Energy gap-opening and Fermi-level tuning in three-dimensional topological Dirac semimetal Na₃Bi films

Huinan Xia¹, Wenhao Zhang¹*, Ying-Shuang Fu¹,#

1. School of Physics and Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, Wuhan 430074, China

Email: *wenhaozhang@hust.edu.cn, #yfu@hust.edu.cn.

Three-dimensional topological Dirac semimetal, exemplified by Na₃Bi, offer an alternative system to reach the two-dimensional topological phase through the quantum confinement effect that can gap out Dirac nodes. Utilizing the combination of molecular beam epitaxy and scanning tunneling microscopy, we measure the electronic structure of Na₃Bi film with a √3×√3 surface reconstruction and its modification as a function of the film thickness. The Fermi energy can be tuned via certain growth process, thus offering an appropriate way for achieving the charge neutrality. We directly demonstrate that a band gap of 67 meV is opened down to 4 ML, converting the Dirac semimetal to a band insulator. By imaging the electronic states with quasiparticle interference, we resolve the Dirac-cone surface states with linear dispersion in momentum space on both gapped and gapless Na₃Bi films. Our work opens up the possibility to exploit the distinct electronic properties of Dirac semimetals, as well as topological phase transitions near the Dirac or charge neutrality point.
Three-dimensional (3D) topological Dirac semimetals (DSMs) realize a 3D analogue of graphene that possess an even number of 3D Dirac fermions in the bulk Brillouin zone (BZ) [1,2], distinctive from the two-dimensional (2D) linear dispersion found on the surfaces of 3D topological insulators (TI) [3] or in graphene [4]. In DSMs, Dirac points appear in pairs that are separated in momentum space, and each can be resolved into two massless Weyl nodes of opposite chirality by breaking some inherent symmetry. As candidates, Cd$_3$As$_2$ and Na$_3$Bi have been theoretically proposed to be DSMs [5,6], and directly verified by observing 3D Dirac fermions that disperse linearly along all three momentum directions around the Dirac points in angle-resolved photoemission (ARPES) [7-9], scanning tunneling microscopy/spectroscopy (STM/STS) [10] and magneto-transport experiments [11,12]. Subsequently, a variety of unusual physical properties, such as strong linear magnetoresistance [13], chiral/quantum anomaly [14] and quantum Hall effect [15,16], have been widely identified related to the topological nature of Dirac quasiparticles. These attractive phenomena make DSM an ideal platform for the realization of exotic quantum states and possible applications of graphene in 3D materials for future functional devices.

In general, the intriguing properties of topological Dirac fermions associated with exotic surface Fermi-arc states in DSMs are topologically protected by time-reversal and inversion symmetries, together with crystalline rotational symmetry. When certain symmetry is broken by the electric field, dimension, chemical doping or external pressure/strain [17,18], DSMs may be driven into many other quantum states, such as the Weyl semimetal, topological superconductor and axion insulator [19,20]. For instance, Na$_3$Bi$_{1-x}$Sb$_x$ and Cd$_3$[As$_{1-x}$P$_x$]$_2$ will undergo a topological phase transition from a DSM to a trivial insulator upon altering Sb or P concentrations [21]. The α-Sn
films grown on InSb(111) will induce the formation of DMS phase under epitaxial strain, where the character of the Dirac cone will change to 2D nature by reducing the film thickness [22]. Particularly, in terms of thin films that are promising for potential electronic devices/transistors, the finite-size effect plays a significant role that will drive a DSM into a trivial band insulator or a quantum spin Hall insulator, depending on the thickness [5,21,23]. Down to the 2D limit, a monolayer (ML) of Na₃Bi is theoretically proposed to possess a large band gap of 0.31 eV, where 2D TI and 2D topological crystalline insulator phase can coexist with spin-valley polarization [24]. The fact that DSMs will open a band gap in ultrathin film has been widely predicted considering the quantum confinement effect [5,6,21,25], whereas direct evidence is presently lacking, except for few secondary hints by transport measurements [15,16,26,27]. In this regard, it is essential to unveil the thickness dependence of Na₃Bi film and image its electronic states in real space from experimental detection, especially by surface-sensitive spectroscopic probes since the broken translational symmetry at the surface will create novel topological Fermi-arcs states [2,5,8]. Moreover, while stable Cd₃As₂ has been intensively studied, Na₃Bi is rarely explored due to its high reactivity and easily ionizability in atmosphere. Therefore, the combination of molecular beam epitaxy (MBE) growth with low-temperature STM experiments is ideally suited to address these crucial details.

In this study, we grow various thicknesses of high-quality Na₃Bi films on a graphene-covered SiC(0001) substrate by molecular beam epitaxy (MBE). By utilizing STM/STS, we show that Na₃Bi surface exhibits a √3×√3 reconstruction independent of growth condition and film thickness. By varying the Na/Bi flux ratio or annealing treatment, we can manipulate the energy position of Dirac point ($E_D$) and uncover a $p$-$n$ transition of dominated carrier densities, crossing the neutrality
point. By measuring the thickness-dependent electronic structure, we find that the Na$_3$Bi film experiences a semimetal-to-insulator phase transition when its thickness is below 5 ML, where a band gap of ~79 meV is opened for 3 ML due to quantum confinement. Quasiparticle interference (QPI) imaging indicates the Dirac-cone linear dispersion survives in the momentum space on both gapped and gapless Na$_3$Bi surfaces, but with a slight anisotropy in the $k_x$-$k_y$ plane. We obtain the Fermi velocity of approximately 2.0 eV·Å (or 3×10$^5$ m/s), comparable to the bulk values reported previously.

Figure 1(a) displays the crystal structure of Na$_3$Bi, which contains two stacked MLs of Na-(Na/Bi)-Na structure in each unit cell. Both Na and Bi atoms constitute a hexagonal lattice with in-plane lattice constant of 5.448 Å, while the height between every two MLs is 9.655 Å. Figure 1(b) shows an atomically resolved STM image of an as-grown Na$_3$Bi island (5 nm), which is regularly arranged in a periodic lattice of 9.5 Å. From the 2D Fourier transformation (FT) of Figure 1(b) inset, we can resolve two categories spots of 5.5 Å and 9.5 Å, marked by yellow and red circles, respectively. While 5.5 Å is the (1×1) Na-terminated atomic lattice [28], the 9.5 Å signal corresponds to a $\sqrt{3} \times \sqrt{3}$ surface reconstruction. This surface reconstruction is always observed in all Na$_3$Bi films, irrespective of the film thickness. Previous ARPES report on the (001) surface of Na$_3$Bi crystal also proposes a $\sqrt{3}$-reconstruction based on the folding bands of Fermi surface features between K and Γ points [29]. We measure the electronic structure with STS on this $\sqrt{3}$-reconstructed surface, whose typical $dI/dV$ spectra is shown by the blue curve in Figure 1(d). The distinct minimal dip (black arrow) is regarded as $E_D$, reflecting the suppressed local density of states (LDOS) at the Dirac point [30,31]. The $E_D$ is ~188 meV above the Fermi level ($E_F$), indicating the as-grown sample is heavily p-doped and the dominated carriers are hole-like.
Besides the $\sqrt{3}$-reconstruction in Figure 1(b), there is a small amount of bright protrusions randomly distributed on the surface. Similar individual defects are observed previously and are referred to Na vacancies [30]. To testify this speculation, we increase the flux of evaporating Na source during the growth process and record the atomically flat surface in Figure 1(c). It’s clearly seen that the surface is also well-ordered in $\sqrt{3}$-reconstruction, with sparse bright defects now. The corresponding STS (the blue curve in Figure 1(d)) shows a minimum at the energy of -73 meV, implying $p$-type doping. This transition from hole- to electron-like carriers is reasonable since Na vacancies are charge acceptors and usually act as sources of hole charges. Inspired by this conjecture, we postanneal the as-grown Na$_3$Bi film in a Na-rich atmosphere. Compared with the as-grown sample ($E_D \sim 188$ meV), the $E_D$ of annealed one (the red curve in Figure 1(d)) shifts to $E_F$ at -5 meV, approaching the charge neutrality point [32]. Thus, the larger Na/Bi flux ratio cannot only improve the quality of Na$_3$Bi films, but also qualitatively tune the position of the Dirac points and dominance of carrier transport in DSMs by reducing the Na vacancies. Such a $p$-$n$ transition of carriers has been also reported by transport measurements, but triggered by temperature, or surface molecular/electrostatic doping [33,34].

It has been theoretically proposed that the Dirac states of Na$_3$Bi will open a band gap for films with a thickness smaller than 4.5 nm (10 ML) [21], we thus investigate the electronic structure of Na$_3$Bi as a function of film thickness. A series of $dI/dV$ spectra is successionally acquired on different thicknesses of Na$_3$Bi islands. As is illustrated in Figure 2(a), the LDOS, together with the position of the Dirac point ($E_D$), are nearly the same when the thickness ranges from 11 to 29 ML. Since all the Na$_3$Bi islands are simultaneously grown under the same condition, we conclude the electronic properties keep undisturbed for film thicker than 10 ML, similar to the bulk limit. On
the other hand, Figure 2(b) displays the STS of thinner Na$_3$Bi islands on another sample with lower coverage. For 5 ML, the Na$_3$Bi is metallic as the thicker ones in Figure 2(a) but with $E_D \sim -14$ meV. However, the LDOS of 4 ML becomes vanished near $E_F$, and a clear gap of $\sim 67$ meV is observed. Down to 3 ML, the thinnest island we can obtain, the gap still exists and becomes larger ($\sim 79$ meV). Obviously, we find the spatial energy gap and the position of $E_D$ distributed inhomogeneously that are traced by the black dashed lines, again a $n$-$p$ transition of carriers near $E_F$. To manifest such gap-opening behavior, we take a STS line cut across the single-ML step edge in Figures 2(c)-(e). Apparently, the energy gap persists on the whole terrace of 4 ML, while it directly closes on 5 ML and the Na$_3$Bi film recovers to be a gapless DSM. The distinct STS characteristics (Figure 2(e)) reveal that Na$_3$Bi experiences a gap-opening transition with decreasing film thicknesses at 5 ML. The thickness-dependent energy gap originates from the interlayer coupling between the two oppositely spin-textured topological surface states, experimentally verifying previous theoretical prediction [5,21,25]. Similar phenomena of Dirac gap opening by varying film thickness have been reported for 3D TI Bi$_2$Se$_3$ films [34,35].

To examine how the energy gap affects the surface Dirac states of Na$_3$Bi, which originates from the bulk band inversion, we further scrutinize their scattering properties. STS maps obtained near the step edges for isolated 3 and 5 ML Na$_3$Bi (Figures 3(a) and 3(b)) are shown in Figures 3(c) and 3(d), respectively. We also present two selected $dI/dV$ curves in Figures 3(e) and 3(f), respectively. Whether or not there is a gap, we can always observe a series of LDOS peaks in each spectrum for both 3 and 5 ML, which are nearly equally spaced in energy above $E_F$. The energy position of these peaks varies dependent on their distances to the step edge, forming standing-wave patterns (Figures 3(c) and 3(d)). These standing-waves in the LDOS are well-understood by interference
scattering of surface states from the step edges, further proving momentum-resolved information on the properties of surface states [10,28].

We perform one-dimensional (1D) FT analysis of $dI/dV$ measurement on the terraces of 3 and 5 ML, respectively, as is shown in Figures 4(a) and 4(b). Both terraces show branches of linear dispersions, which coincides with the scattering modes of cone-like dispersed surface states, in agreement with the 3D Dirac band structure of Na$_3$Bi [7]. Specifically, the Dirac-cone dispersion (black dashed lines in Figure 4(b)) in the momentum space is intact in the whole energy ranging from -500 to 400 mV for 5 ML. We directly extract the Dirac position with $E_D \approx 10$ meV, similar to the STS dip in Figure 3 (f), thus validating our aforementioned judgment that the minimum of LDOS reflects the Dirac point. On the terrace of 3 ML, however, there is an obvious band gap of \sim 75 meV opened near -100 mV, in accordance with Figure 2(b). Consequently, the bands in the vicinity of the gap are no longer linear but with slight curvatures. Additionally, several branches of bulk bands in Na$_3$Bi are visible (red dashed lines). We calculate the slopes of the dispersions by linear fitting and obtain the Fermi velocities are 2.20 eV·Å (or 3.34×10$^5$ m/s) for 3 ML and 1.94 eV·Å (or 2.95×10$^5$ m/s) for 5 ML, in the same order of magnitude previously reported by ARPES, STM and transport measurements [7,28,31], thus proving the Dirac-cone bulk band structure of Na$_3$Bi.

To demonstrate the 3D nature of the Dirac-cone band structure in DSM Na$_3$Bi, we record a series of STS mappings over a hexagonal 5 ML island at various energies in Figures 4(c)-(e). There exhibit signatures of spatially modulated interference patterns, known as QPI that originates from the states scatter from potential barriers caused by lattice defects or atomic steps. We find the length of the scattering wavevector increases from 500 to 300 mV, and the QPI signal can hardly
be resolved at the energy below -100 mV. We carried out the corresponding FT analysis of the spectroscopic mappings in Figures 4(f)-(h). While six symmetrized spots appear along the Γ-K direction for 500 mV and 300 mV, there are only FT signals along the Γ-M direction at -500 mV. By extracting the energetic-dependent FT signals along both Γ-K and Γ-M directions, we plot the evolutions of QPI dispersion in momentum space in Figures 4 (i) and 4(j), respectively. Again, both directions show linearly dispersing bands as a function of energy. The Dirac velocities by slope fitting are 1.96 eV·Å (or 2.98×10^5 m/s) for Γ-K and 1.89 eV·Å (or 2.87×10^5 m/s) for Γ-K, respectively, indicating a slight anisotropy in the k_x-k_y plane [9]. Moreover, there exist energy-independent FT intensities along the Γ-M direction with the wave number of 0.66 Å^-1, equating to the √3 ×√3 surface reconstruction (9.5 Å) in the STM images (Figure 1). We note the exact energy position of E_D is different in these two directions, possibly the result of spatial inhomogeneity of E_D (Figure 3(d)) and in-plane anisotropy.

To conclude, we have investigated the electronic properties of various thicknesses of Na_3Bi films by STM/STS. A phase transition from semimetal to insulator is demonstrated at the critical thickness of 5 ML, below which a direct energy gap is observed that increases with decreasing thickness. We can successfully tune the doping level and the type of dominated carrier densities in a controllable way via proper growth condition, including reaching the neutrality point for transport properties. However, all films exhibit a √3×√3 surface reconstruction. We further image the linear energy-momentum relations of surface states by QPI patterns, characteristic of the 3D topological Dirac nature of Na_3Bi. This persists whether or not the surface is gapped. Our work opens up a route toward novel topological phenomena, including manipulations of Dirac points, the realization of quantum spin Hall states and topological quantum phase transition in the 2D
limit. Future explorations on fabricating functional devices are also expected by engineering the carrier density transistors for low-energy logic circuits.

Note: During the preparation of the manuscript, we are aware of a closely related study reporting the topological phase transition of Na$_3$Bi ultrathin films through applying electric field by doping with potassium or by close approach of the scanning tunnelling microscope tip, which is recently published in *Nature* [37].
**Experimental Section**

To prepare a uniform graphene substrate, a commercial 6H-SiC(0001) wafer, was firstly degassed at 600°C for 3 hours, and then annealed at 950°C under a Si flux for 5 cycles. The SiC substrate became atomically flat terminated with graphene by flashing to 1400°C for 10 minutes. High-purity of Na (99.95%) and Bi (99.999%) were simultaneously co-evaporated from two homemade thermal effusion sources onto the substrate, whose temperature was held at 200°C. During the growth, the Bi:Na flux ratio, controlled by the temperatures of Bi (380°C) and Na (245°C) sources, was kept larger than 1:10. There are two ways to achieve the n-doped Na₃Bi films: by raising the Na source to 260°C with a larger flux or by annealing the sample at the growth temperature for 10 minutes in a Na overflux.

STM/STS measurements were performed on a Unisoku STM system operating at 4.5 K. A W tip with electrochemical etching was cleaned by e-beam heating and calibrated on Ag islands before all measurements. All topographic images were taken in a constant-current mode, and the tunneling dI/dV spectra and conductance mappings were acquired by standard lock-in technique at 983 Hz with modulation voltage amplitude of 5 mV.

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Figure captions:

Figure 1. (a) Crystal structure of Na₃Bi in the top and side view, respectively, with interleaved Na atom and two inequivalent Na(1) and Na(2) atoms. A ML is defined as a Na-(Na/Bi)-Na triple-layer with the height of c/2. (b),(c) The atomic-resolution STM image with a periodic lattice of 9.5 Å on the as-grown Na₃Bi films under growth condition of small and large Na flux, respectively. Scanning condition: $V_{bias} = +100$ mV, $I_t = 100$ pA (b) and $V_{bias} = +50$ mV, $I_t = 100$ pA (c). Inset of (b): 2D FT of (b). Yellow and red circles correspond to the $1 \times 1$ Na-terminated lattice the $\sqrt{3} \times \sqrt{3}$ surface reconstruction, respectively. (d) $dI/dV$ spectra taken on the as-grown Na₃Bi films with a small (black) and large (red) Na flux, respectively, as well as on Na₃Bi films annealed with extra Na flux (blue). The corresponding arrows mark the positions of $E_D$ as 188 mV, -73 mV and -5 mV, respectively.

Figure 2. (a) A series of d$I$/d$V$ spectra recorded on Na₃Bi terraces with different thickness ranges from 11 ML to 29 ML. All spectra are shifted vertically and taken on the same sample as the inserted STM image. Scanning condition: $V_{bias} = +3.0$ V, $I_t = 10$ pA. (b) The same as (a) but acquired on 3 ML, 4 ML, and 5 ML Na₃Bi film. (c) (a) Topographic image of a Na₃Bi film containing both 4 and 5 ML terraces. Scanning condition: $V_{bias} = +3.0$ V, $I_t = 10$ pA. (d) The corresponding line profile across Na₃Bi step edges by the black line in (c). The height of a single-ML step is 0.49 nm. (e) 2D plot of tunneling spectra measured along the black line in (c). The vertical magenta lines mark the positions of single-ML step edges.
Figure 3. (a),(b) STM topography images of isolated 3 ML and 5 ML Na$_3$Bi islands, respectively, supported on a graphene substrate. Scanning condition: $V_{\text{bias}} = +3.0$ V, $I_t = 10$ pA. (c),(d) $dI/dV$ spectra taken along the cyan and red dashed lines in (a) and (b), respectively. The dashed yellow lines trace the spatially distributed evolution of the energy gap and the position of $E_D$ in (a) and (b), respectively. The dashed black line indicates the position of $E_F$. (e),(f) Selected $dI/dV$ spectra of different locations obtained on 3 ML (A and B sites) and 5 ML (C and D sites), respectively. The corresponding arrows mark the energy positions of $E_D$.

Figure 4. (a),(b) Energy dispersion relation of the standing-waves in Figures 2(c) and 2(d) by 1D Fourier transformation, respectively. Black and red dashed curves are guides to the eye that trace the linearly dispersed surface states and bulk states, respectively. (c)-(e) Real-space conductance mappings of a Na$_3$Bi island at 500 mV, 300 mV and -500 mV, respectively. (f)-(h) The corresponding 1D FT of (c)-(e). Inset of (f) is the 3D Brillouin zone projected onto the 2D (001) surface. (i),(j) Plots of QPI peaks along $\Gamma$-K and $\Gamma$-M directions, respectively. The red dashed curves are Dirac dispersions guiding to the eye. The yellow arrows mark the $\sqrt{3} \times \sqrt{3}$ surface reconstruction that is dispersionless in the energy ranges below $E_F$. 
Figure 1
Figure 2
Figure 3
Figure 4