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Nano Electronics on Atomically Controlled van der Waals Quantum Heterostructures

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14. ABSTRACT

We report molecular beam epitaxial growth and electronic transport properties of high quality topological insulator Bi2Se3 thin films on hexagonal boron nitride. We present a comprehensive study on topological insulator (TI) Bi2Se3 thin films on hexagonal boron nitride (h-BN): careful heteroepitaxial growth using molecular beam epitaxy (MBE) and thorough characterizations of their structural and electrical properties. TIs have been spotlighted for their exotic charge and spin transport properties through topologically protected Dirac surface states. Bi2Se3 has in particular attracted an intense attention due to its well-separated topological surface states (TSSs) located in the bulk band gap energy, the

largest among the group V2-VI3 TI family. However, experimental efforts on Bi2Se3 have been frequently resulted in the bulk conduction being dominant over TSSs in transport due to bulk doping effects of defect sites. The usual approach to avoid this problem is compensation-doping or alloying. While this approach has been successful in probing the various novel phenomena exhibited by TSSs, it unavoidably results in energy gap smaller than that of pristine Bi2Se3 or an increased degree of disorder, potentially degrading its merits in device applications. On the other hand, high quality TI Bi2Se3 with a reduced concentration of defects can be achieved by the heteroepitaxial growth on a substrate with a compatible lattice structure. h-BN is one of the ideal substrates for Bi2Se3 in this purpose since they share the hexagonal lattice symmetry and dangling-bond-free two-dimensional (2D) van der Waals (vdW) layered structure.

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Abstract: We report molecular beam epitaxial growth and electronic transport properties of high quality topological insulator Bi2Se3 thin films on hexagonal boron nitride. We present a comprehensive study on topological insulator (TI) Bi2Se3 thin films on hexagonal boron nitride (h-BN): careful heteroepitaxial growth using molecular beam epitaxy (MBE) and thorough characterizations of their structural and electrical properties. TIs have been spotlighted for their exotic charge and spin transport properties through topologically protected Dirac surface states. Bi2Se3 has in particular attracted an intense attention due to its well-separated topological surface states (TSSs) located in the bulk band gap energy, the largest among the group V2-VI3 TI family. However, experimental efforts on Bi2Se3 have been frequently resulted in the bulk conduction being dominant over TSSs in transport due to bulk doping effects of defect sites. The usual approach to avoid this problem is compensation-doping or alloying. While this approach has been successful in probing the various novel phenomena exhibited by TSSs, it unavoidably results in energy gap smaller than that of pristine Bi2Se3 or an increased degree of disorder, potentially degrading its merits in device applications. On the other hand, high quality TI Bi2Se3 with a reduced concentration of defects can be achieved by the heteroepitaxial growth on a substrate with a compatible lattice structure. h-BN is one of the ideal substrates for Bi2Se3 in this purpose since they share the hexagonal lattice symmetry and dangling-bond-free two-dimensional (2D) van der Waals (vdW) layered structure.

Introduction: In this project, the team at SNU successfully demonstrate the molecular beam epitaxial growth of high quality Bi2Se3 thin films on a h-BN substrate and their atomic structural and electrical transport properties. The high-resolution transmission electron microscopy (TEM) study showed an atomically abrupt and epitaxial interface formation between the h-BN substrate and Bi2Se3. The Harvard team uses this high quality film to show the Dirac nature of the high mobility TSS at the Bi2Se3/h-BN interface as proved by observation of Shubnikov-de Haas oscillations. This work presents noticeable novelty and originality in the growth of high quality TI thin films on h-BN only possible through close collaboration between the Korean and US teams. Most significantly, we developed a new method for characterizations of the TI/h-BN vdW heterostructures. Microfabrication combined with the crystal growth and TEM enables us to investigate microstructural properties of the grown films without any destructive post-growth process and obtain fast feedback on the MBE growth. We are currently extending this work to create superconducting/TI hybrid structures to realize novel electronic devices based on topologically protected superconductivity.

Experiment:

MBE growth Bi2Se3 TI thin films on hBN. Bi_2Se_3 thin films were grown on h-BN layers using a custom-built UHV MBE system dedicated to $(Bi_xSb_{1-x})_2(Se_yTe_{1-y})_3$ materials. The base pressure of the growth chamber was in the range of low 10^{-10} Torr. For substrate preparation, h-BN layers were transferred by the mechanical exfoliation technique either onto TEM compatible chips or a Si wafer covered with a 300-nm-thick SiO_2 layer. A typical lateral size and thickness of h-BN crystallites are ~10–50 μm and 10–100 nm, respectively. Prior to Bi_2Se_3 growth, thermal cleaning was carried out at 700 K for 30 min in an ultrahigh vacuum. High purity Bi (99.999%) and Se (99.9999%) fluxes were provided by Knudsen cells. The typical Se/Bi flux ratio during the growth was 15–20, measured by a quartz crystal microbalance. The growth rate was maintained at 0.2–0.3 QL/min, solely determined by the Bi flux.

The morphological and microstructural characteristics of Bi_2Se_3 films on h-BN were investigated using SEM, AFM, and HR-TEM. For plan-view TEM observations, the h-BN transferred onto a SiN_x/Si membrane chip or a holey carbon TEM grid was employed as a substrate. For the SiN_x/Si membrane chip, low stress Si_3N_4 membrane windows were used. E-beam lithography was employed to define a suspension region on the membrane, and the region was entirely etched through by plasma etching using the e-beam resist as the etch mask. Few layer h-BN was mechanically exfoliated and identified on 90 nm SiO_2, which offers the greater optical contrast for thin h-BN identification, through optical microscopy. The ultrathin h-BN was then picked up with PPC on PDMS, and transferred onto the etched hole in the SiN_x membrane. On the other hand, poly(methyl methacrylate) (PMMA) and polyvinyl chloride (PVA)-assisted transfer was employed to prepare h-BN on holey carbon TEM grids. Samples for cross-sectional TEM imaging were prepared by a focused ion beam milling. A 200 kV field-emission TEM (JEOL JEM-2100F) was used for SAED, BF imaging, and HR imaging. Crystal structure of Bi_2Se_3/h-BN was visualized using VESTA software.

Electrical transport measurements were performed on Hall bar devices fabricated by following steps. 10 QL Bi_2Se_3 films grown on h-BN transferred on a SiO_2/Si chip were used for electrical characterizations where the heavily doped bulk Si can be used as a global back gate. For the first step, standard e-beam lithography was performed, and ohmic contacts were formed by e-beam evaporation of Cr (10 nm) / Au (40 nm). Then hydrogen silsesquioxane (HSQ) was spun coated as both a negative tone e-beam resist and a etch mask, and second e-beam lithography was followed to pattern the HSQ layer into a Hall bar geometry. The films were then etched using Ar/CF_4 plasma. Here, e-beam exposed HSQ serves as a capping layer. Final e-beam lithography and a subsequent e-beam evaporation of Cr (10 nm) / Au (110 nm) were used to put down contact pads and to connect them with the 1st contacts.

The magnetotransport measurements were carried out in a Quantum Design physical property measurement system by low-frequency AC lock-in technique with an excitation current of 100 nA.

Specular interband Andreev Reflection between graphene and NbSe2. Injecting superconducting Cooper pairs into non-superconducting materials has been one of the most exciting condensed matter physics problems. The recent surge of research interest of creating and manipulating unique quasi particles with topologically exceptional properties, such as Majorana particles, has added new opportunities of studying novel physical phenomena. In this manuscript, we demonstrate that extremely clean interface between graphene and quasi 2-dimensional superconductor NbSe2 has been realized. Utilizing the vdW interfaces, we realize a superconductor and graphene interface, where the Fermi level of normal channel is much smaller than superconducting energy gap. In this unusual limit, the holes are expected to be reflected specularly at the superconductor-graphene interface due to the onset of interband Andreev processes. We find that the conductance across the graphene-superconductor interface exhibits a suppression when the Fermi energy is tuned to values smaller than the superconducting gap, a hallmark for the transition between intraband retro- and interband specular- Andreev reflections.

In this project, we employ a novel non-invasive approach to fabricate normal metal (N) and superconductor (SC) interfaces with an unprecedent energy resolution close to the the neutrality of graphene. The hBN/BLG/NbSe2 hetero-structures are assembled by fabricating hBN/BLG Hall-bar devices following the standard recipe. In this process we intentionally do not contact one end of the patterned BLG channel with a Ti/Au electrode, and leave it uncovered for the deposition of NbSe2). The mechanically exfoliated NbSe2 flake is then transferred onto the device in such a way that it creates an overlap region with the BLG from one side, and four gold electrodes from the other side. The so created gold/NbSe2 and BLG/NbSe2 junctions have Ohmic interfacial resistances with typical values. Since the resistance of graphene channel underneath of the superconductor is many orders of magnitude larger than superconducting pathway, the current from the NbSe2 flake directly inject into the BLG Hall-bar at the boundary between NbSe2 and graphene.

Results and Discussion:

MBE growth Bi2Se3 TI thin films on hBN. We report the molecular beam epitaxial growth and characterization of single crystalline topological insulator Bi2Se3 thin films on hexagonal boron nitride (h-BN). A two-step growth was developed, enhancing both the surface coverage and crystallinity of the films on h-BN. High-resolution transmission electron microscopy study showed an atomically abrupt and epitaxial interface formation between the hBN substrate and Bi2Se3. We performed gate tuned magnetotransport characterizations of the device fabricated on the thin film and confirmed a high mobility surface state at the Bi2Se3/hBN interface. The Bery phase obtained from Shubnikov-de Haas oscillations suggested this interfacial electronic state is a topologically protected Dirac state.

We performed the magnetotransport measurements to investigate the electronic properties of the Bi_2Se_3 thin films grown on h-BN. Using a standard electron beam (e-beam) lithography followed by depositing metal electrodes and lift-off procedure, we fabricated electrical contacts on the Bi_2Se_3 thin films. Further plasma etching procedure protected by patterned resist resulted in a Hall bar shaped device where magnetotransport can be measured (inset of Fig. 1(a)). Highly doped silicon substrate supporting h-BN substrate serves as a back gate, tuning the carrier density in the film. Fig. 1(a) shows the longitudinal resistance (R_{xx}) as a function of back gate voltage (V_g) at the zero applied magnetic field (B = 0). R_{xx} decreases as V_g increases within the range of gate voltage we applied (-120 – 80 V), suggesting that the film is overall *n*-type. Correspondingly, the Hall resistance (R_{xy}) measured as a function of magnetic field B (Fig. 1(b)) exhibits negative slope ($dR_{xy}/dB < 0$) at various fixed gate voltages, also suggesting the *n*-type

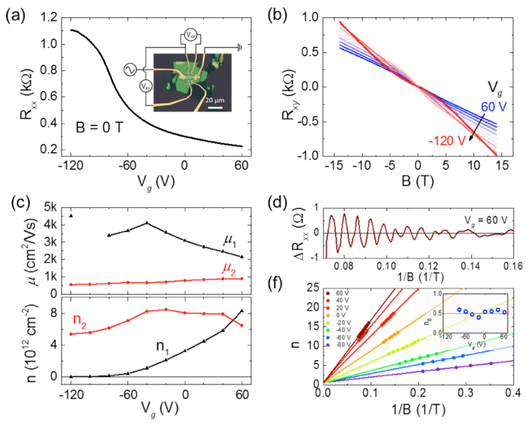

FIG. 1. Electrical transport properties of 10 QL Bi_2Se_3/h-BN. (a) Gate voltage dependence of R_{xx}. The inset shows an optical microscope image of the Hall bar sample and measurement configuration. (b) R_{xy} *vs.* B taken at different gate voltages. (c) Carrier mobilities μ and carrier densities n *vs.* V_g, obtained by the multiple channel conduction model while the single channel model (n_1 = 0) gives the best fit for V_g = -100 V. (d) Amplitude of SdH oscillations *vs.* $1/B$ at V_g = 60 V. (f) Landau fan diagram of the peaks from TSS at the Bi_2Se_3/h-BN interface. The inset shows the intercept *vs.* gate voltages. All graphs are taken at 1.75 K

conduction in the film. However, we also observed that $R_{xy}(B)$ exhibits nonlinearity in B, especially at the negative V_g values. Nonlinear $R_{xy}(B)$ is often attributed to the presence of multiple conduction channels by carriers with different natures.

The Dirac nature of the high mobility TSS at the Bi_2Se_3/h-BN interface was proved by pronounced SdH oscillations observed at high magnetic fields. Fig. 1(d) shows SdH oscillations in background-subtracted $\Delta R_{xx}(1/B)$ at $V_g = 60$ V, where the contribution of the TSS at the Bi_2Se_3/h-BN interface to the total conduction is the strongest. Clear observation of oscillatory features in $1/B$ suggests well-quantized Landau orbits in the bottom TSS. In Fig. 1(e), the Landau level index n is plotted as a function of the position $1/B$ of the most prominent SdH maxima and minima at each gate voltage. Linear fits provided the n-axis intercepts of 0.5 as seen in the inset, a prominent result due to the π–Berry phase carried by Dirac fermions in the TSS.

To obtain fast microstructural feedback on MBE growth of the films on h-BN, we employed a TEM-compatible MBE technique. Bi_2Se_3 thin films with atomically smooth terraces over a large area have been obtained by employing a two-step growth method. The optimized samples exhibited high crystallinity, epitaxially oriented Bi_2Se_3 film on a h-BN substrate with atomically sharp interfaces, as confirmed by TEM studies. Furthermore, magnetotransport experiments revealed that the dominant channel of transport was *via* the TSS at the Bi_2Se_3/h-BN interface with an enhanced carrier mobility. More generally, we believe that the experimental scheme demonstrated in this report can serve as a promising method for the preparation of high quality TI thin films as well as many other heterostructures based on 2D vdW layered materials.

Specular interband Andreev Reflection between graphene and NbSe2. Quantitative comparison between the experiment and theoretical model in the small energy regime $|\varepsilon_F| \sim \Delta$ can be performed by re-plotting the experimental $G_{1.7K}/G_{10K}$ map as a function of ε_F and V_{ns} (see SI for the conversion scheme) (Fig. 1 (a)). In both graphs, one can identify four regions of enhanced conductance (colored blue): two of them for $|\varepsilon_F| > |eV_{ns}|$ and two for $|\varepsilon_F| < |eV_{ns}|$. These regions are separated from each other by connected regions of reduced conductance (colored red) that are approximately following the dependence $|\varepsilon_F| \sim |eV_{ns}|$, forming diagonal lines that are roughly symmetrically arranged with respect to $\varepsilon_F = eV_{ns} = 0$ in the conductance maps. Several representative line cuts, showing $G_{1.7K}/G_{10K}(\varepsilon_F)$, clearly exhibit similar features for both experimental and theoretical traces, with good quantitative

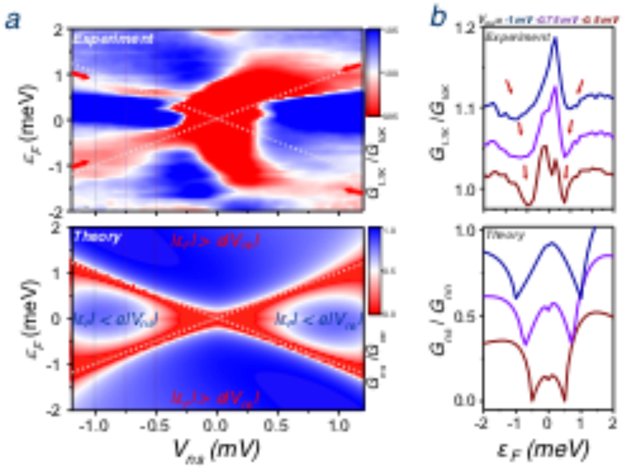

FIG. 2. Experimental and theoretical normalized conductance as a function of bias and Fermi energy. A continuous region of lower conductance (red) that is subdivides the map into four disconnected regions of comparatively high conductances (blue). (b) Experimental and theoretical normalized conductance with line-traces demonstrate the evolution of the conductance dips (red arrows) with varying Vns.

agreement for the positions of the conductance dips (Fig. 3 (b)).

We believe our result to be particularly significant for following reasons: (i) while the possibility to achieving a smaller Fermi energy than a superconducting gap has been theoretically identified as one of the fundamentally unique interests of the Dirac matter research, this effect has not previously been experimentally accessible due to the technical difficulty to realize such system experimentally; (ii) our finding of specular Andreev reflection help to draw a general picture of the exact physical processes underlying Cooper pair interaction with normal electrons, which can lead into a new venue of creating novel hybrid Dirac matter-superconducting devices.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:
a) papers published in peer-reviewed journals,

“Selective excitation of Fabry-Perot or whispering-gallery mode-type lasing in GaN microrods,” J. Y. Park, G.-H. Lee, J. Jo, A. K Cheng, H. Yoon, K. Watanabe, T. Taniguchi, M. Kim, P. Kim and G.-C. Yi, 2D Materials 3, 035029 (2016)

“Specular Interband Andreev Reflections in Graphene,” D. K. Efetov, L. Wang, C. Handschin, K. B. Efetov, J. Shuang, R. Cava, T. Taniguchi, K. Watanabe, J. Hone, C. R. Dean, and P. Kim, Nature Physics 12, 328–332 (2016).

b) papers published in peer-reviewed conference proceedings,
None
c) papers published in non-peer-reviewed journals and conference proceedings,
None
d) conference presentations without papers,

- Invited Speaker, Winter Conference at Aspen Center for Physics, Aspen, CO (2017)
- Plenary Speaker, Recent Progress of Graphene Research (RPGR), Seoul, Korea (2016)
- Invited Speaker, International Conference of Physics of Semiconductor (ICPS), Beijing, China (2016)
- Invited Speaker, European Materials Research Society Meeting, Lille, France (2016)
- Materials Science Society Meeting, Boston (2015)

e) manuscripts submitted but not yet published, and
None

Attachments: Publications a), b) and c) listed above if possible.

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