Rapid Surface Oxidation as a Source of Surface Degradation Factor for Bi$_2$Se$_3$


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**ABSTRACT**

Bismuth selenide (Bi$_2$Se$_3$) is a topological insulator with metallic surface states (SS) residing in a large bulk bandgap. In experiments, synthesized Bi$_2$Se$_3$ is often heavily n-type doped due to selenium vacancies. Furthermore, it is discovered from experiments on bulk single crystals that Bi$_2$Se$_3$ gets additional n-type doping after exposure to the atmosphere, thereby reducing the relative contribution of SS in total conductivity. In this article, transport measurements on Bi$_2$Se$_3$ nanoribbons provide additional evidence of such environmental doping process. Systematic surface composition analyses by X-ray photoelectron spectroscopy reveal fast formation and continuous growth of native oxide on Bi$_2$Se$_3$ under ambient conditions. In addition to n-type doping at the surface, such surface oxidation is likely the material origin of the degradation of topological SS. Appropriate surface passivation or encapsulation may be required to probe topological SS of Bi$_2$Se$_3$ by transport measurements.

**KEYWORDS:** topological insulator · nanoribbon · transport · oxidation · doping · bismuth selenide

Based on X-ray photoelectron spectroscopy (XPS) characterizations, we show native oxide growth on Bi$_2$Se$_3$, both for nanoribbons and bulk crystals, which we surmise as the likely material origin of surface degradation and environmental doping. Possible mechanisms for the surface oxidation induced doping are discussed.

Transport measurements on Bi$_2$Se$_3$ nanoribbons provide additional evidence for n-type doping by air exposure. Synthesis and device fabrication of Bi$_2$Se$_3$ nanoribbons were reported previously, with details given in the Experimental Section. Four-probe magnetoresistance, $R_{xx}$ (Figure 1a), and Hall resistance, $R_{xy}$ (Figure 1b), are measured by PPMS (Quantum Design), with a magnetic field applied perpendicular to the nanoribbon surfaces corresponding to the (0001) plane of Bi$_2$Se$_3$. SdH oscillations are observed both in $R_{xx}$ and $R_{xy}$. The oscillation period, $(\Delta(1/B))^{-1}$, is determined as 86 T (Supporting Information). According to the band structure of Bi$_2$Se$_3$, SdH oscillations of the surface electrons are expected to have a...
much larger period when the Fermi level is near the bottom of the conduction band,\textsuperscript{23} so we ascribe the observed oscillations to bulk electrons. In addition, cyclotron effective mass, $m^* = 0.13 \ m_e$, obtained by fitting the thermal damping of the SdH oscillation amplitude (Figure 1c; details of the analyses are provided in the Supporting Information), is consistent with the value of bulk electrons from bulk single-crystal measurements.\textsuperscript{20,24} For moderately doped samples ($n \leq 5 \times 10^{18} \ \text{cm}^{-3}$), the Fermi surface of bulk states is approximately a prolate ellipsoid in momentum space.\textsuperscript{24,25} Consequently, the SdH oscillation period should be proportional to $n^{2/3}$ (see Supporting Information for derivation). Figure 2 shows previous bulk crystal SdH oscillation data fitted with this relation.\textsuperscript{23,24,26}

By fitting the curve, we estimate the bulk electron density in the nanoribbon as $n_{3D}^{SdH} = 4.7 \times 10^{18} \ \text{cm}^{-3}$ (Figure 2). On the other hand, effective areal electron concentration in the nanoribbon is $n_{3D}^{Hall} = 1.5 \times 10^{14} \ \text{cm}^{-2}$, obtained from the Hall slope of $4.28 \ \Omega/T$ (Figure 1b). Hence, bulk electron concentration is $n_{3D}^{Hall} \approx 1.7 \times 10^{13} \ \text{cm}^{-3}$, as the nanoribbon has a thickness of 88 nm measured by atomic force microscopy (AFM, Figure 1b inset). Apparently, $n_{3D}^{Hall}$ is much higher than $n_{3D}^{SdH}$, indicating the existence of low-mobility carriers inside the nanoribbon. The “discrepancy” between $n_{3D}^{Hall}$ and $n_{3D}^{SdH}$ is because these low-mobility carriers will not take part in the SdH oscillations, while present in the Hall measurements. We note that the Ti SS is not expected to be the dominant source of the additional carriers owing to the relatively low density of 2D electronic states. Transport measurements on bulk single crystals typically show consistency between the carrier concentration estimated by the Hall slope and SdH oscillation period.\textsuperscript{18,20} A few bulk crystal experiments reveal lower carrier concentration from the Hall slope compared to that from the SdH oscillation,\textsuperscript{24} which is expected for the Hall measurement on a multicarrier material at low field limit. The large Hall carrier concentration $n_{3D}^{Hall}$ with a factor of $\sim 3.6$ larger than $n_{3D}^{SdH}$ observed in our Bi$_2$Se$_3$ nanoribbon is rarely seen in bulk crystals. It was reported previously that excessive electrons accumulate on the surface of Bi$_2$Se$_3$ crystals over time.\textsuperscript{18,20} In a lightly doped Bi$_2$Se$_3$ bulk crystal ($n \approx 10^{17} \ \text{cm}^{-3}$), the Fermi energy at the surface acquired by ARPES increases to a degenerate level upon exposure to air, which corresponds to the accumulation of electrons that bend the bulk band near the crystal surface.\textsuperscript{20} In addition, time-dependent transport studies on lightly doped bulk crystals exposed to humid atmosphere reveal the continuous n-type doping from the environment.\textsuperscript{18} For the nanoribbon case, the environmentally doped electrons contribute to the transport with a much more pronounced effect due to the large surface-to-volume ratio in nanostructures. It is therefore reasonable to ascribe the excessive electrons revealed in the Hall measurement to environmentally doped carriers, possibly with low mobility, that do not contribute to the SdH oscillations.

Figure 2. Plot of $n_{3D}^{2/3}$ versus $(\Delta(1/B))^3$ fitted with a linear relation. Open circles are data collected from previous measurements on bulk single crystals.\textsuperscript{23,24,26} Carrier concentration of the nanoribbon device is thus obtained, as marked by the red stars. Upper inset: Schematic band structure of Bi$_2$Se$_3$, with different Fermi levels for environmentally doped layer (red) and crystal inner region (black). Lower inset: Structure of Bi$_2$Se$_3$ nanoribbons consisting of a surface oxide layer, topological insulator surface states, a heavily doped layer from environmental doping (low mobility), and a moderately doped inner region (high mobility). Diagram of Fermi level, conduction, and valence band edges through the nanoribbon is also shown. The existence of surface oxide is revealed by XPS characterizations (shown in Figure 3).
To examine the physical origin of the environmental doping on Bi$_2$Se$_3$, surface chemistry probe XPS (SSI S-Probe XPS spectrometer with Al Ka source) is used to characterize the composition at the surface of Bi$_2$Se$_3$ nanoribbons and bulk single crystals. Silicon substrates with full coverage of nanoribbons are selected for XPS study to avoid the substrate contribution in the final spectra. For as-grown nanoribbons (Figure 3a and b), a bismuth oxide (BiO$_x$) peak is observed.$^{27}$ Here, we cannot exclude the possibility that the observed surface oxide exists in the hydroxide form, which is difficult to distinguish from the oxide due to the broadness of the oxide peak overlapping the energy range of the hydroxide. We note that previous energy dispersive X-ray spectroscopy (EDS) characterizations on Bi$_2$Se$_3$ nanoribbons, performed in a transmission electron microscope (TEM), reveal negligible oxygen content with respect to the bismuth and Se.$^{17,21,22}$ XPS is a surface-sensitive technique, whereas TEM-EDS probes the compositions of the whole nanoribbon since the electron beam transmits through the sample. Comparison between XPS and EDS analyses indicates the oxide is formed on the surface of the nanoribbons. Time evolution of the surface oxide is studied with XPS and EDS characterizations of the Bi$_2$Se$_3$ nanoribbons exposed in air for 5 days, revealing a dramatic increase in the oxide thickness for samples with relatively short time exposure to air. The thickness of the surface oxide is estimated as $\sim$0.38 nm, by assuming a bilayer structure with BiO$_x$ on top and Bi$_2$Se$_3$ underneath. The oxide peak can be reduced by a short argon (Ar) ion etching for 5 min (10 mA, 5 kV); the weight of the BiO$_x$ peak decreases from 19% to 13% after Ar etch, further confirming the surface origin of the oxide. Spectra of the cleaved bulk crystal with longer air aging of 2 days are also acquired, revealing a dramatically increased BiO$_x$ peak. The SeO$_x$ peak is also observed in such long time aged samples, similar to the nanoribbon case. The surface oxide thickness of 2-day air-exposed samples is estimated as $\sim$1.94 nm (Experimental Section). Interestingly, the elemental Se peak is also present in the same spectra. A tentative explanation is that some Se in the Bi$_2$Se$_3$ crystal grown with excessive Se powder tends to gradually precipitate out, since a Se-deficient state is more thermodynamically favorable under ambient conditions.

The growth of native oxide (or hydroxide) on Bi$_2$Se$_3$ nanoribbons and bulk crystals may account for many challenges in transport measurements of TIs. Environmental doping from surface oxide growth is known for many semiconductors, such as germanium (Ge) and gallium nitride (GaN)$^{28,29}$ Semiconductor bulk bands bend near the oxide/semiconductor interface. It may directly come from the induced charges in the semiconductor from the trapped charges in the oxide or at the semiconductor/oxide interface$^{29,30}$ or the formation of interfacial defect states giving rise to the Fermi level pinning at the interface and bulk bands bending. We note that surface oxidation involving only oxygen is a p-type doping process for Bi$_2$Se$_3$. With moisture-assisted surface oxidation of Bi$_2$Se$_3$ in air may exhibit distinctive interfacial defects or trapped charges different from the pure oxygen case, which results in the reversed doping
effect. Another possibility is an indirect mechanism. The surface oxide is expected to be decorated with hydroxyl groups as surface impurities under ambient conditions, especially at defect sites. Hydroxyl impurities are typically electron donors that lead to n-type band bending. The dominant contributor to the n-type surface doping for Bi$_2$Se$_3$ requires further study. For continuous surface oxide growth, oxygen atoms need to diffuse into the crystal and locally distort the perfect layered crystal structure, increasing disorder on the surface. Furthermore, continuous surface oxide growth is also observed in bismuth telluride (Bi$_2$Te$_3$), another layered TI with a structure close to that of Bi$_2$Se$_3$. Such surface oxidation appears to be general for this family of TIs. The current study does not exclude alternative mechanisms contributing to the environmental doping and surface degradation process. For example, absorbed water (H$_2$O) serves as an electron donor for certain layered chalcogenide semiconductors, even without appreciable surface reactions. The aging of the Bi$_2$Se$_3$ surface in the atmosphere is likely the collective effect from multiple factors.

We can qualitatively evaluate the transport properties of the Bi$_2$Se$_3$ nanoribbons. The conductance of the nanoribbon comes from parallel contributions from the environmentally doped band bending region, nondoped inner region, and TI SS (schematic shown in Figure 2). The doped region is expected as a thin layer encapsulating the nanoribbon, due to the strong screening in metallic Bi$_2$Se$_3$. Topological SS exist at the interface between the doped layer and surface oxide. The effective Hall mobility of the nanoribbon $\mu_H$ is $630 \text{ cm}^2/(\text{V} \cdot \text{s})$, determined by the measured Hall slope of 4.28 $\Omega$/T and the sheet resistance of 68 $\Omega$. The Hall mobility is the averaged mobility of different types of carriers. The mobility of the nondoped inner bulk region is extracted from thermal damping of the amplitude of the SdH oscillations (details in the Supporting Information). The isotropic scattering time for inner bulk electrons, $\tau_{\text{iso,3D}}$, is 0.08 ps, corresponding to a mobility, $\mu_{\text{iso,3D}}$, of 1100 $\text{cm}^2/(\text{V} \cdot \text{s})$. The conductance of the inner region is determined by the transport mobility, $\mu_{\text{3D}}$, which is larger than $\mu_{\text{iso,3D}}$ for a 3D electron gas. The ratio of $\mu_{\text{3D}}/\mu_{\text{iso,3D}}$ varies depending on microscopic scattering processes. Recent measurements on bulk single crystals show the ratio can be as large as 4. $\mu_{\text{3D}}$ is expected to be a few thousand $\text{cm}^2/(\text{V} \cdot \text{s})$. A comparison between $\mu_H$ and $\mu_{\text{3D}}$ indeed reveals that a significant amount of low-mobility carriers exist in the nanoribbon. The major source of such low-mobility electrons is from the doped band bending region, since it holds the largest population of the carriers. The decrease of the mobility in the band bending layer is ascribed to the addition of interface defects during oxide growth. The mobility of topological SS may vary with the surface condition. In bulk Bi$_2$Se$_3$ crystals with minimal air exposure, SdH oscillations of SS are observed in pulse field measurements, with a relatively high isotropic scattering mobility of 1750 $\text{cm}^2/(\text{V} \cdot \text{s})$. Nevertheless, the environmental doping as well as the increase of surface scattering, associated with the oxidation process, adds challenges in probing topological SS. As shown in Figure 2, environmental doping induces band bending at the Bi$_2$Se$_3$ surface and shifts the Fermi level deeper into the conduction band. Under extreme cases, the topological SS may merge into the bulk conduction band and become nondistinguishable from bulk states in transport measurements. In addition, even though TI SS are protected by the time reversal symmetry and are insensitive to a backscattering process, they are not completely immune to other scattering routes. The increase of surface disorders therefore would still lower SS mobility. The smearing of SS SdH oscillations of Bi$_2$Se$_3$ after 1–2 h air exposure and the absence of surface transport signature in high-quality single crystals reveal such a degradation process of topological SS transport properties after Bi$_2$Se$_3$ interaction with the ambient environment. Certainly, these results implore extreme caution in handling Bi$_2$Se$_3$ samples, to minimize the extraneous SS degradation effects from atmosphere exposure. The extent of the surface chemical reactions and their influence on the transport properties of TI SS may depend on the sample quality or growth conditions. This study does not exclude the opportunity to obtain Bi$_2$Se$_3$ crystals with relatively robust surface transport properties under ambient conditions.

**CONCLUSION**

In summary, the observed discrepancy between the Hall- and SdH-estimated carrier concentrations in Bi$_2$Se$_3$ nanoribbons indicates n-type doping by air exposure, consistent with previous measurements on bulk single crystals. XPS charcterizations on Bi$_2$Se$_3$ nanoribbons and bulk single crystals reveal the rapid formation and continuous growth of surface oxide under ambient conditions. This oxide growth may serve as the physical origin of surface degradation and environmental doping on Bi$_2$Se$_3$. It presents a practical challenge for probing TI SS by transport measurements. Appropriate encapsulation or surface passivation to inhibit the surface oxidation may be required.

**EXPERIMENTAL SECTION**

Bi$_2$Se$_3$ Nanoribbon Synthesis and Device Fabrication. Bi$_2$Se$_3$ nanoribbons are synthesized by metal-catalyzed vapor phase growth in a horizontal tube furnace. As-grown Bi$_2$Se$_3$ nanoribbons are grown by using 20 nm gold nanoparticles as catalyst. Sn-doped Bi$_2$Se$_3$ nanoribbons are grown with Sn/Au (5 nm/2 nm)

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**KONG ET AL.**

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4701
double-layer alloy catalysts, where the dopant is introduced by the diffusion from the catalyst during the growth. Nanoribbons exhibit a well-defined structure, with very smooth top and bottom surfaces perpendicular to the (0 0 0 1) trigonal axis. The synthesis is based on a combined vapor–liquid–solid (VLS) and vapor–solid (VS) mechanism, in which the VLS process promotes one-dimensional growth from the metal catalyst, and the VS process favors direct deposition on the side surface of the nanoribbon for two-dimensional growth. The involvement of the VS process for the growth of wide nanoribbons is supported by the catalyst-free growth of Bi$_2$Se$_3$ nanoribbons with conditions close to the nanoribbon synthesis. As-grown Bi$_2$Se$_3$ nanoribbons using gold particles have a higher yield than Sn-doped Bi$_2$Se$_3$ nanoribbons. Hence we used gold-catalyzed nanoribbons, which can completely cover a substrate, for XPS measurements, to improve the signal-to-noise ratio and avoid contributions from the substrate. Sn-doped nanoribbons are selected for transport study. Sn effectively compensates residual bulk electrons induced from Se vacancies and improves the transport mobility, allowing us to observe Aharonov–Bohm oscillations reported previously and Shubnikov–de Haas oscillations discussed here. Sn-doped nanoribbons still remain metallic. EDS characterizations on Sn-doped nanoribbons reveal little signal of Sn within the detection limit (~1–2%). Typically, only a trace amount of the dopant is introduced to the nanostructures by diffusion from the catalyst. Therefore, Sn-doped nanoribbons are expected to exhibit similar surface chemical properties to as-grown nanoribbons with a relatively low concentration of Sn dopants.

Bi$_2$Se$_3$ nanoribbons are mechanically transferred from the growth substrate onto a 150 nm thick silicon nitride on Si substrate. Titanium (Ti)/Au (5 nm/195 nm) or chromium (Cr)/Au (5 nm/195 nm) ohmic contacts are patterned on nanoribbons to form six-terminal configurations, through standard e-beam lithography followed by thermal evaporation of the metals.

Bi$_2$Se$_3$ Bulk Single Crystal Growth. Single crystals of Bi$_2$Se$_3$ have been grown by slow cooling a binary melt. Elemental Bi and Se are mixed in alumina crucibles in a molar ratio of 35:65. The mixtures are sealed in quartz ampules, raised to 750 °C, cooled slowly to 550 °C, and then annealed for an extended period. Crystals grown with such nominal composition ratio containing excessive Se exhibit reduced defect density and low carrier concentration.

Transport Measurements. Standard low-frequency (1000 Hz) four-probe magnetoresistance measurements are carried out in a Quantum Design PPMS-7 instrument equipped with a 9 T magnet. The field is applied to the normal direction of the nanostructures, and a Keithley 6100 data acquisition system is used. The measurements are carried out in the temperature range of 2 K to 300 K, and the magnetic field is up to 9 T. The field is applied to the normal direction of the nanoribbon surfaces, corresponding to the (0001) plane of Bi$_2$Se$_3$.

XPS Sample Preparation and Surface Oxide Thickness Estimation. XPS characterizations on nanoribbons are performed directly on as-grown substrates. High-yield substrates with full coverage of the nanoribbons are selected, to eliminate the contribution from the substrates to the final spectra. The flat surface of Bi$_2$Se$_3$ bulk single crystals is available by cleaving the crystal along its natural cleavage plane (perpendicular to its trigonal axis).

To estimate the thickness of the oxide layer on the nanoribbons, we prepared a bilayer structure with the surface oxide on top and Bi$_2$Se$_3$ underneath. We obtain the atomic percentage of Bi$_2$Se$_3$+BiO$_x$ as 81.4%:18.7%, from areas under the Bi$_2$Se$_3$ and BiO$_x$ peak in Bi 4f transitions. Using the electron escape depth of 1.8 nm (typical for Al Kα source), the attenuation of the Bi$_2$Se$_3$ peak from 100% to 81.4% due to the surface oxide gives the oxide thickness of ~0.38 nm for samples with minimum air exposure. After 5 min etching, the BiO$_x$ peak is reduced to 13%. We note that it is difficult to accurately estimate the amount of remaining BiO$_x$ after etching since the Bi peak widens. For crystals aged in air for 2 days, we observe an increased BiO$_x$ peak as well as SeO$_x$ peak. Assuming again the bilayer structure with the surface oxide on top and Bi$_2$Se$_3$ underneath, the attenuation of the Bi$_2$Se$_3$ peak from 100% to 34.1% gives the surface oxide thickness of ~1.94 nm for a 2-day-exposed sample.

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Supporting Information Available: EDS spectrum of Sn-doped nanoribbons of Bi$_2$Se$_3$ and details on the analyses of SdH oscillations. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES