Coherent Heteroepitaxy of Bi$_2$Se$_3$ on GaAs (111)B

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We report the heteroepitaxy of single crystal thin films of Bi$_2$Se$_3$ on the (111)B surface of GaAs by molecular beam epitaxy. We find that Bi$_2$Se$_3$ grows highly c-axis oriented, with an atomically sharp interface with the GaAs substrate. By optimizing the growth of a very thin GaAs buffer layer before growing the Bi$_2$Se$_3$, we demonstrate the growth of thin films with atomically flat terraces over hundreds of nanometers. Initial time-resolved Kerr rotation measurements herald opportunities for probing coherent spin dynamics at the interface between a candidate topological insulator and a large class of GaAs-based heterostructures.

The narrow band gap semiconductor Bi$_2$Se$_3$ has recently emerged as a promising basis for creating a state of matter known as a topological insulator (TI) wherein protected states can be produced at the surface of the material via the locking of spin and momentum by the constraints of time reversal symmetry. The prediction that it has the requisite electronic structure for forming these special conducting surface states spanning its bulk electronic energy gap has been confirmed by angle resolved photoemission spectroscopy. With a bulk band gap ($\sim 0.3$ eV) larger than other relevant materials, Bi$_2$Se$_3$ is one of the best candidate materials for engineering of the Fermi energy into the bulk band gap so that transport can occur only through these surface states. However, this simple prescription has proved hard to realize because of an inherent tendency of the material to form Se vacancies or antisites that serve as donors, moving the Fermi energy far above the gap and making the contribution of the surface states to transport properties difficult to detect.

The growth of Bi$_2$Se$_3$ by molecular beam epitaxy (MBE) provides a potentially attractive solution for minimizing such defects by allowing for flexible control of growth conditions. To date, MBE growth of Bi$_2$Se$_3$ has been demonstrated on several substrates, including silicon, graphene and SrTiO$_3$, albeit without complete removal of midgap states. For silicon, the MBE growth of single crystal Bi$_2$Se$_3$ requires the introduction of an intermediate layer (e.g. a monolayer of Bi or amorphous layers) that improves the film quality by effectively decoupling it from the substrate, while graphene is conductive, complicating transport measurements of the surface states. In this Letter, we report the heteroepitaxy of Bi$_2$Se$_3$ thin films upon another technologically important substrate material, GaAs. Notably, we show that the epitaxial growth is coherent with the substrate, thus opening routes for exploring the coupling of spin polarized TI states with electronic states in a wide variety of advanced semiconductor heterostructures, including magnetically doped III-V and II-VI semiconductors.

We carried out MBE growth of Bi$_2$Se$_3$ thin films on epiready, semi-insulating GaAs (111)B substrates using thermal evaporation of high purity (5N) elemental Bi and Se from conventional Knudsen cells. After thermal desorption of the native oxide on the substrate under an arsenic flux, we first deposited a very thin GaAs buffer layer ($\sim 18$ monolayers), yielding a very flat GaAs surface without the pitting of the surface that occurs with desorption of the oxide or the three dimensional hillocks that form with thicker buffers. Bi$_2$Se$_3$ was then grown at a substrate thermocouple temperature of 400 $^\circ$C (corresponding to an estimated actual substrate temperature of $\sim 320^\circ$C) and a Se:Bi beam equivalent pressure ratio ranging from $\sim 10:1$ to $\sim 30:1$.

Bi$_2$Se$_3$ has a tetradymite, trigonal crystal structure

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a) Electronic mail: nsamarth@psu.edu
Intensity
800
600
400
200
0
Intensity
50
40
30
20
10
2 (deg)
5000
4000
3000
2000
1000
0
Intensity
10.0
9.5
9.0
8.5
8.0
(003)
(006)
(0,0,12)
(0,0,15)
(0,0,18)
(0,0,21)
GaAs (111)
(009)
FIG. 2. (Color online) X-ray diffraction of a ~25 nm thick Bi₂Se₃ film. The (003) family of reflections shows that the films are highly c-axis oriented. Bi₂Se₃ peaks are labeled from ICDD PDF file 00-033-0214. Inset shows the rocking curve of the (006) reflection giving a FWHM of 0.1°.

The morphology of the films was studied ex-situ by atomic force microscopy (AFM). For some films, like the 25 nm thick film shown in Fig. 1(b), we grew a second buffer of ZnSe, only a few monolayers thick, by atomic layer epitaxy. While we were unable to directly confirm the presence of ZnSe in these samples by x-ray diffraction (XRD) or Raman spectroscopy, they did tend to result in very flat Bi₂Se₃ surfaces with RMS roughnesses of ~0.5 nm. Samples without the ZnSe buffer were slightly rougher with an average RMS roughness of a few nm. Very thin films of 2-3 QLs appear to exhibit island-like growth, similar to observations made for growth of Bi₂Se₃ on graphene. XRD measurements show reflections only from the (003) family of planes of the film, indicating that the films are highly c-axis oriented along the growth direction (Fig. 2). The rocking curve yielded a full width half maximum of 0.1°, significantly better than those reported for growth on vicinal Si substrates with an amorphous layer. While including a ZnSe buffer resulted in a flatter film, it also resulted in a wider rocking curve.

RHEED measurements during growth of Bi₂Se₃ indicate an unreconstructed surface (Fig. 1(a)). We have also observed RHEED oscillations of the specular spot (data not shown), with each oscillation corresponding to the growth of a QL, indicating that the Bi₂Se₃ thin films grow layer-by-layer.

The lattice fringes of the phase contrast images show a good registry between the film and substrate without any amorphous growth or secondary phases occurring at the interface. The inset shows a selected area diffraction (SAD) pattern from just the GaAs substrate. Fig. 3(b) shows the SAD pattern from the whole region spanning the interface. Besides the pattern due to GaAs (blue indexes), the new spots (red indexes) are consistent with a single crystal Bi₂Se₃ film that has grown epitaxially on the GaAs. The interplanar distance between Bi₂Se₃ (2240) and GaAs (440) is found to be 0.336 nm⁻¹ in reciprocal space yielding a lattice mismatch in the ab plane of 3.62%, consistent with the expected value of 3.55%, and indicating that the film is relaxed. Surprisingly, we do not find any evidence of twinning or dislocations in the TEM study, despite the large lattice mismatch. Both the HRTEM images and the diffraction patterns from several different areas show that the Bi₂Se₃ thin films are generally high-quality single crystals with a low density of defects.

Electrical transport studies were carried out at 4.2 K using lithographically patterned and wet etched Hall bars (with dimensions of 650 μm × 400 μm) in perpendicular magnetic fields up to 4 T. Electrical and Hall conductivity measurements reveal that all the samples studied are n-doped with carrier densities in the range $8.06 \times 10^{18}$
cm$^{-3}$ \lesssim n \lesssim 4 \times 10^{19}$ cm$^{-3}$ and mobilities in the range $\sim 100-\sim 1000$ cm$^2$(V.s)$^{-1}$, consistent with previous reports of MBE growth. Thus, we are still faced with unintentional background doping, presumably from a lack of stoichiometry and perhaps some contributions from unintentional Cd contamination from an earlier source in our MBE chamber. Magnetoresistance (MR) curves are shown in Fig. 3(a) for various film thicknesses. All show a positive MR cusp, consistent with weak anti-localization corrections to diffusive transport and typical of measurements of Bi$_2$Se$_3$ reported in the literature. A systematic analysis of the temperature, magnetic field and sample thickness dependence of the MR will be reported elsewhere.

Finally, we discuss preliminary magneto-optical measurements that probe spin-dependent phenomena associated with the interface in these heterostructures. We used a well-established time-resolved Kerr rotation (TRKR) technique to demonstrate a possible method of probing spin polarization in a TI via coupling to spin states in a conventional semiconductor. Figure 4(b) shows TRKR curves for optically-injected spins in the GaAs substrate precessing in an in-plane magnetic field. Data measured through an 8 nm layer of Bi$_2$Se$_3$ are shown at two temperatures, along with reference data from an area where the Bi$_2$Se$_3$ layer was wet-etched away. By fitting the TRKR to a damped sinusoid we deduce the g-factor and the inhomogeneous spin lifetime ($T_2^*$). While the g-factor of spins in GaAs ($g = -0.44$) is unchanged by overgrowth of Bi$_2$Se$_3$, $T_2^*$ is significantly shorter at the Bi$_2$Se$_3$ interface: at $T = 30$ K, $T_2^*$ = 160 ps at the interface, compared with $T_2^*$ = 450 ps in the reference region.

In summary, we have demonstrated the coherent epitaxial growth of the candidate TI material Bi$_2$Se$_3$ on GaAs (111)B substrates. The ability to synthesize Bi$_2$Se$_3$ epitaxial films with high quality heterointerfaces on GaAs and ZnSe opens the door to a host of interesting heterostructure applications, including TI-magnetic semiconductor interfaces, where magnetic monopoles or Majorana fermions at domain walls could be studied.

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