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Role of oxidation on surface conductance of the topological insulator Bi_2Te_2Se

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ABSTRACT

We investigated the effect of surface oxides on charge transport properties in a topological insulator (Bi_2Te_2Se) 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. The current density varied with applied load on the oxidized surface, which implies that the topological surface states respond to tip-induced pressure even though surface oxide is present. From these results, we conclude that surface oxidation in air has a negligible effect on surface conductance in topological insulators.

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_2O_3 and TeO_2 formed on the Bi_2Te_3 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_2Se_3 and Bi_2Te_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_2Se_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_2Se_3 and Bi_2Te_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_2O 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_2O [25]. V. A. Golyachov et al. surveyed the inertness of the Bi_2Se_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_2Te_2Se (BTS) appears to contribute highly to surface current, compared with binary compounds such as Bi_2Te_3 and Bi_2Se_3, due to the suppression of intrinsic defects [15,16,27]. Single crystals of BTS were grown using self-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 changes to the tip radius took place soon after the initial contact; 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

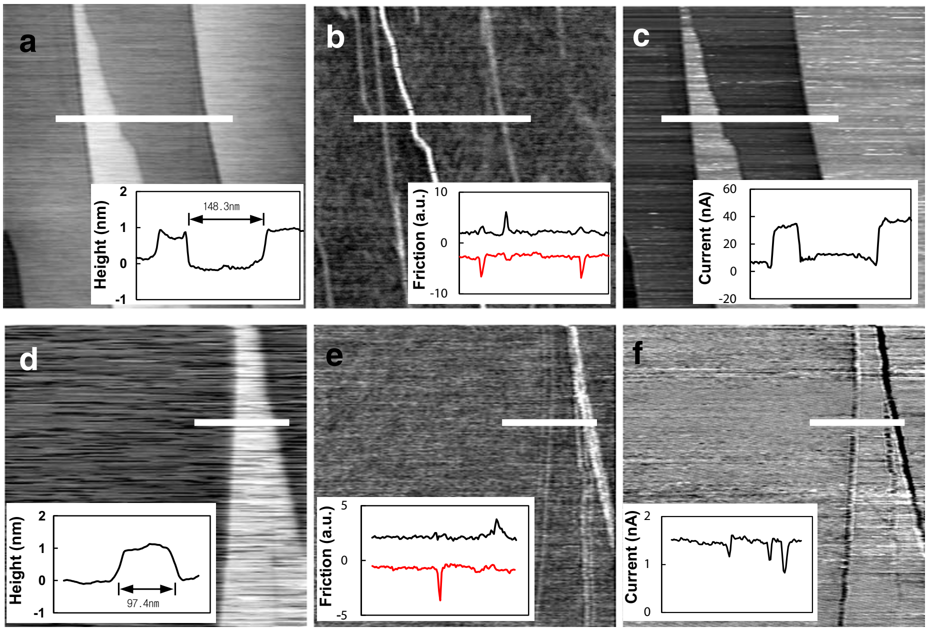

Fig. 1. 500×500 nm^2 images of (a) topography, (b) friction, and (c) current taken in contact AFM mode on the cleaved Bi_2Te_2Se surface (applied load = 9.21 nN, sample bias = 0.67 V). After air exposure, (d) topography, (e) friction, and (f) current on the oxidized Bi_2Te_2Se surface were taken (applied load = 8.2 nN, sample bias = 0.67 V). Insets are the line profiles of the white line in each figure. The trace (red) and retrace (black) curves are shown in friction line profile (b, e). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)