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Synthesis of 2D semiconducting single crystalline Bi₂S₃ 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 Bi₂S₃ 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 cm² V^{-1} 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 Bi₂S₃ that shows low sulfur vacancies and atomic ratio close to the ideal value (2:3) under a rich sulfur growth process using H₂S gas instead of sulfur powder. The synthesis method will provide a platform to realize high performance electronics and optoelectronics based on 2D semiconductors.

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 highpower consumption, heat dispassion, 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 MoS₂ have been attracting great attention due to their unique physical and chemical properties.¹⁻⁵ Among these materials, 2D semiconducting materials such as MoS2, WSe2 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 (0.1-10 cm² V⁻¹ S⁻¹) at room temperature that critically impedes their application in electronic devices. 16-18,29 Although phosphorene exhibits outstanding electrical mobility (1000 cm² V⁻¹ S⁻¹), it is not an appropriate candidate for nextgeneration electronic devices due to significant instability in the air. 19,20

Bi₂S₃ (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, Bi₂S₃ 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 Bi₂S₃ 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 Bi₂S₃ by chemical vapor deposition (CVD). Bi₂S₃ was grown

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Table 1 Comparisons of mobility and current on/off ratio between the synthesized Bi₂S₃ with other conventional 2D materials using the chemical vapor deposition (CVD) method

2D materials (CVD)	Progress	Layer	Mobilities (cm ² V ⁻¹ S ⁻¹)	On/off ratio	Ref.
MoS_2	$MoO_3 + S$ (powder)	Monolayer	~4	$\sim 10^{7}$	Van Der Zande <i>et al.</i> , Nature materials, (2013) ⁴¹
WS_2	$H_2WO_4 + NaCl + S$ (powder)	Monolayer	~28	_	F. Reale <i>et al.</i> , Scientific reports, (2017) ⁴²
ReS_2	Re + S (powder)NH ₄ ReO ₄ +	Monolayer bilayer	~9	$\sim 10^{6}$	X. He <i>et al.</i> , Small, (2015) ⁴³
	S (powder)		$\sim 7.2 \times 10^{-2}$	$\sim 10^{3}$	K. Keyshar et al., Advanced Materials, (2015) ⁴⁴
Bi ₂ S ₃ (nano wire)	$Bi_2O_3 + S$ (powder)	_	~ 0.563	$\sim 10^{3}$	F. Lu et al., ChemPhysChem, (2015) ⁴⁵
Bi ₂ S ₃ (nano sheet)	Bi + S (powder)	_	~28	$\sim 10^3$	K. A. Messalea <i>et al.</i> , Advanced Materials Interfaces, (2020) ⁴⁶
Bi ₂ S ₃ (single crystal)	$Bi_2O_3 + H_2S$ (gas)	Few layer	~ 100.4	$\sim 10^4$	This work

directly on a SiO₂ substrate using Bi₂O₃ powder and H₂S gas instead of conventional sulfur powder. Sulfur powder is broadly used to synthesize 2D materials such as MoS₂, WS₂ and ReS₂ (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 MoS₂, WS₂ and ReS₂.

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 H₂S 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. H2S was used to improve the crystallinity and solve the critical problem of sulfur vacancies of 2D materials such as MoS2 and WS2, 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 Bi₂S₃ 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 Bi₂S₃ exhibited a high charge-carrier mobility of 100.4 cm² V⁻¹ 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 Bi₂S₃. These results demonstrate the feasibility of application of synthesized Bi₂S₃ in high performance and low voltage electronics and optoelectronics.

2. Results and discussion

2.1. Synthesis and improvement of the crystallinity of Bi₂S₃ using the LPCVD system

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

As depicted in the figure, 2D Bi₂S₃ 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

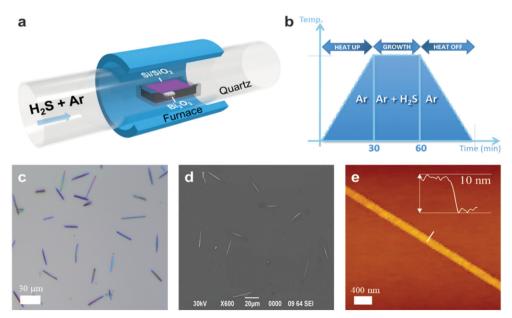


Fig. 1 The synthesis method of Bi_2S_3 and its characterization. (a) Schematic illustration of experimental set-up of Bi_2S_3 , (b) diagram of synthesis process of Bi₂S₃, (c) OM image of as-grown Bi₂S₃, (d) SEM image of as-grown Bi₂S₃, and (e) AFM image and height profile of as-grown Bi₂S₃.

using H₂S and Bi₂O₃ powder as precursors and Ar gas was used as a transporting material in whole CVD process. Bi2S3 was directly grown on a SiO2/Si substrate (300 nm SiO2) by sulfurization of Bi₂O₃ after injection of H₂S gas (Fig. 1(a and b)). During the whole growth process, the density and supply duration of H₂S gas were exactly adjusted using a mass flow controller and CVD system. While sulfur powder is rapidly vaporised within several min, H₂S can provide a rich and steady sulfur environment until the end of the duration of growth. Although Bi₂S₃ can be synthesized within 10 min, the duration of H₂S gas supply increased up to 30 min including annealing process to reduce the sulfur vacancies and improve crystal quality.

2.2. Characterization and structure of Bi₂S₃

Fig. 1(c) and (d) show optical and electron microscopy images of Bi₂S₃ multilayer crystals which were grown on the SiO₂/Si substrate. The optical microscope image exhibits the contrast of multilayer Bi₂S₃ with the size of 10-50 micrometers. Also, the shape of synthesized Bi₂S₃ presents a highly anisotropically structured 1D nanowire. AFM measurements were performed to observe surface states and thicknesses as shown in Fig. 1(e).

Fig. 1(e) reveals the highly uniform and clean surface of Bi₂S₃ crystals without chemical residue and critical defects. The synthesized Bi₂S₃ samples show a thickness of about 10 nm and a width of about 200 nm.

Raman spectroscopy was used to characterize qualitative physical properties of Bi₂S₃ samples. As shown in Fig. 2(a), the Raman spectrum was obtained from the sample with approximately 10 nm thickness under a 532 nm wavelength laser and excitation power of 1 mW. The Raman system was

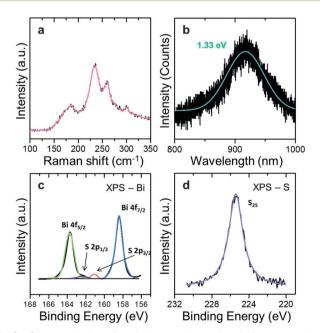


Fig. 2 Characterization of optical properties and stoichiometry analysis of Bi₂S₃ (a) Raman spectrum of Bi₂S₃, (b) PL spectrum of Bi₂S₃, (c) XPS spectrum of Bi 4f peaks and S 2p peaks, and (d) XPS spectrum of S 2s

calibrated using the Si peak at 520 cm⁻¹. The Raman spectrum shows well-defined main peaks at 185 and 235 cm⁻¹ of A_g phonon mode and 260 cm $^{-1}$ of B_{1g} phonon mode. 32 The A_{g} and B_{1g} vibration modes are associated with transverse and longitudinal optical phonons respectively. These peak positions match well with those values reported in both of previous theoretical works and experimental results.³³ PL spectroscopy was also performed using a 532 nm excitation source. To avoid thermal damage from laser irradiation, 1 mW of power was used for this work. The relatively weak signal of the PL spectrum results from a smaller width of the Bi₂S₃ sample (~ 200 nm) than the spot size of the Raman laser (~ 1 μ m). As shown in Fig. 2(b), the PL spectrum has the main peak at 917 nm (1.33 eV) which corresponds well to the expected value of the optical band gap. 34,35

XPS measurements were carried out to characterize the chemical stoichiometry of the synthesized Bi₂S₃ crystals and prove low sulfur vacancies of Bi₂S₃ crystals (Fig. 2(c) and (d)). To obtain exact peak values, the experimental data were fitted with 4 peaks as shown in Fig. 2(c). The 4f spectrum of Bi³⁺ presents dominant peaks at 163.7 and 158.4 related to $4f_{5/2}$ and $4f_{7/2}$ respectively.

Similarly, Fig. 2(c) reveals two peaks at 162.3 and 161.1 eV representing S $2p_{1/2}$ and S $2p_{2/3}$. In Fig. 2(d), the 2s spectrum of S exhibits the peak at 225.3 eV. These results correspond well to the chemical bond between sulfur and bismuth of Bi₂S₃.³³ The Bi 4f orbitals, which result from inherent oxide in Bi₂O₃ can appear at high binding energy levels.³⁶

The Bi 4f spectrum shows no signal arising from the Bi_xO_y radicals or Bi₂O₃ residues. The atomic ratio of Bi to S is about 0.67 (Fig. 2(c) and (d)), which closely corresponds to the ideal stoichiometry of Bi₂S₃ and proves the presence of a few sulfur vacancies that result in critical low crystal quality. Furthermore, this result shows lower ratio of sulfur vacancies than CVD-grown Bi₂S₃ using sulfur powder.³⁷

The electronic band structure of bulk Bi2S3 is plotted in Fig. 3. It displays a semiconducting character with a bandgap of 1.29 eV, in excellent agreement with the previously reported value of 1.3 eV as well as our PL peak value of 1.33 eV. 47 The carrier effective mass is calculated by a parabolic fit to the band edge. The hole and electron effective mass from VBM and CBM are 0.39 m_0 and 0.25 m_0 , respectively, where m_0 is the free electron mass. Compared with the value of MoS_2 ($\approx 0.5 m_0$), such a smaller electron effective mass suggests a comparable or higher electron mobility than that of MoS₂ (10-50 cm² V⁻¹ S⁻¹).⁴⁸

HR-TEM was used to analyze the crystal structure and evaluate the crystalline quality of a synthesized Bi₂S₃ sample. The Bi₂S₃ flakes synthesized on the SiO₂/Si substrate were coated with polymethylmethacrylate (PMMA) in a spin-coater. The PMMA coating with the flakes was removed from the substrate in a buffered oxide etchant (BOE) and rinsed in deionized water (DIW) several times.

The PMMA-supported Bi₂S₃ was transferred onto a TEM copper grid. PMMA was removed in acetone solution and the grid was rinsed in IPA several times. Fig. 4(a) shows the image of HR-TEM of a Bi₂S₃ flake transferred onto the copper TEM

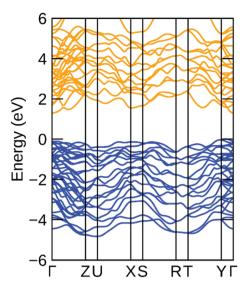


Fig. 3 Electronic band structure of bulk Bi₂S₃. Blue/orange lines for valence/conduction band. The VBM is set to be E = 0.

grid. Fig. 4(b) and (c) show the selected area electron diffraction (SAED) pattern and the HR-TEM image of the Bi₂S₃ flake, respectively. The SAED pattern in Fig. 4(b) presents a periodic orthogonal feature that is associated with a classical anisotropic orthorhombic structure of Bi₂S₃.

HR-TEM image shows no impurities and defects in the Bi₂S₃ crystal. Above all, the SAED pattern reveals a high-quality and perfect single crystal of a synthesized Bi₂S₃ 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 Bi2S3 which is the orthorhombic crystal system with the lattice parameters of

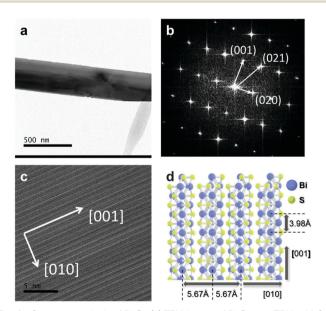


Fig. 4 Structure analysis of Bi₂S₃. (a) TEM image of Bi₂S₃ on a TEM grid, (b) SAED patterns of single crystalline Bi₂S₃, (c) HRTEM image of anisotropic Bi₂S₃ structure, and (d) schematic illustration of Bi₂S₃ crystal structure.

 $a = 0.112 \text{ nm}, b = 1.125 \text{ nm}, c = 0.397 \text{ nm}, \alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ}$ 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 Bi₂S₃ along a main axis of the [001] direction which is perpendicular to the [010] direction due to the anisotropic orthorhombic structure of Bi₂S₃ (Fig. 4(d)).

2.3. Electrical performance of a Bi₂S₃ FET

A FET was fabricated to evaluate the electronic properties of the synthesized Bi₂S₃ sample.

In this work, an as-grown multilayer Bi₂S₃ 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 dropcasting an ionic liquid onto the Bi₂S₃ 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(trifluoromethylsulfonyl)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 $\mu = (L/WV_DC_{ion-gel}) (\Delta I_D/\Delta V_G)$, 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 $\Delta I_{\rm D}/\Delta V_{\rm G}$ 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 cm² V⁻¹ S⁻¹, and a high current on/off ratio of $\sim 10^4$ at $V_D = 1$ V, which are superior to those of other conventional 2D materials such as

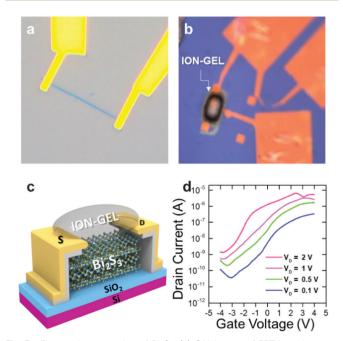


Fig. 5 Electronic properties of Bi₂S₃: (a) OM image of FET based on asgrown Bi₂S₃, (b) OM image of the ion-gel gated transistor of Bi₂S₃, (c) schematic diagram of ion-gel gated Bi₂S₃ FET, (d) transfer characteristics of Bi₂S₃ transistor.

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 Kα 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 planewave energy cutoff of 600 eV were set for the structural optimization (electronic band structure calculation). The calculated lattice constants of the relaxed bulk Bi_2S_3 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-beamlithography. 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 Bi_2S_3 (~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 $\sim 10^4$ 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.

Acknowledgements

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