Topological insulator Bi$_2$Se$_3$ thin films grown on double-layer graphene by molecular beam epitaxy

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Three dimensional (3D) topological insulators (TIs) such as Bi$_2$Se$_3$ and Bi$_2$Te$_3$ are characterized by a bulk energy gap of strong spin-orbit coupling origin and metallic surface states protected by time-reversal symmetry. Without external doping, the Fermi level of the materials resides in the bulk energy gap and thus only intersects the Dirac cone topological surface states, which we call as “intrinsic” TI hereafter. A major experimental breakthrough in the emergence of strong spin-orbit coupling origin and metallic surface states protected by time-reversal symmetry is the material realization of high-quality TIs via layer-by-layer growth of epitaxial Bi$_2$Se$_3$ films. The as-grown films without doping exhibit a low defect density of 1.0 $\pm$ 0.2 $\times$ 10$^{11}$/cm$^2$, and become a bulk insulator at a thickness of ten quintuple layers, as revealed by in situ angle resolved photoemission spectroscopy measurement. © 2010 American Institute of Physics.

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Atomically flat thin films of topological insulator Bi$_2$Se$_3$ have been grown on double-layer graphene formed on 6H–SiC(0001) substrate by molecular beam epitaxy. By a combined study of reflection high energy electron diffraction and scanning tunneling microscopy, we identified the Se- rich condition and temperature criterion for layer-by-layer growth of epitaxial Bi$_2$Se$_3$ films. The as-grown films without doping exhibit a low defect density of 1.0 $\pm$ 0.2 $\times$ 10$^{11}$/cm$^2$, and become a bulk insulator at a thickness of ten quintuple layers, as revealed by in situ angle resolved photoemission spectroscopy measurement.

Our MBE growth and characterization of Bi$_2$Se$_3$ thin films were conducted in an ultrahigh vacuum (UHV) MBE-ARPES-STM combined system (Omicron) with a base pressure of 1 $\times$ 10$^{-10}$ Torr. The double-layer graphene was prepared on a nitrogen-doped SiC(0001) substrate with a resistivity of $-0.1$ $\Omega$ cm using the well-established recipe. High purity Bi (99.999%) and Se (99.999%) were evaporated from standard Knudsen cells. ARPES spectra were collected at room temperature by a Gammadata Scienta SES-2002 analyzer with a HeI light source of 21.2 eV. We also used a low temperature STM system to characterize the as-grown films (Unisoku). An MBE chamber is attached to the STM system and Bi$_2$Se$_3$ films were grown by using the same conditions mentioned above. STM images were taken at 4.8 K at a constant current of 0.1 nA with a polycrystalline W tip. The $dI/dV$ mapping was acquired using a lock-in technique with a bias modulation of 10 mV at 987.5 Hz.

The optimal conditions for layer-by-layer growth of bulk insulating Bi$_2$Se$_3$ films were established by a systematic investigation of the growth dynamics, surface morphology, and thickness-dependent electronic structure with RHEED, STM, and ARPES. Similar to those for GaAs (Ref. 19) and Bi$_2$Te$_3$, the optimal growth can be achieved under Se-rich atmosphere (Se/Be beam flux ratio $\theta$=10) and $T_{Bi} > T_{Se}$ (the Bi-cell, substrate, and Se-cell temperatures, respectively). The former not only assures nucleation of the Bi$_2$Se$_3$ phase, but also minimizes the formation of Se vacancy, which is difficult in self-flux method. Under Se-rich condition, there always exist extra Se molecules on the growing front. However, these molecules cannot be incorporated into the film and will desorb since $T_{Se} > T_{Bi}$. The optimal growth is demonstrated in Fig. 1. The film shown in this figure was grown at $\theta$=11, $T_{Bi}$=550 °C, $T_{Se}$=136 °C, $T_{ substrate}$=220 °C and has a nominal thickness of 26 QL. The characteristic RHEED intensity oscillation recorded during film deposition indicates

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an ideal layer-by-layer growth [Fig. 1(a)], where each circle of the oscillations corresponds to deposition of 1 QL of Bi₂Se₃. Therefore, the growth rate can be precisely measured, which is \( \approx 0.3 \) QL/min in this case. The atomically flat nature of the film is first evidenced by the sharp 1×1 RHEED pattern in Fig. 1(b) and further demonstrated by the STM image in Fig. 1(c). As expected, the steps seen in the STM image have a height of 0.95 nm, exactly the QL unit cell size of Bi₂Se₃ along the \( c \) axis. The Se-rich condition results in very few defects in the as-grown samples. A typical STM image of the film is shown in Fig. 1(d). Only two defects can be found in an area of 50×50 nm². The dominant defects are Se vacancies [the dark depressions in Fig. 1(d)], which can be identified by their registry with respect to the topmost Se lattice. The areal defect density in this sample is \( \approx 1.0 \pm 0.2 \times 10^{11} \) cm², which is much lower than that on the cleaved samples. Further investigation indicates fewer vacancy defects if higher Se/Bi flux ratio is used.

The electronic structure of the film is studied by ARPES and shown in Fig. 2(a). The Dirac cone (the dashed red lines) can be clearly seen, and the Dirac point is located at 130 meV below \( E_F \). While the position of the Dirac point can change (several tens of millielectron volts) with film thickness, what is important here is that the intense electronic pocket from the bulk conduction band observed in the cleaved crystal does not appear, suggesting that the film at this thickness is already a bulk insulator. Given the conditions we used, it is found that the minimum thickness for the film being an intrinsic TI is 11 QL. The details of this result has been discussed elsewhere.

We also tried another substrate Si(111)-7×7. To avoid possible formation of SiSe₂ and other selenides at the interface, the Bi-terminated \( 3 \times 3 \) structure was first grown. In spite of it, the morphology of the Bi₂Se₃ films on the Bi-terminated \( 3 \times 3 \) surface, especially in the very thinner regime, is ill-defined. Moreover, the films suffer from stronger electron-doping, which can be seen by a comparison of the ARPES data on both substrates [Fig. 2(b)]. Clearly, the Bi₂Se₃(111) films on graphene show much quicker development to the bulk insulating state than those on the \( 3 \times 3 \) Bi/Si(111) substrate, suggesting more defects and poorer film quality in the latter case. The critical thickness for intrinsic TIs on the Bi-terminated Si(111) surface is as high as 24 QL.

Now we discuss the role of the double-layer graphene. In a heteroepitaxial growth, the interface plays very critical roles in growth mode, strain relaxation, and formation of defects such as misfit and screw dislocations. The situation becomes even more severe when a film is being deposited on a substrate of different material, for example, Bi₂Se₃ on Si in which strong surface selenidization by Se molecules may occur. By using inert graphene substrate, we found that not only is the interface reaction completely suppressed but also could the strain relaxation be complete at the very first epi-

![Fig. 1](image1.png)

**FIG. 1.** (Color online) (a) RHEED intensity of the (0, 0) diffraction vs growth time. (b) RHEED pattern along Γ–K direction and (c) STM image of the 26 QL Bi₂Se₃ film acquired at a sample bias (\( V_s \)) of 1.0 V. (d) STM image (\( V_s=10 \) mV) showing the Se vacancies (arrows).

![Fig. 2](image2.png)

**FIG. 2.** (Color online) (a) ARPES intensity map of the 26 QL film along the Γ–K direction. The dotted line indicates the Fermi level, and the topological surface states, respectively. (b) Thickness-dependent surface Dirac point of Bi₂Se₃ films on graphene and Si substrates.
The growth criteria established in this study, intrinsic Ti films can be easily obtained when the thickness is above 10 QL. We emphasize that the growth conditions presented here can be applied to growth of other V-VI topological thin films and their heterostructures by standard MBE technique.

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FIG. 3. (Color online) (a) Large scale ($V_r=4.0$ V) and (b) atomic resolution STM images ($V_r=10$ meV) of double-layer graphene on SiC(0001) substrate. (c) STM image ($V_r=1.0$ V) recorded after deposition of 1.5 QL Bi$_2$Se$_3$ on graphene. (d) High-resolution STM image ($V_r=10$ meV) of 1 QL Bi$_2$Se$_3$ film. The bright spot corresponds to a topmost surface Se atom. (e) $dI/dV$ mapping of 1 QL Bi$_2$Se$_3$ film at $V_r=-0.35$ V, revealing a Morié pattern with a period of 7.10 nm. (f) Simulated Morié pattern by assuming a fully relaxed Bi$_2$Se$_3$ on graphene.

The exposed graphene is 0.41 nm thick, implying an incomplete wetting of the graphene surface. The observation of the bulk Bi$_2$Se$_3$ surface. The observation of the strained graphene. This leads to a well-defined Morié pattern with a period of 7.10 nm, as observed from $dI/dV$ mapping of 1 QL Bi$_2$Se$_3$ film at $V_r=-0.35$ V, revealing a Morié pattern with a period of 7.10 nm. (f) Simulated Morié pattern by assuming a fully relaxed Bi$_2$Se$_3$ on graphene.

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