Fabrication of Graphene/Bi$_2$Se$_3$/Graphene heterostructure without the surface oxidation of Bi$_2$Se$_3$

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Abstract

Graphene/Bi$_2$Se$_3$/Graphene (G/Bi$_2$Se$_3$/G) sandwich hybrids were fabricated via chemical vapor deposition. The medium graphene layer is used to synthesize the high-quality Bi$_2$Se$_3$, benefitting from the smaller lattice mismatch between graphene and Bi$_2$Se$_3$. The covering graphene layer is designed to inhibit the surface oxidation of Bi$_2$Se$_3$ layers which are easily changed to BiO$_x$ in the atmosphere. The Raman spectroscopy, scanning electron microscopy and X-ray diffraction confirm the high-quality and uniform Bi$_2$Se$_3$ film. The Raman spectroscopy and X-ray diffraction investigates antioxidant ability of the G/Bi$_2$Se$_3$/G structure. We conclude that the graphene can effectively improve the crystal quality of Bi$_2$Se$_3$ and inhibit the surface oxidation of it.

Graphical abstract

The method to improve the crystal quality and inhibit the surface oxidation is important for the application of the Bi$_2$Se$_3$ films. Graphene/Bi$_2$Se$_3$/Graphene (G/Bi$_2$Se$_3$/G) sandwich hybrids were fabricated here via chemical vapor deposition. The medium graphene layer is used to synthesize the high-quality Bi$_2$Se$_3$, benefitting from the smaller lattice mismatch between graphene and Bi$_2$Se$_3$. The covering graphene layer is designed to inhibit the surface oxidation of Bi$_2$Se$_3$, layers which are easily changed to BiO$_x$ in the atmosphere. We conclude that the graphene can effectively improve the crystal quality of Bi$_2$Se$_3$ and inhibit the surface oxidation of it.

Introduction

Bi$_2$Se$_3$, an ideal topological insulator (TI) with a single Dirac cone residing in a large bulk bandgap (~0.3eV), has attracted extensive scientific interests to experimental and theoretical communities [1]. Layer-structured Bi$_2$Se$_3$ materials may be applied for the future spintronics and quantum computing devices due to large ratio of surface-to-volume, thus it is urgent to synthesize high-quality Bi$_2$Se$_3$, with defined sizes [2-4]. Various methods have been tried to fabricate Bi$_2$Se$_3$ thin film, such as molecular beam epitaxial (MBE) [5,6], solvothermal synthesis [7], mechanical exfoliation [8], metal-organic chemical vapor deposition (MOCVD) [9] and chemical vapor deposition (CVD) [10-13]. Compared with other methods, CVD is an inexpensive and effective strategy to obtain Bi$_2$Se$_3$ materials. Directly fabricated the large-area high-quality Bi$_2$Se$_3$ film on SiO$_2$ is difficult due to the larger lattice mismatch between Bi$_2$Se$_3$ and SiO$_2$. Graphene film, a 2-D atomic-scale honeycomb lattice made of carbon atoms, can be used to fabricate the high-quality epitaxial layer benefiting from that the van der Waals interactions between epitaxial layer and graphene can efficiently suppress the negative effects of the lattice mismatch [12]. Here, we fabricated large-area high-quality Bi$_2$Se$_3$ thin film in a Se-rich environment via a catalyst-free CVD method on the graphene/SiO$_2$ substrate.

However, the synthesized Bi$_2$Se$_3$ thin film gets doped after being exposed to the atmosphere and the content of BiO$_x$ increased with the increase of the exposed time. Such rapid surface oxidation reduces the relative contribution of surface states, which greatly limits the development of the Bi$_2$Se$_3$ devices [14]. Therefore, a method to inhibit the surface oxidation is urgently required. Graphene is capable of...
both scavenging free-radicals [15-18] and can serving as gas barriers [19-23], these dual effects make graphene be effective in improving oxidation stability of Bi$_2$Se$_3$. In this study, we fabricated high-quality G-Bi$_2$Se$_3$-G heterostructure via CVD. There are two advantages of this heterostructure: (1) the 2D growth single-crystal Bi$_2$Se$_3$ thin film can be successfully deposited on the graphene film; (2) the oxidation process of the Bi$_2$Se$_3$ is significantly delayed compared with that without the protection of the graphene.

**Experimental method**

The monolayer graphene film was synthesized on the Cu foil via a CVD method and immediately transferred to the SiO$_2$ substrate using wet-etching process. Bi$_2$Se$_3$ thin film was grown on the monolayer graphene substrate along the lateral direction with the help of Se powder in the source materials via CVD method in a horizontal quartz tube (~3.5 inch in diameter), which has been investigated by our previous work [13]. As shown in Figure 1, high purity powder of Bi$_2$Se$_3$ and Se as the precursor for evaporation was located in the constant-temperature zone and the G/SiO$_2$ substrate was placed on a quartz boat in the down-stream zone. The horizontal quartz tube was pumped to 1.0×10$^{-6}$ Torr by mechanical pump and aerated Ar gas with ~50 sccm flow rate to remove any oxygen residue. The constant-temperature zone of the furnace was heated and maintained at 550°C for 15 min. The furnace was naturally cooled down to the ambient temperature with the Ar gas flowing (~50 sccm). The fabricated Bi$_2$Se$_3$/G is immediately covered by another graphene layer to get the G/Bi$_2$Se$_3$/G sandwich hybrid structure. Following the fabrication, the morphology, chemical analysis, structural properties and single-crystalline structure of the G/Bi$_2$Se$_3$/G were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy and X-ray diffraction (XRD).

**Results and discussion**

Graphene layer plays a vital role in forming uniform Bi$_2$Se$_3$ thin film. Figure 2a exhibits the SEM image of the Bi$_2$Se$_3$ deposited on the SiO$_2$ substrates with and without the graphene film. From the right of the Figure 2a, only Bi$_2$Se$_3$ nanoplates were obtained in the case of no graphene serving as medium layer, which can be easily observed from SEM image under a high magnification (shown in the Figure 2b). As can be seen, the Bi$_2$Se$_3$ nanoplates grow along the lateral direction with the help of the Se powder in the source materials serving as growing point. However, the large lattice mismatch with SiO$_2$ substrates makes it impossible to form Bi$_2$Se$_3$ film. Large area high-quality Bi$_2$Se$_3$ thin film was synthesized on the graphene/SiO$_2$ on the left of the images, which benefits from the van der Waals interactions between the graphene and Bi$_2$Se$_3$ layer. Figure 2c shows the SEM images of Bi$_2$Se$_3$ samples grown on SiO$_2$ substrate with the graphene layer under 10× magnification, symmetric triangular and hexagonal morphologies with a smooth multi-layered structure aligned in the same orientation. Individual Bi$_2$Se$_3$ plates deviated from the main orientation may be introduced by the lattice mismatch or defects of the graphene substrate. The EDX spectrum of the samples displayed in Figure 2d shows that the energy signal peak of Se and Bi are detected on the G/SiO$_2$ substrate. (c) High magnification SEM image of the Bi$_2$Se$_3$ nanoplates grown on the G/SiO$_2$ substrate. (d) EDX spectrum of the Bi$_2$Se$_3$/G hybrid materials. (e) 20-ω X-ray diffraction pattern of the prepared sample. (f) The Raman spectra of the graphene and Bi$_2$Se$_3$/G.

| Element | Weight% | Atomic% |
|---------|---------|---------|
| C       | 0.39    | 2.68    |
| O       | 10.53   | 34.02   |
| Si      | 20.78   | 38.24   |
| Se      | 22.52   | 14.74   |
| Bi      | 45.77   | 10.32   |
| Total   | 100.0   |         |

**Table 1.** Quantitative atomic analysis of the Bi and Se elements.

![Figure 1. Schematic of the hot-wall CVD system used in this study.](image)

![Figure 2.](image)
related with the SiO$_2$ substrates. The spectrum of the Bi$_2$Se$_3$ reveals three characteristic bands of the Bi$_2$Se$_3$ thin film: ~72, ~131 and ~174 cm$^{-1}$ respectively correspond to the $A_g$, $E'_g$ and $A'_g$ vibrational modes [25]. The symmetric Lorentzian line shape of all of the Raman peaks means that the Bi$_2$Se$_3$ thin film samples have a crystal structure. Obvious G and 2D bands at ~1585 and ~2700 cm$^{-1}$ representing for graphene film, were also detected in the high frequency region. The intensity ratio of the 2D peak to G peak was measured to be around 2.0, which are typical signatures of a monolayer graphene film. In addition, after the deposition of the Bi$_2$Se$_3$ thin film, the 2D band of the monolayer graphene film becomes broader and up shifts by ~28 cm$^{-1}$, which probably be attributed to the van der Waals interaction of the Bi$_2$Se$_3$ thin film and graphene. These features imply the fact that the graphene film still possesses perfect structural properties after the deposition of the Bi$_2$Se$_3$ thin film.

Quintuple layer (QL) in Bi$_2$Se$_3$ is ordered in a Se–Bi–Se–Bi–Se sequence via covalent bond and adjacent layer are connected by weak van der Waals force. Dangling bonds appeared in the surface of Bi$_2$Se$_3$ film as a result of the Se vacancies make Bi$_2$Se$_3$ easily react with oxygen atoms of environment and form BiO$_x$ [11,14], which great limit the application of Bi$_2$Se$_3$. The stability of the Bi$_2$Se$_3$ sample as a function of exposure time in air as shown in Figure 3a, the Raman modes at 72 cm$^{-1}$, 131 cm$^{-1}$, 174 cm$^{-1}$ attributed to Bi$_2$Se$_3$ are clearly seen. However, the modes of BiO$_x$ at 250 cm$^{-1}$ and 328 cm$^{-1}$ [26] appears when the sample is left in air over ten days. To further demonstrate the formation of BiO$_X$ XRD measurement was carried out as shown in Figure 3b, the diffraction peaks of BiO$_x$ at 2θ= 27.377, 40.053 and 41.884 appears respectively [11], which correspond well with the Raman spectrum (shown in Figure 3a). It illustrates that the formation of BiO$_X$ is very fast.

In order to delay the oxidation of Bi$_2$Se$_3$ film, we transfer a covering graphene on it again to fabricate a G/Bi$_2$Se$_3$/G sandwich Dirac heterostructure. The covering graphene can be mixed with Bi$_2$Se$_3$ thin film at a molecular level to maximize the contact between them by the van der Waals interaction [22]. The monolayer graphene are stable under ambient conditions and its pore size is far less than the size of oxygen molecules, which make it a perfect gas barrier. In addition, it is capable of scavenging free-radicals, thus the covering graphene layer can effectively delay the process of surface oxidation of Bi$_2$Se$_3$ [23]. The Raman spectrum signal of the G/Bi$_2$Se$_3$/G sample shown in Figure 4a is different from the spectra changes of the Bi$_2$Se$_3$/G sample exposed in air over ten days. At 72, ~131 and ~174 cm$^{-1}$, the intensity of all known, the intensity of the out-of-plane vibrational mode, $A'_g$ and $E'_g$, is more sensitive to the thickness [25]. The thickness of the G/Bi$_2$Se$_3$/G films can be identified by the Raman band mappings with the different color. As can be seen from Figure 4c, 4d and 4e, relatively smooth $A'_g$, $E'_g$ and $A'_g$, band mappings of Bi$_2$Se$_3$ thin film with uniform colour are formed, indicating the large-area layer-controlled Bi$_2$Se$_3$ thin film. In Figure 4b, the red spectrum is taken from the red region marked by the yellow triangle (red) and white dot (black). (c)-(e) The scanning Raman $A'_g$, $E'_g$ and $A'_g$ band mappings of the G/Bi$_2$Se$_3$/G sample exposed in air for different days.

In conclusion, we have demonstrated that high-quality and uniform Bi$_2$Se$_3$ thin film can be obtained with graphene serving as medium layers and the covering graphene can effectively delay the process of surface oxidation of Bi$_2$Se$_3$. This method presents a simple and economical technique to fabricate Bi$_2$Se$_3$ film with chemistry stable under ambient conditions. It presents a practical help for probing topological insulator surface state by transport measurements and pave the way for applying in the spintronics and quantum computing.

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**References**

1. Cui HM, Liu H, Wang JY, Li X, Han F, Boughton RI (2004) Sonochemical synthesis of
bismuth selenide nanobelts at room temperature. J Cryst Growth 271: 456-461.
2. Peng HL, Lai KJ, Kong DS, Meister S, Chen YL, et al. (2010) Aharonov-Bohm interference in topological insulator nanoribbons. Nat Mater 9: 225-229. [Crossref]
3. Tang HL, Liang D, Qu RLJ, Gao XPA (2011) Two-dimensional transport-induced linear magneto-resistance in topological insulator Bi2Se3 nanoribbons. ACS Nano 5: 7510-7516. [Crossref]
4. Xiu FX, He L, Wang Y, Cheng YL, Chang LT, Lang MR, et al. (2011) Manipulating surface states in topological insulator nanoribbons. Nano Lett 6: 216-222. [Crossref]
5. He L, Xiu FX, Wang Y, Alexei V, Fedorov G, et al. (2011) Epitaxial growth of Bi2Se3 topological insulator thin films on Si. J Appl Phys 109: 103702
6. Tabor P, Keenan C, Urazhdin S, Lederman D (2010) Plasmon-enhanced electron-phonon coupling in Dirac surface states of the thin-film topological insulator Bi2Se3. Nature Physics 6: 584-588.
7. Zhang GQ, Wang W, Lu XL, (2009) Solvothermal Synthesis of V− VI Binary and Ternary Hexagonal Platelets: The Oriented Attachment Mechanism. Growth Des 9: 145-150.
8. Checkelsky JG, Hor YS, Liu MX, Qu DX, Cava RJ, Ong NP (2009) Quantum interference in macroscopic crystals of nonmetallic Bi 2 Se 3. Phys Rev Lett 103: 246601. [Crossref]
9. Alegria LD, Schroer MD, Chatterjee A, Poirier GR, Preto M, et al. (2012) Structural and Electrical Characterization of Bi2Se3 Nanostructures Grown by Metal-Organic Chemical Vapor Deposition. Nano Lett 12: 4711-4714. [Crossref]
10. Dang WH, Peng HL, Li HL, Wang P, Liu ZF (2010) Epitaxial heterostructures of ultrathin topological insulator nanoplate and graphene. Nano Lett 10: 2870-2876. [Crossref]
11. Liu FY, Liu M, Liu AH, Yang C, Chen CS, et al. (2015). J Mater Sci 26: 3881-3886
12. Zhang C, Liu M, Man BY, Jiang SZ, Yang C, Chen CS, et al. (2014) Crystal Eng Comm 16: 8941.
13. Liu M, Liu FY, Man BY, Bi D, Xu XY (2014) Multi-layered nanostructure Bi 2 Se 3 grown by chemical vapor deposition in selenium-rich atmosphere. Appl Surf Sci 317: 257-261.
14. Kong DS, Cha JJ, Lai KJ, Peng HL, Analytis JG, Meister S, et al. (2011) Evaporative Trimming: A facile synthesis method for high quality ultrathin layers of 2D crystals. Am Chem Soc 5: 4698-4703. [Crossref]
15. Qiu Y, Wang Z, Owens AC, Kulaots I, Chen Y, et al. (2014) Antioxidant chemistry of graphene-based materials and its role in oxidation protection technology. Nanoscale 6: 11744-11755. [Crossref]
16. Denis PA, Irabarne F (2012) A First Principles Study on the Interaction between Alkyl Radicals and Graphene. Chem Eur J 18: 7568-7574. [Crossref]
17. Wang FT, Chen L, Tian CJ, Meng Y, Wang ZG, et al. (2011) Interactions between free radicals and a graphene fragment: Physical versus chemical bonding, charge transfer, and deformation. J Comput Chem 32: 3264-3268. [Crossref]
18. Yang Y, Huang Y, Lv Y, Zhao P, Yang Q, et al. (2013). Mater Chem A 41: 11184-11191.
19. Kim H, Miura Y, Macosko CW (2010) Graphene/polyurethane nanocomposites for improved gas barrier and electrical conductivity. Chem Mater 22: 3441-3450.
20. Wu JR, Huang GS, Li HL, Wu, SD, Liu YF, et al. (2013) Enhanced mechanical and gas barrier properties of rubber nanocomposites with surface functionalized graphene oxide at low content. Polymer 54: 1930-1937.
21. Potts JR, Shankar O, Du L, Ruoff RS (2012) Processing-morphology-property relationships and composite theory analysis of reduced graphene oxide/natural rubber nanocomposites. Macromolecules 45: 6045-6055.
22. Tang MZ, Xing W, Wu JR, Huang GS, Xiang KW, et al. (2015) Graphene as a prominent antioxidant for diolefin elastomers. J Mater Chem A 3: 5942.
23. Chen ZS, Biscarasia J, Shukla A (2015) A high performance graphene/few-layer InSe photo-detector. Nanoscale 7: 5981. [Crossref]
24. Zhang M, Yang LQ, Yang XS, Zhao Y (2013) Materials Review 27: 7.
25. Zhang J, Peng ZP, Soni A, Zhao Y, Xiong Y, et al. (2011) Raman spectroscopy of few-quintuple layer topological insulator Bi2Se3 nanoplatelets. Nano Lett 11: 2407-2414. [Crossref]
26. Salazar-Pérez AJ, Camacho-López MA, Morales-Luckie RA, Sánchez-Mendieta V (2005) Structural evolution of Bi2O3 prepared by thermal oxidation of bismuth nanoparticles. Superficies y Vacio18: 4-8.

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