm⁻¹ before measurement. XPS was performed to determine the chemical stoichiometry and bonding states of Bi₂S₃ with an Al K α X-ray source (ESCALAB 220i-XL, VG Scientific Instruments). AFM was used for surface analysis and measurement of the thickness of the samples. AFM measurements (Seiko instrument) were taken with a Si tip (NT-MDT). To make the TEM sample, a Bi₂S₃ on SiO₂/Si wafer was coated with polymethylmethacrylate (PMMA) in a spin-coater. It was immersed in BOE solution to remove SiO₂ and then was rinsed in DIW several times. The PMMA-supported Bi₂S₃ was transferred onto a TEM copper grid and the PMMA was removed in acetone for 30 min and rinsed in IPA several times. The TEM images and SAED patterns were obtained using a JEM-2100F, Cs corrector.

3.3. Structure relaxation and electronic band structure calculations

All the DFT calculations were performed using the Vienna *ab initio* Simulation Package (VASP).⁴⁹ For the ion-electron interaction, projector augmented wave (PAW) pseudopotentials were used. For the exchange-correlation functional, the Perdew-Burke-Ernzerhof (PBE) type generalized gradient approximation (GGA) was adopted.⁵⁰ The van der Waals interactions were described by the DFT-D3 Grimme method.⁵¹ The Γ -centered k -mesh of $4 \times 12 \times 5$ ($9 \times 25 \times 9$) and the plane-wave energy cutoff of 600 eV were set for the structural optimization (electronic band structure calculation). The calculated lattice constants of the relaxed bulk Bi₂S₃ are $a = 11.12$ Å, $b = 11.29$ Å and $c = 4.00$ Å, in very good agreement with the experimental values ($a = 11.2$ Å, $b = 11.25$ Å and $c = 3.97$ Å).

3.4. Device fabrication

A FET based on as-grown Bi₂S₃ was fabricated using e-beam lithography. The metal electrodes of Cr/Au (5/50 nm) were deposited by using an e-beam evaporator. To make the gate insulator, the ionic liquid was drop-cast onto the FET. The gate dielectric layer was formed by drop-casting an ion-gel solution comprising poly(ethyleneglycol) diacrylate (PEGDA, Sigma-Aldrich), 2-hydroxy-2-methylpropiophenone (HOMPP, Sigma Aldrich), and 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide ([EMIM][TFSI]) ionic liquid (Merck) in a weight ratio of 2 : 1 : 22. After drying, the ion gel layer in a patterned photomask was exposed to UV light (365 nm, 100 mW cm⁻²) for five seconds. The area exposed to UV light became chemically crosslinked, while the unexposed region was removed by rinsing in DIW.

4. Conclusions

In conclusion, we have developed the CVD method for the synthesis of single crystalline Bi₂S₃. The crystals have the shapes of 1-dimensional nanowires or nanorods with a width of ~200 nm and a thickness of tens of nanometers. TEM and SAED patterns revealed anisotropic properties and high crystallinity in the orthorhombic structure of Bi₂S₃. The optical band gap of Bi₂S₃ (~1.33 eV) was confirmed by PL spectroscopy. AFM and SEM images showed clean and uniform surfaces of Bi₂S₃. Above all, ion-gel gated FETs based on as-grown Bi₂S₃ displayed superior electronic properties with a charge carrier mobility of 100.4 cm² V⁻¹ S⁻¹, a current on/off ratio of ~10⁴ and a low voltage operation below 4 V. The CVD method to grow Bi₂S₃ single crystals paves a new way for high performance electronics with 2D semiconducting materials.

Author contributions

Y. K. developed the synthesis method of Bi₂S₃ and carried out the analysis of CVD-grown Bi₂S₃, M. J. conducted the electronic band structure calculation of Bi₂S₃ and E. J. fabricated the device of Bi₂S₃ and conducted the electrical test. All authors contributed the discussion and preparation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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