Spatial charge inhomogeneity and defect states in topological Dirac semimetal thin films of Na$_3$Bi

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Topological Dirac semimetals (TDSs) are three-dimensional analogs of graphene, with carriers behaving like massless Dirac fermions in three dimensions. In graphene, substrate disorder drives fluctuations in Fermi energy, necessitating construction of heterostructures of graphene and hexagonal boron nitride (h-BN) to minimize the fluctuations. Three-dimensional TDSs obviate the substrate and should show reduced metallic screening and higher dielectric constants. We map the potential fluctuations in TDS Na$_3$Bi using a scanning tunneling microscope. The rms potential fluctuations are significantly smaller than the thermal energy room temperature ($\Delta E_{F,\text{rms}} = 4$ to 6 meV = 40 to 70 K) and comparable to the highest-quality graphene on h-BN. Surface Na vacancies produce a novel resonance close to the Dirac point with surprisingly large spatial extent and provide a unique way to tune the surface density of states in a TDS thin-film material. Sparse defect clusters show bound states whose occupation may be changed by applying a bias to the scanning tunneling microscope tip, offering an opportunity to study a quantum dot connected to a TDS reservoir.

INTRODUCTION

Three-dimensional (3D) topological Dirac semimetals (TDSs), such as Na$_3$Bi and Cd$_3$As$_2$, (1–4), express the pseudorelativistic physics of 2D Dirac material graphene but extended to three dimensions. TDSs can yield ultrahigh mobilities (5) and new physics such as the chiral anomaly (6). The close approach of the Fermi energy $E_F$ of a Dirac semimetal to the Dirac point $E_D$ is limited by fluctuations in the Fermi energy due to charge puddling. Thus, low Fermi-energy fluctuations are critical for the observation of new Dirac point physics such as velocity renormalization (7–9) and the Dirac plasma (10, 11) at $|E_D - E_F| < k_BT$, where $k_BT$ is the thermal energy. Potential fluctuations arise in Dirac semimetals when the Fermi energy $E_F$ measured relative to the Dirac point energy $E_D$ approaches zero, meaning that the carrier density tends to zero and metallic screening disappears. Poorly screened disorder induces spatial fluctuations in the local $E_D$ and, hence, fluctuations $\Delta E_F$ corresponding to local electron and hole “puddles.” The carriers in puddles, in turn, screen the disorder, with $\Delta E_F$ determined self-consistently by the disorder and the screening properties of the Dirac materials (12, 13). Puddles have been visualized in graphene using scanning single-electron transistor microscopy (14) and scanning tunneling spectroscopy (STS) (15–17), where the fluctuations are largely governed by the underlying substrate, and have also been measured in the Dirac surface state of a topological insulator (18).

RESULTS AND DISCUSSION

Here, we use 20-nm Na$_3$Bi thin films grown via molecular beam epitaxy (MBE) on both semiconducting [Si(111)] and insulating [$\alpha$-Al$_2$O$_3$(0001)] substrates in ultrahigh vacuum (UHV) to probe $\Delta E_F$ fluctuations using scanning tunneling microscopy (STM) and STS. Figure 1A shows a large-area (400 nm × 380 nm) topographic STM image of a thin 20-nm film of Na$_3$Bi on Si(111), with several atomically flat terraces >100 nm in size. The inset of Fig. 1A reveals the (1 × 1) Na-terminated atomic lattice ($a = 5.45$ Å) with an individual Na vacancy. Figure 1B (45 nm × 45 nm taken immediately after growth) and C (30 nm × 30 nm taken 7 days after growth) shows the topography of two atomically flat regions away from step edges or the screw dislocations seen in Fig. 1A. Figure 1D shows an atomically flat region (30 nm × 30 nm) of Na$_3$Bi grown on sapphire [$\alpha$-Al$_2$O$_3$(0001)]. Whereas atomically flat regions of Na$_3$Bi up to 100 nm × 100 nm can be obtained on Si(111), sparse defect cluster sites (few per 100 nm × 100 nm) give rise to tip-induced ionization ring features (19–22) that will be discussed further below. This necessitated focusing on smaller areas free of ionization rings to unambiguously determine the variation in Dirac point.

Figure 1E shows area-averaged scanning tunneling spectra of the Na$_3$Bi film. STS measures the differential conductance $dI/dV$ as a function of sample bias $V$, proportional to the local density of states (LDOS) at energy $eV$ relative to $E_D$. STS was performed at points on a grid encompassing the entire regions shown in Fig. 1 (B and C), along with two other regions not shown. Figure 1E shows the averaged spectra of these four areas. Two key features are prominent in all spectra: a distinct minimum in the LDOS corresponding to the Dirac point energy ($E_D$) and a resonant feature ~30 meV below $E_D$, labeled D. As-grown, the Dirac point is located ~20 meV above the Fermi level, indicating p-type doping. Similar doping (~25 meV) has been reported on similar thickness Na$_3$Bi films on Si(111) measured with angle-resolved photoelectron spectroscopy, validating our assumption that the minimum in the LDOS reflects the Dirac point (23). Seven days after growth, the Dirac point has shifted to approximately 15 meV below the Fermi level, reflecting a gradual global n-type doping of the Na$_3$Bi due to the adsorption of atomic species present in UHV. Photoelectron spectroscopy (not shown) shows the emergence of carbon-related species (such as CO and CH) after several days in UHV. This adsorption results in the formation of intermittent impurity clusters on the surface; hence, all topography and spectroscopic measurements were deliberately performed away from these sites. The resonance...
feature D is unambiguously tied to $E_D$, and not to $E_p$, because the relative energy shift of D with respect to $E_D$ remains unchanged within experimental accuracy during the transition from p-type to n-type doping.

We first turn to the spatial variation of the Dirac point energy, $E_D$, found by tracking the position of the minimum differential conductance in STS (regions B and C) or, alternatively, the shift in the defect resonance D (region A; see discussion provided in section S2). Figure 2 (A and B) shows the spatial variation of $E_D$ for regions A and B corresponding to Fig. 1 (B and C, respectively). In both Dirac point energy maps, it can be seen that a clear, continuously connected local potential modulation emerges, correlated on a scale much larger than the crystal lattice or point-spectroscopy grid pixel size (0.5 nm). This modulation in $E_D$ represents the puddling of charge density at the surface. The individual Na vacancy sites are shown as black dots in Fig. 2 (A to C). The local variation in $E_D$ is found to be positively correlated with the individual Na vacancy sites that have a more positive Dirac point energy (we have verified this statistically; see the Supplementary Materials); this indicates that the Na vacancies act as acceptors and a significant source of charge disorder. In addition, Fig. 2C shows the local $E_D$ of 20-nm Na$_x$Bi on α-Al$_2$O$_3$(0001) (labeled region C), which has a larger n-type doping. The upper, middle, and lower panels of Fig. 2D show histograms of $E_D$ relative to $E_p$ for the scans in Fig. 2 (A to C, respectively). From spatial autocorrelation analysis of the puddle maps, we determine spatial coherence lengths $\xi$ of 13.4 ± 5.2, 9.3 ± 2.4, and 5.1 ± 1.9 nm for regions A, B, and C, respectively (see the Supplementary Materials for calculation details). The observed histograms of $E_D$ have mean values of 19.7 ± 1.7 meV (region A), −15.4 ± 1.3 meV (region B), and −47.2 ± 0.6 meV (region C) and SD $E_p$ of 5.6, 4.2, and 3.5 meV, respectively. These values are comparable to the 5.4 meV observed for graphene on hexagonal boron nitride (h-BN) (15). However, undersampling results in an underestimate in the magnitude of $\Delta E_p$ by a factor $(L/\xi)^2/((L/\xi)^2 - 1)$, where L is the scan size in each region [also likely in the study of Xue et al. (15)]; hence, the corrected $\Delta E_p$ values are 6.1 and 4.6 meV for regions A and B, respectively, whereas region C remains essentially unchanged because of the small coherence length.

Figure 2E plots the measured $\xi$ as a function of $E_p$. The shaded region shows the coherence length estimated within the Thomas-Fermi (TF) approximation $\xi = \sqrt{\frac{\pi}{2\alpha \hbar v_F}}$, where the spin/valley degeneracy $g = 4$, $\alpha$ is the fine structure constant, and $v_F$ the average Fermi velocity of the $k_x$, $k_y$, and $k_z$ directions. Both $\alpha$ and $v_F$ are expected to be universal material parameters; however, experimental measurements have not yet tightly constrained them, with $\alpha$ predicted to be between 0.069 and 0.174 and $v_F$ to be between $1.4 \times 10^5$ and $2.4 \times 10^5$ m/s (2, 24). Given this uncertainty, Fig. 2E plots the theoretical upper bound as a solid line (using $v_F = 2.4 \times 10^5$ m/s and $\alpha = 0.069$) and the lower bound as a dashed line (using $v_F = 1.4 \times 10^5$ m/s and $\alpha = 0.174$). The agreement is good within uncertainty but closer to the lower bound, implying a larger $\alpha$ (that is, a more strongly interacting system), consistent with previous studies (24, 25). Assuming $\alpha = 0.174$, we can calculate an impurity density and mobility for regions A, B, and C using the TF approximation and random-phase approximation (RPA) (see section S6 for the full calculations and results). For region C, we infer an $n_{imp}$ of $3.6 \times 10^{13}$ cm$^{-3}$ from RPA, in good agreement with the doping measured by the Hall effect (4.35 × 10$^{18}$ cm$^{-3}$), demonstrating that the dopants are charged impurities. However, the experimental mobility (3540 cm$^2$ V$^{-1}$ s$^{-1}$) is significantly lower than expected (19,000 cm$^2$ V$^{-1}$ s$^{-1}$) for charged impurity scattering alone, indicating that other sources of disorder (for example, point defects and grain boundaries) are important and suggests that ultrahigh-mobility thin-film Na$_x$Bi could be achieved, provided that these other sources of disorder can be eliminated.

We now turn to the resonance feature (labeled D) observed in the scanning tunneling spectra in Fig. 1E. Figure 3A plots the peak
differential conductance of the resonant feature D, with the red markers indicating the position of defect sites observed in the topography of region A (Fig. 1B). The high degree of correlation indicates that the defect sites are the origin of the resonance feature (see fig. S6 for further analysis). Figure 3B plots $dI/dV$ point spectra taken at a defect site and up to 7 nm away. It is clear the resonance is never completely suppressed, demonstrating that the resonance is not atomically localized at defect sites and has an extended state. These defects correspond to Na surface vacancies (inset of Fig. 1A) in position Na(2) of the crystal structure of Na$_3$Bi shown in Fig. 3C. To better understand the origin of the resonance feature, density functional theory (DFT) calculations including spin-orbit coupling were performed (see Materials and Methods and section S7 for details). Figure 3D compares an experimental STS for Na$_3$Bi on Si(111), where $E_D$ is shifted to 0 eV (green curve) with the calculated DOS $D(E)$ for the following Na$_3$Bi structures with an Na(2) vacancy: bulk Na$_3$Bi with one Na(2) vacancy per 8 unit cells (black curve), an Na$_3$Bi slab ($2 \times 2 \times 2$ unit cells) containing an Na(2) vacancy in the interior of the slab (blue curve), and an Na$_3$Bi slab ($2 \times 2 \times 3$ unit cells) containing an Na(2) vacancy at the surface (red curve). The associated band structures for each of the structures are shown in Fig. 3E. In all cases, the Na(2) vacancy accepts one electron. In addition, we find that Na(2) vacancies at the surface produce a peak in $D(E)$ at an energy close to the experiment (red curve), due to the formation of a “Mexican hat”-shaped valence band edge (see Fig. 3E). This structure and associated $D(E)$ peak are not present for Na(2) vacancies in the bulk or in the interior of confined slabs (see the additional discussion in the Supplementary Materials). Because the enhanced $D(E)$ at the surface results from a band structure effect, we expect that it is not atomically localized at defect sites but rather varies on a length scale set by the Fermi wavelength, in agreement with observations. The extended nature of the resonant state is confirmed from DFT calculations by projecting the DOS on different surface atoms and also somewhat penetrates the bulk (calculations are shown in section S7 and figs. S9 and S10). The Na(2) surface vacancy concentration thus provides a unique knob to tune the surface DOS of this Dirac material, which could be used, for example, to tune electron-electron interactions or the coupling to magnetic impurities.

Qualitatively different behavior was observed for occasional defect clusters. Figure 4A, where the STM topography of a 60 nm × 60 nm region of Na$_3$Bi, shows a large concentration of singular-defect sites, as well as one defect that appears in topography to consist of a multi-vacancy cluster. The spectroscopic signature of these defects is very different from the quasi-bound resonant state of the singular defects (see Fig. 3), as shown in the fixed-bias $dI/dV$ maps (Fig. 3, B to D) taken at

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**Fig. 2. Charge puddling profiles of p-type and n-type Na$_3$Bi.** (A) Dirac point energy map of the 45 nm × 45 nm (90 pixels × 90 pixels) region of p-type Na$_3$Bi on Si(111) ($V = 250$ mV and $I = 250$ pA), corresponding to region A represented in Fig. 1B. Scale bar, 15 nm. (B) Dirac point energy map of the 30 nm × 30 nm (60 pixels × 60 pixels) region of n-type Na$_3$Bi Si(111) corresponding to region B of Fig. 1C ($V = 150$ mV and $I = 200$ pA). Scale bar, 10 nm. (C) Dirac point energy map of the 30 nm × 30 nm (60 pixels × 60 pixels) region of n-type Na$_3$Bi Si(111) grown on α-Al$_2$O$_3$(0001) (labeled region C) ($V = 150$ mV and $I = 200$ pA). Scale bar, 10 nm. (D) Upper, middle, and lower panels representing histograms of the Dirac point energy maps in (A) to (C), respectively. The histograms are color-coded to reflect the intensity scale in the corresponding Dirac point energy map. (E) Plot of spatial coherence length as a function of Fermi energy, comparing the experimental data for region A (red triangle), region B (blue triangle), and region C (purple diamond) to theoretical predictions (shaded region) where the upper bound (solid line) is defined using $\nu_F = 2.4 \times 10^5$ ms$^{-1}$ and $\alpha = 0.069$, whereas the lower bound (dashed line) uses $\nu_F = 1.4 \times 10^5$ ms$^{-1}$ and $\alpha = 0.174$. (24).
−196, −216, and −236 meV, respectively. Because of the long-ranged electrostatic interaction of the defect with the scanning tip, a ring-like structure emerges that increases in spatial extent as the tip-sample potential becomes more negative. $dI/dV$ maps were also performed at fixed bias while varying the tunneling current and also showed this ring-like structure that varied in width with changing tunneling current, excluding the possibility of a static LDOS feature. This phenomenon has also been observed for defects in graphene (19), dopants in semiconductors (20, 21), and topological insulator systems (22) as a tip-induced "ionization charging ring," where the sudden increase in charge of a bound defect state at a particular tip potential affects the screening cloud in the substrate at the tip position. In this case, the defect state is truly localized, in contrast to the quasi-bound state observed for single Na vacancies, and offers an opportunity to study a quantum dot connected to a TDS reservoir, an area of significant theoretical interest (26–28).

**CONCLUSION**

We have demonstrated, using STM and STS, the existence of charge puddles in the TDS, Na$_3$Bi. The ultralow Dirac point energy fluctuations, which occur over length scales of approximately 5 to 15 nm, are of the order of 4 to 6 meV = 40 to 70 K, well below room temperature and comparable to the highest-quality graphene on h-BN. The ultralow potential fluctuations in this 3D Dirac system will enable the exploration of novel physics associated with the Dirac point (7–11). In addition, we observed defect-associated quasi-bound and bound

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**Fig. 3. Determining the bound state defect resonance.** (A) Map of the $dI/dV$ magnitude at the defect resonance energy, where defects are shown as red circles. (B) $dI/dV$ point spectra (taken on region B) on/off the defect site, at locations corresponding to the defect site (black), then 1 nm (red), 3 nm (purple), 5 nm (green), and 7 nm (brown) away from the defect. (C) Crystal structure of Na$_3$Bi, with the surface-terminated Na labeled Na(2) (gold), with the remaining Na atoms in blue with the Na bonded to Bi in the hexagonal lattice labeled Na(1) and the Bi atoms in gray. (D) Comparison between DFT calculations of the DOS for Na$_3$Bi with an Na(2) vacancy at the surface of a 2 × 2 × 3 cell (red curve), an Na(2) vacancy inside a 2 × 2 × 2 cell (blue curve), and a bulk Na(2) vacancy (black curve) and the experimental STS curve for a 20-nm Na$_3$Bi film (green curve). Energy scales of all spectra have been corrected so that 0 eV reflects the Dirac point. A vertical offset has been applied for clarity. (E) Accompanying electronic band structures for bulk Na$_3$Bi with an Na(2) vacancy (left), an Na(2) vacancy inside a 2 × 2 × 2 cell (middle), and an Na(2) vacancy at the surface of a 2 × 2 × 3 cell (right).

**Fig. 4. Tip-induced ionization rings around large defects.** (A) STM topography ($V = −250$ mV and $I = 250$ pA) on a 60 nm × 60 nm region of Na$_3$Bi. Fixed-bias $dI/dV$ maps taken at (B) −196 mV, (C) −216 mV, and (D) −236 mV over the same region as (A) showing a ring-like feature centered around a large vacancy site highlighted by the dashed circle in (A).
states in a 3D TDS, which opens the possibility to tune electron-electron interactions or tune the coupling to magnetic impurities by varying the sodium surface vacancy concentration.

MATERIALS AND METHODS

Growth and measurements

The 20-nm Na3Bi thin films were grown in a UHV (10⁻¹⁰ torr) MBE chamber and then transferred immediately after the growth to the interconnected CreaTec low-temperature scanning tunneling microscope operating in UHV (10⁻¹¹ torr) for STM/STS measurements at 5 K. For Na3Bi film growth, effusion cells were used to simultaneously evaporate elemental Bi (99.999%; Alfa Aesar) in an overflow of Na (99.95%; Sigma-Aldrich) with a Bi/Na flux ratio of not less than 1:10, calibrated by quartz microbalance. The Bi rate used was ~0.03 Å/s, and the Na rate was ~0.7 Å/s. The pressure during growth was less than 3 × 10⁻⁹ torr.

Growth on Si(111)

To prepare an atomically flat substrate, a Si(111) wafer was flash-annealed to achieve 7 × 7 surface reconstruction, confirmed using STM. During the growth, the substrate temperature was 330°C for successful crystallization. At the end of the growth, the sample was left at 330°C for 10 min in an Na overflux to improve the film quality before cooling to room temperature.

Growth on sapphire

The sapphire substrate was annealed in atmosphere at 1350°C and then in pure oxygen atmosphere at 1050°C to achieve an atomically flat surface. Ti/Au (5/50 nm) contacts were deposited on the corners of the substrate and wire-bonded to a contact busbar on the sample plate to allow for in situ transport measurements in a 1-T perpendicular magnetic field at 5 K. The sapphire was annealed in UHV at 400°C for 1 hour to remove atmospheric species. Na3Bi films were then grown using a two-step growth method, as reported previously by Hellerstedt et al. (24) and Edmonds et al. (25). The Na3Bi film used in this study had a final growth temperature of 330°C.

A PtIr STM tip was prepared and calibrated using an Au(111) single crystal and the Shockley surface state at ~−0.5 V and flat LDOS near the Fermi level before all measurements. STM differential conductance (dI/dV) was measured using a 5-mV ac excitation voltage (673 Hz) that was added to the tunneling bias. Differential conductance measurements were made under open feedback conditions with the tip in a fixed position above the surface. Data were prepared and analyzed using MATLAB and WSxM software (29).

DFT methods

First-principles calculations based on DFT were used to obtain electronic bands and DOS of bulk, bilayer, and trilayer Na3Bi, with and without Na(2) vacancies. The first-principles approach is based on Kohn-Sham DFT (30), as implemented in the Quantum ESPRESSO code (31). The exchange correlation energy was described by the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional (32). Interactions between valence and core electrons were described by Troullier-Martins pseudopotentials (33). The Kohn-Sham orbitals were described in a plane-wave basis with a cutoff energy of 50 rydberg (Ry), and for the charge density, a cutoff of 200 Ry was used. The Brillouin zone was sampled using Γ-centered grids, following the scheme proposed by Monkhorst and Pack (34). For the convergence of charge density, an 8 × 8 × 4 grid was used for the bulk, whereas a 6 × 6 × 1 grid was used for the bilayer and trilayer. For the DOS, a finer grid of 32 × 32 × 16 (26 × 26 × 1) was used for the bulk (bilayer and trilayer). The calculation of the spin-orbit splitting was performed using noncollinear calculations with fully relativistic pseudopotentials. For the bilayer and trilayer models, we used periodic boundary conditions along the three dimensions, with vacuum regions of 10 Å between adjacent images in the direction perpendicular to the layers. Convergence tests with greater vacuum spacing guaranteed that this size was enough to avoid spurious interactions between neighboring images.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/12/eaa06661/DC1

section S1. Determining the Dirac point position from dI/dV spectra

section S2. Demonstrating the spatial and energy correspondence between STS measurements of the Na3Bi Dirac point and defect quasi-bound state

section S3. Demonstrating that charge puddling is correlated with Na(2) vacancies

section S4. Correlation of resonance state in dI/dV spectra with lattice defects

section S5. Calculation of puddle coherence length from autocorrelation analysis

section S6. Theory discussion on correlation length, impurity density, and mobility

section S7. DFT calculations of Na vacancies in the Na3Bi lattice

fig. S1. Determining the Dirac point position from the dI/dV spectra.

fig. S2. STM topography of region A (as in Fig. 1C) showing the 1 × 1 Na3Bi (001), Na(2)-terminated surface, with vacancy point defects and unidentified impurities visible.

fig. S3. Frequency histogram of the measured Dirac point and Na(2) vacancy quasi-bound state (STS peak, ~−30 mV below the Dirac point) features extracted from STS of region A.

fig. S4. Radially averaged correlation profiles for spatial profiles of key STS features in region A.

fig. S5. STM topography and charge puddling map of p-type Na3Bi on region A.

fig. S6. Spatial dependence of defect resonance.

fig. S7. Electronic structure of pristine and defective Na3Bi.

fig. S8. Total DOS of pristine and defective Na3Bi.

fig. S9. Comparison of calculated total DOS and projected DOS on surface for Na3Bi with Na(2) vacancy.

fig. S10. Comparison of calculated total DOS and projected DOS on individual atomic layers for Na3Bi with Na(2) vacancy.

table S1. Charged impurity density for both region A, B, and C.

table S2. Mobility for E_r × E_m calculated using Thomas–Fermi and RPA for both region A, B, and C.

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