Role of oxidation on surface conductance of the topological insulator Bi$_2$Te$_2$Se

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**Abstract**

We investigated the effect of surface oxides on charge transport properties in a topological insulator (Bi$_2$Te$_2$Se) using conductive probe atomic force microscopy in an ultrahigh vacuum environment. Uniform distribution of the measured friction and current were observed over a single quintuple layer terrace after exposure to the ambient environment, which is an indication of uniform surface oxide coverage. An oxide-free topological insulator surface was exposed using tip-induced etching. By comparing surface conduction on a fresh surface versus a surface exposed to air, we observed a minor change in resistance when surface oxide was present.

**1. Introduction**

Three-dimensional topological insulators (TI), characterized by a nontrivial Z$_2$ topology of the bulk wave function, are insulating in the bulk with unusual metallic surface states that consist of spin-polarized Dirac fermions [1–4]. Surface states of the TIs are protected by time-reversal symmetry and the spin–orbit interaction [2,4]. Such spin-helical states are insensitive to disorder or local perturbations because no states are available for backscattering [5,6]. Low energy dissipation can therefore be expected during electron transport processes [7,8]. The characteristics of electron transport phenomena with low energy loss make a dramatic increase in energy efficiency possible, which will be a key technology for future energy industries. Thus far, many attempts have been made to achieve TI-based electronic devices, including the ambipolar field effect, flexibility, and superconducting transport [7,9–12]. Recently, it was shown that charge transport on TI is influenced by moisture and oxygen in the surrounding environment [13,14]. Since most of the transport studies were carried out in air, these transport studies on TI materials are subject to air oxidation [14–16]. For example, Bi$_2$O$_3$ and TeO$_2$ formed on the Bi$_2$Te$_2$ surface were measured by X-ray photoemission spectroscopy and Raman spectra [17]. While the effect of air oxidation on the TI layer is significant, the role of surface oxide in charge transport is barely known. For further applications, it is necessary to discover the role of oxidation on surface conductance of TIs.

Bismuth-based compounds have long been studied to verify unusual topological states. Bi$_2$Se$_3$ and Bi$_2$Te$_3$ were widely used for their large 0.3 eV band gap with a single Dirac cone inside [18–21]. While measurements using angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM) are normally performed on a fresh surface obtained by cleaving samples in situ under ultrahigh vacuum, the surface is usually exposed to ambient conditions during transport measurements. Transport techniques are widely used to investigate the intrinsic quantum behaviors of the surface states; however, several groups still dispute the effect of surface oxides. From experiments on bulk single crystals, D. Kong et al. discovered that Bi$_2$Se$_3$ has additional n-type doping after exposure to the atmosphere, thereby reducing the relative contribution of the surface states in total conductivity [13]. ARPES measurements show that the surface states of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ are strongly modified after exposure to air at room temperature and that two-dimensional quantum well states form near the surface [22,23]. B. Zhou et al. further insisted that bi-polar control of surface carriers by gaseous or alkaline surface doping did not affect the topological nature of these materials when using H$_2$, CO, and O$_2$ [24]. H$_2$O and O$_2$ have been reported to be the main sources of surface deterioration by chemical reactions, but L. V. Yashina et al. made ARPES measurements and found that no chemical reactions occur in O$_2$ and H$_2$O [25]. V. A. Golovach et al. surveyed the inertness of the Bi$_2$Se$_3$ surface to oxidation using X-ray photoelectron spectroscopy, STM, and density functional theory calculations [26].

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In our view, the effect of air oxidation should be separated from the effect of aging mainly due to bulk defects (e.g., vacancies and antisite defects). Thus, we directly measured the charge transport of clean and oxidized TI surfaces using conductive probe atomic force microscopy (CP-AFM) in ultrahigh vacuum (UHV). Contact mode AFM allowed us to measure friction and conductance simultaneously, so we could determine the relative surface composition from the friction. We removed the oxide layer by applying a high voltage, allowing us to uncover the effect of surface oxide on surface conductance and friction. The current density on the TI surface as a function of local pressure was employed to verify the topological surface states.

2. Experimental details

The bismuth-based ternary compound Bi$_2$Te$_2$Se (BTS) appears to contribute highly to surface current, compared with binary compounds such as Bi$_2$Te$_3$ and Bi$_2$Se$_3$, due to the suppression of intrinsic defects [15, 16, 27]. Single crystals of BTS were grown using self-basix flux methods. High-purity elements—Bi(5 N), Te(6 N), and Se(5 N)—were sealed in an evacuated quartz ampoule with a stoichiometry of Bi:Te:Se = 2:1.95:1.05 [15]. After the mixture was heated to 850 °C and annealed for two days for homogeneity, the mixture was slowly cooled to 600 °C for a week. The furnace was kept at 600 °C for one additional week before cooling the furnace to ensure high crystallization.

A commercial RHK-Tech UHV AFM system was used for the AFM experiments. To avoid forces originating from capillary water between the tip and sample at ambient pressure, the chamber was maintained at a base pressure of 1.0 × 10$^{-10}$ Torr. TiN-coated cantilevers with a force constant of 0.1 N/m (NT-MDT) were utilized to measure the conductance and friction. The measurements were performed using hybrid combinations of CP-AFM and friction force microscopy (FFM) for simultaneous detection of atomic-scale forces and conduction properties [28–30]. Conventional contact mode AFM uses cantilever deflection as the feedback signal to regulate the tip–sample distance. When electrically conductive AFM tips are connected to a current pre-amplifier, the tip–sample current is obtained as an additional independent signal when a bias voltage is applied between the conducting tip and a conduction substrate [29]. The radii of the metal-coated tips were 30–50 nm before contact, as measured by SEM. However, when measured after a contact experiment, the radii were found to be 35 ± 10 nm. Because the measured friction force does not show time-dependent behavior during the experiments, we assume that the range of stress is in the elastic regime with minimal changes during subsequent contact measurements. By analyzing the topographical and frictional images after the contact AFM experiment, we confirm that the loads are sufficiently small such that the neither the tip nor the surface was damaged.

3. Results and discussion

We prepared two kinds of samples: a sample cleaved inside the vacuum chamber, and a sample cleaved outside that results in surface oxidation. Fig. 1(a)–(c) is the clean surface, and Fig. 1(d)–(f) is the oxidized surface; from the left, the images represent topography, friction, and conductance, respectively. The AFM images were obtained using 9.21 nN of applied load and 0.67 V of sample bias on the clean surface and 8.5 nN of applied load and 1 V of sample bias on the oxidized surface for contact mode AFM imaging. We were able to observe atomic steps in most areas of the two samples, and each terrace extended from several micrometers to a few nanometers. Friction measurements of back and forth scanning of the AFM tip produced the friction images of the sample; the friction images did not show any differences between one step and another for either clean or oxidized surfaces. However, the current images showed a conductance contrast between neighboring terraces.

According to the X-ray diffraction study, a single layer of BTS consists of Te–Bi–Se–Bi–Te with covalent bonds and each layer is connected by van der Waals (vdW) forces [15, 27]. The height of a single step is 1.0 ± 0.2 nm, which is consistent with our topographic measurements. Due to weak interbonding and layer composition, we expect that Te atoms terminate the step terraces in the clean surface. When a clean surface is exposed to air, Te atoms will form Te-related defects on the oxidized surface. Identical friction between neighboring terraces
implies that terraces separated by steps are chemically the same for either clean or oxidized surfaces. However, we only observed a contrast in conductance between neighboring terraces in the clean surface. The conductance contrast for the clean surface is not clearly understood. One possible explanation is a difference in carrier density due to an internal field generated by a non-uniform distribution of defects. We suppose that different amounts of point defects and defect types generate an internal field between the neighboring terraces in the clean surface. According to a previous study of Bi$_2$Se$_3$, the density of state can vary because of the internal field or the level of doping in light of electronic band structures [31]. The self-flux growth of Bi$_2$Se$_3$ could contain nonstoichiometric intercalated Bi/Se domains in the vdW gap and a high density of antisite defects could exist near the surface layer [32]. Although BTS is reported to have high bulk resistivity due to effective carrier compensation, TeBi antisite defects have been found on the BTS surface using STM [9,33]. Even though a variation of density of states and Bi/Se antisite domains were reported in Bi$_2$Se$_3$, we assume that Te$_{Bi}$ antisite defects play a role in the conductance domain. Compared with the clean surface, no contrast was found on the oxidized surface. From these results, the sample exposed to air is oxidized and the modified surface may play an important role in surface conductance.

To shed light on the effect of surface oxide on BTS, we investigated the mechanical and electrical properties of the fresh surface obtained by scanning probe lithography. We were able to observe nanosized surface etching by sweeping the AFM tip on the BTS surface in ultrahigh vacuum, as illustrated in Fig. 2(a). The etching was made with 5 V of sample bias and 10.7 nN of applied load, which allows us to expose an oxide-free trench region on the surface. A similar approach was used to study the role of an oxide or passivating layer in nanomechanical properties [34,35]. Fig. 2(b) clearly shows an etched area (100 × 50 nm$^2$) in a wide view of the topography image (500 × 500 nm$^2$). After surface etching, the depth of the trench was about 5 nm, which makes us suppose that the tip-induced etching removed the oxide layer as well as other loose-bound materials adsorbed onto the sample.

Fig. 2(c)–(e) shows the line profiles of topography, friction, and current taken between points A and B shown in Fig. 2(b). Here, friction is proportional to the gap between the trace (red) and retrace (black) curves in the friction profiles. The fresh surface exposed 5.11 ± 0.09 nm below the surface is compared with the oxidized surface, revealing high friction and current. The applied load and sample bias for image scanning were 10.7 nN and 2.5 V, respectively. We obtained the oxidation effect from the line profiles of the images. We summarized the changing friction and current in the Table 1. Friction on the fresh surface was six times higher than that on the oxidized surface. The increase in friction implies the elimination of the oxide on the BTS surface. In spite of oxide removal, the current increased by only 38.1%.

**Fig. 2.** (a) Schematic of scanning probe lithography of nanoscale Bi$_2$Te$_2$Se layers using high voltage (applied load = 10.7 nN, sample bias = 5 V), (b) Wide scan images (500 × 500 nm$^2$) of the topography of the etched Bi$_2$Te$_2$Se (applied load = 10.7 nN, sample bias = 2.5 V). Line profiles of (c) topography, (d) friction, and (e) current revealing high friction and current on the etched surface between points A and B shown in (b). The trace (red) and retrace (black) curves are shown in the friction image (d). I–V curves for both the etched and unetched (oxidized) Bi$_2$Te$_2$Se surface show symmetric behavior, as shown in (f).
Friction and current were measured using 10.7 nN of applied load and 2.5 V of sample bias. Friction changed markedly due to the removal of the surface oxide, while current increased only 38.1%.

Although the oxide suppressed the current flow, electron transport changed slightly. We obtained the current–voltage (I–V) curve of a fresh surface, shown in Fig. 2(g). The red and black curves indicate fresh and oxidized surfaces, respectively. The fresh surface shows a slightly higher current at the identical sample bias. The higher conductance on the etched region is associated with the removal of oxide layers as well as disorder caused by the tip-induced etching. Because atomic-scale defects typically decrease conductance and the shape of the I–V curve measured on the exposed area is quite similar to that on the oxidized area, we suppose that the removed oxide layer is mainly responsible for the increased current.

Mechanical exfoliation would be another way to investigate the clean surface; however, the focus of this study is to directly compare the oxidized region with the etched region in one AFM image, which is not possible on an exfoliated sample. We note that we carried out the tip-induced etching experiment more than five times and that in all of the cases, we obtained a higher friction force and moderately higher current on the etched region. From direct comparison of the surfaces, fresh and oxidized surfaces, respectively. The fresh surface shows a nearly symmetric I–V curve measured on the exposed area is quite similar to that on the oxidized area, we suppose that the removed oxide layer is mainly responsible for the increased current.

We previously measured the correlation between nanomechanical properties and charge transport from an AFM tip to the sample [28,29,36]. The oxidized surface kept those unique properties due to the topological band structure when we measured the load dependence of the I–V curve at the junction between the conductive tip and BTS in the elastic regime, as shown in Fig. 3. The I–V curve shows a nearly symmetric curve, which suggests that the TI surfaces have a metallic nature. Enlargement of current flow was observed as the strain increased when loading the tip until the normal force was at 8.5 nN. At high load, however, the increase in current was saturated, as shown in the figure inset. This behavior may represent electron transport specifically on the TI surface. Subsequently, we measured friction and current simultaneously as a function of applied load. The following measurement clearly shows that the current responses depend on pressure.

Fig. 4(a) shows friction and conductance measured at the center of the terrace on the oxidized BTS surface in the elastic regime. The measurements were taken with 2 V of sample bias. The blue and red squares indicate current and friction, respectively. While friction increased moderately, current increased and saturated when the normal force was over 15.7 nN. We increased the current until the normal force was 8.5 nN, which corresponded to the I–V curve. In the wearless regime, friction at a single asperity (j) is described by \( f = \frac{A}{2}\pi r^2 \), where A is the contact area and \( \tau \) is the shear stress at the interface. Thus, we can regard friction as the contact area since shear stress (\( \tau \)) is not a function of applied load, but rather is a constant value determined by material and surface conditions [37]. We calculated the contact area using the Derjaguin–Müller–Toporov (DMT) continuum mechanical model [38–40]. The elastic modulus (\( E_{\text{BTS}} \)) of 40.2 GPa for BTS was measured by nanoindentation with 0.3 for Poisson’s ratio (\( v_{\text{BTS}} \)). A combined modulus of 41.2 GPa (from \( E_{\text{TiN}} = 600 \) GPa, \( E_{\text{TiN}} = 0.25 \)) [28] and tip radius of 35 nm were used for DMT fitting. The adhesion force of \( 11.1 \pm 0.7 \) nN was measured from force–distance curves on the BTS surface. From the calculated contact area and current, we obtained the current density (A/cm²) as a function of effective pressure (GPa) after considering the adhesion force, as shown in Fig. 4(b). We identified two regimes in the current density that depend on applied pressure. In the low-pressure regime (less than 0.55 GPa), the current density increased, while the current density decreased by 38.1% in the high-pressure regime.

Crossover behavior of the current density implies that the local density of states and the scattering component are significantly influenced by local strain. A cleaved surface shows current density variation by tip-induced strain [41], which explains the combined effect of changes in the in-plane conductance due to spin–orbit coupling and hexagonal warping [42–45]. As the pressure increased, the effects of inter-layer coupling and contact resistance may also contribute to increasing the

![Fig. 3. Current–voltage curves between a TiN tip and the oxidized Bi₂Te₂Se surface as a function of apparent applied load. I–V curves on the Bi₂Te₂Se show nearly symmetric behavior. The inset shows the change in current at 2 V of sample bias.](Image)

![Fig. 4. (a) Current and lateral force as a function of applied load measured on the oxidized Bi₂Te₂Se surface (sample bias = 2 V). The tip–sample contact area (black line) is calculated using the DMT model. (b) Current density was obtained as a function of effective pressure from (a).](Image)
current density in the low-pressure regime. Conductance variation as a function of pressure is a unique property of topological surface states, implying that the oxidized surface keeps the characteristics of TIs. Because the experiment was carried out at room temperature, thermally excited bulk carriers can contribute to the total conductance, even though the quantitative assessment of the ratio of surface to bulk conductance is challenging. However, in our measurement, we clearly observed a change in current density as the pressure changed, indicating that surface conductance is significant. Other narrow band gap semiconductors (e.g., Si) do not exhibit such dependence on pressure [46].

We note that a similar crossover behavior of current density was observed on the cleaved Bi2Te3 surface. The similar result between cleaved Bi2Te3 and oxidized BTS suggests that the crossover behavior of the current density is general for topological insulator materials. These results imply that topological surface states play a major role in nanoscale charge transport and are correlated with mechanical deformation at atomic scale, even when surface oxide is present.

4. Conclusion

In conclusion, we studied the influence of surface oxide on the charge transport properties of BTS surfaces using conductive probe AFM. Each terrace of a clean BTS surface has different levels of conductance, but the variation in conductance disappears after surface oxidation. To identify that surface conductance is significantly affected by the quantitative assessment of the ratio of surface to bulk conductance can contribute to the total conductance, even though the oxidative assessment of the ratio of surface to bulk conductance is challenging. However, in our measurement, we clearly observed a change in current density as the pressure changed, indicating that surface conductance is significant. Other narrow band gap semiconductors (e.g., Si) do not exhibit such dependence on pressure [46].

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