Surface relaxation of topological insulators: Influence on the electronic structure

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The surface structure of topological insulators Bi_2Te_3(111) and a single bilayer bismuth on it was studied by low-energy electron-diffraction analysis. The topmost quintuple layer of Bi_2Te_3 showed only a slight relaxation ($\sim$1% contraction). On the other hand, the bilayer Bi was strongly distorted compared to bulk Bi (3.5% in-plane contraction and $\sim$7% out-of-plane expansion). First-principles calculation reveals that this distortion has a large influence on the electronic structure and can enlarge the band gap.

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Topological insulators (TIs) have been attracting many researchers since their existence was predicted theoretically[1–3] and later confirmed experimentally in a HgTe/CdTe quantum well as a two-dimensional TI,[4] and BiSb alloy as a three-dimensional TI.[5] One of the most remarkable and interesting features of TIs is that the bulk is an insulator with a band gap, while there are spin-split gapless bands localized at the edge or surface. Furthermore, these edge states form a Dirac cone in the simplest case, which indicates the high carrier mobility due to the zero effective mass. Therefore they are interesting not only in terms of basic science but also in industrial applications.

Bismuth telluride (Bi_2Te_3) is currently one of the most extensively studied three-dimensional TIs along with Bi_2Se_3.[6–8] The Te trigonal-lattice layer and Bi trigonal-lattice layer alternate to form a quintuple layer (QL) [see Figs. 1(b) and 1(c)], which is the stacking unit along the ⟨111⟩ direction. The interaction between neighboring QLs is weak (the gap between QLs is called the van der Waals gap) and therefore they can easily be cleaved along the (111) plane. It has been known that surface relaxation has a significant influence on the electronic structure of these layered materials. For example, it was debated whether the surface of Bi(111), which is another stacking material, has a significant surface relaxation or not in relation with the spin-orbit split-band dispersion. In Ref. 9, it was shown that the topmost Bi bilayer was nearly isolated from the underlying bulk, but the low-energy electron-diffraction (LEED) analysis shown in Ref. 10 indicated that there was only slight relaxation. In a more recent study, it was found that by depositing Ag on Bi_2Se_3, intercalation takes place and Ag goes inside the crystal and resides between the first and second QLs.[11] They predicted the expansion of the van der Waals gaps and the detachment of topmost QLs from the bulk crystal. It was concluded that this will lead to a relocation of the topological state beneath the detached quintuple layers. So it seems that understanding the surface relaxation is crucial to discuss the surface-state band dispersion accurately.

A single bilayer Bi(111) was previously theoretically predicted as a candidate of a two-dimensional TI.[12] The bilayer (BL) of Bi consists of two atomic layers and forms a hexagonal lattice. It cannot be formed on a Si(111) surface due to the formation of a pseudocubic {012}-oriented film below the critical coverage of $\sim$6 BL.[13] But recent research confirmed that Bi(111) can be grown on Bi_2Te_3(111) from 1 BL (Ref. 14) due to the relatively small lattice mismatch and similar crystal structure. Although it was shown that this Bi 1 BL/Bi_2Te_3 (Bi1BL hereafter) has a quite intriguing band dispersion, it is not still clear how the atomic structure is altered from the bulk Bi(111) due to this lattice mismatch.

As mentioned above, there are many works that have investigated the electronic structure of TIs and explored the exotic band dispersion. On the other hand, although it seems important to identify the atomic structures of TIs precisely, there are hardly any reports on them. Therefore in this paper, we studied the surface structures of Bi_2Te_3(111) and Bi1BL by LEED analysis (symmetrized automated tensor LEED, SATLEED). We found that the topmost quintuple layer of Bi_2Te_3(111) showed only a small relaxation compared to the bulk. In contrast, Bi1BL showed drastic expansion along the surface-normal direction which is likely a result of the contraction in the in-plane lattice constants. *Ab initio* calculations were also performed and the result indeed suggests that the band dispersion will change according to the degree of the surface relaxation of the Bi1BL.

All the film fabrication and measurements were done *in situ*. First, a clean Si(111)-7 × 7 surface was prepared on an *n*-type substrate (P-doped, 1–10 Ω cm at room temperature) by a cycle of resistive heat treatments. Then in a Te-rich atmosphere, Bi was deposited on the substrate at 215 °C to grow an 18 QL Bi_2Te_3 thin film. After postannealing for 100 min at the same temperature, the Bi_2Te_3(111) sample was obtained. The Bi1BL sample was prepared by depositing additional Bi on the Bi_2Te_3(111) film at room temperature. The surface structure analysis of Bi_2Te_3 and Bi1BL was performed with the LEED intensity vs voltage (IV) analysis. IV curves were obtained at 80 K, and their variations were within 1 K during the measurements. The LEED patterns with incident energy from 80 to 400 eV were recorded in steps of 1 eV by a digital CCD camera. IV curves of 14 inequivalent diffraction spots were obtained. In order to determine the surface structure, we calculated the IV curves in the tensor LEED to fit the experimental IV curves using the SATLEED package of Barbieri/Van Hove.[15] As shown in Figs. 1(c) and 3(c), each atomic layer was treated differently according to their environments. The in-plane lattice constant was determined from positions of the LEED spots. Angular momentum up to 17 ($l_{max} = 17$) was taken into account because of the strong

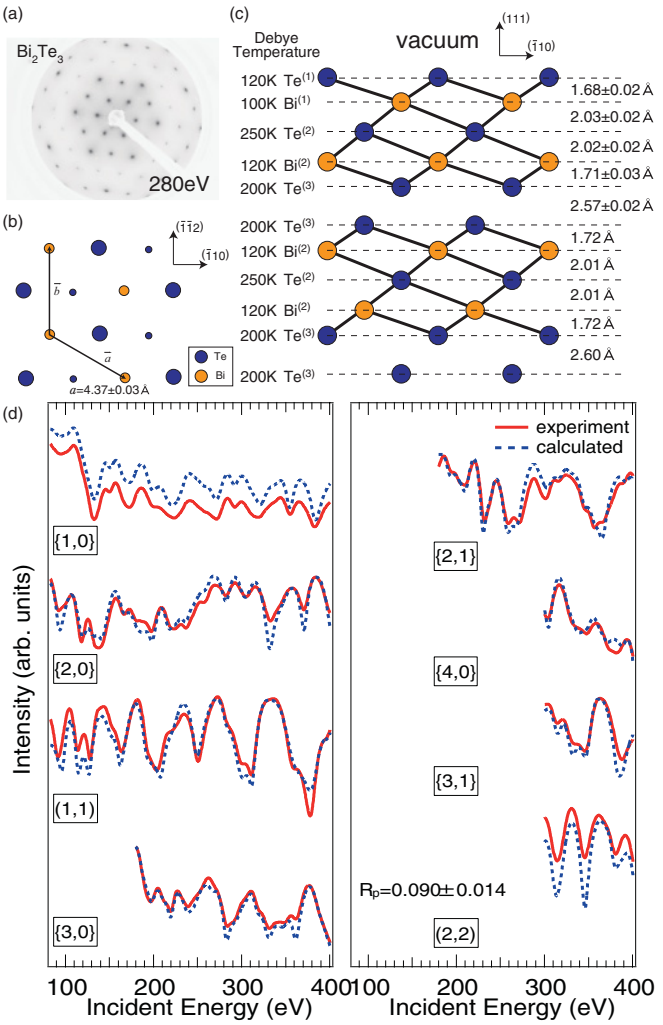

FIG. 1. (Color online) (a) LEED pattern of the 1×1 Bi_2Te_3(111) surface at 80 K. [(b), (c)] Top (b) and side (c) view of the Bi_2Te_3(111) surface. The orange (light gray) circles represent Bi and blue (dark gray) ones represent Te. (d) *IV* curves of the Bi_2Te_3(111) surface. The solid lines are experimentally obtained ones and dashed lines are calculated ones.

scattering of the heavy Bi atom ($Z = 83$). Considering the mean penetration depth of the incident electrons of ∼10 Å, only the surface QL (and the additional Bi 1BL in the case of the Bi1BL sample) was allowed to relax. In search of the optimal structure, the out-of-plane lattice constant of the underlying QLs was changed from 2% contraction to 2% expansion compared to the bulk value, and the Debye temperature of each atom was changed in steps of 10 K from 50 K up to 300 K.

First-principles calculations were performed using the WIEN2K computer code on the basis of the augmented plane wave + local orbitals method taking into account the spin-orbit interaction, and the generalized gradient approximation[17] has been used for the description of exchange-correlation potential.

Figure 1(a) is a LEED pattern of the 1×1 Bi_2Te_3(111) surface. Figure 1(d) shows the experimentally observed *IV* curves of symmetrically inequivalent spots and calculated ones for the optimized surface structure. Despite the $p3m1$

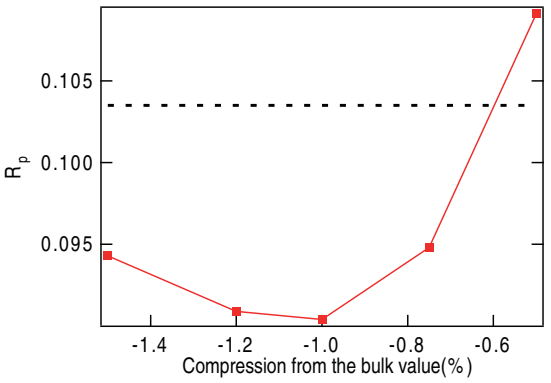

FIG. 2. (Color online) *R* factor vs the out-of-plane lattice compression of Bi_2Te_3. The dashed line indicates the upper limit of the reliability of R_p. The data points below this line is the uncertainty of the lattice constant.

symmetry of the Bi_2Te_3(111) surface, the symmetrically inequivalent spots, such as (1,0) and (0,1) spots, exhibited almost the same *IV* curves. This is because there are twin domains on the surface, which are related by a 180° rotation, and thus their superposition leads to the apparent twofold symmetry. Taking this double-domain surface into account, we took the average of the *IV* curves both in the calculation and in the experimental data such that $\{h,k\}$ is the average of (h,k) and (k,h) spots. Note that spots having the same mirror indices of h and k do not need averaging.

As shown in Fig. 1(d), there was excellent agreement between the measured *IV* curves and calculated ones for the Bi_2Te_3 surface. The Pendry reliability factor (*R* factor, R_p), which determines the degree of the agreement between the experimental *IV* curves and the calculated ones,[16] was 0.090. The in-plane lattice constant was determined as 4.37 ± 0.03 Å, which is equal to the bulk value 4.38 Å within the error [Fig. 1(b)]. Figure 2 shows the dependence of R_p on the out-of-plane lattice constant for the layers below the topmost QL. The optimized out-plane lattice constant was 30.19 ± 0.18 Å, which was slightly smaller than that of bulk Bi_2Te_3, which is 30.49 Å, by 1 ± 0.3%.[18]

The interlayer lattice parameters for the first QL are shown in Fig. 1(c) together with the Debye temperature. It can be seen that $Te^{(1)}$-$Bi^{(1)}$ atomic plane distance shrinks a little bit and the distance of the van der Waals gap (between $Te^{(3)}$-$Te^{(3)}$) becomes a bit smaller than the bulk value. The change is again only within 2%. Therefore it seems that there is only a slight relaxation at the topmost QL for Bi_2Te_3(111). Concerning the Debye temperature also shown in Fig. 1(c), the atoms near the surface tend to have lower Debye temperatures than those inside the bulk crystal [the bulk Debye temperature of Bi_2Te_3 (not layer resolved) is 160 K (Ref. 20)]. This tendency can be seen in many single-crystal surfaces, such as NaCl(100), KCl(100) (Ref. 19), and Bi(111).[10] As a consequence, there seems to be no significant relaxation on the surface of Bi_2Te_3.

Now let us move on to the Bi1BL sample. The LEED pattern is shown in Fig. 3(a) and is very much similar to that of the pristine Bi_2Te_3(111) [Fig. 1(a)]. This implies that the deposited Bi(111) 1 BL preserves the in-plane lattice constant of Bi_2Te_3, 4.37 ± 0.03 Å [Fig. 3(b)]. By comparing Figs. 1(d) and 3(d), it is found that the deposition of Bi1BL

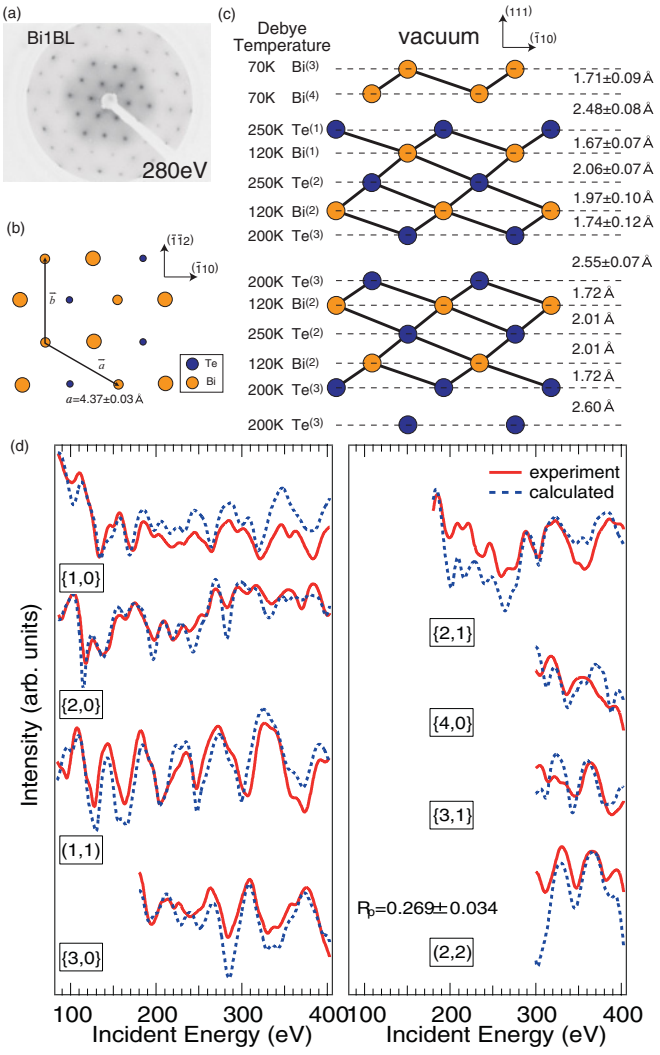

FIG. 3. (Color online) (a) LEED pattern of the bilayer Bi on Bi_2Te_3. [(b),(c)] Top (b) and side (c) view of the Bi bilayer on Bi_2Te_3. The orange (light gray) circles represent Bi and the blue (dark gray) ones represent Te. (d) IV curves of the bismuth bilayer on Bi_2Te_3. The solid lines are experimentally obtained ones and the dashed lines are calculated ones.

affected the shape of the IV curves a little bit. In particular, the {2,1} spot shows some change. The best-fit model is shown in Figs. 3(c) and 3(d) shows that the calculated IV curves agree fairly well with the experimental ones. The minimum R_p was 0.269 and the optimized out-of-plane lattice constant for the layers under the second QL was the same as that of the Bi_2Te_3 sample. The optimized intrabilayer ($Bi^{(3)}$-$Bi^{(4)}$) and interbilayer ($Bi^{(4)}$-$Te^{(1)}$) distance in Bi1BL was 1.71 and 2.48 Å, respectively. The corresponding values for bulk Bi are 1.59 and 2.35 Å, meaning that the Bi1BL is expanded by 7.5 and 5.5%, respectively. Figure 4 shows the R_p dependence on these parameters. There was no significant relaxation in the surface-normal direction in the underlying Bi_2Te_3. As a whole, the expansion is $7 \pm 3\%$. Compared to the $Te^{(3)}$-$Te^{(3)}$ distance between QLs (2.55 Å), the topmost interlayer $Bi^{(4)}$-$Te^{(1)}$ distance (2.48 Å) is smaller [Fig. 3(c)]. This can be qualitatively understood as follows. A calculation based on the density functional theory suggests that both

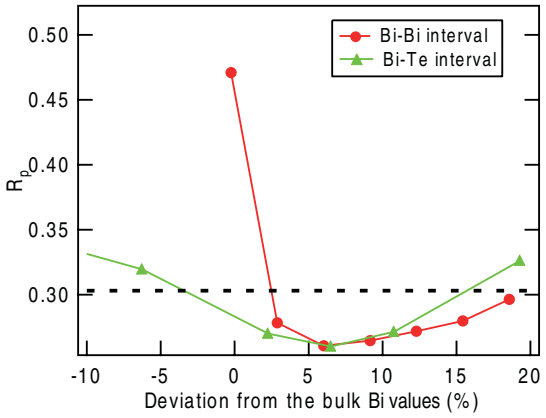

FIG. 4. (Color online) R factor as a function of the lattice expansion for the intrabilayer Bi distance (red or dark gray circles) and the distance between the bottom of the Bi bilayer and the topmost Te layer of Bi_2Te_3 (green or light gray triangles). The values are compared to bulk Bi values. The dashed line indicates the upper limit of the trustworthy R_p value.

covalent bonds and ionic bonds are formed between Bi atoms and Te atoms in a Bi_2Te_3 QL.[21] Since the electronegativity of Te is a little larger than Bi, Te atoms are negatively charged and Bi atoms are positively charged. Thus when the Te layer is replaced by a Bi layer, it can be expected that the $Bi^{(4)}$-$Te^{(1)}$ distance will be shorter than the $Te^{(3)}$-$Te^{(3)}$ (QL-QL) distance. Interestingly, $Te^{(1)}$ of the Bi_2Te_3 surface shows the same Debye temperature as $Te^{(2)}$ in Fig. 3(c), which is in contrast to that in the pristine Bi_2Te_3 [see Fig. 1(c)]. Probably this is because the Bi overlayer makes a similar environment for $Te^{(1)}$ and $Te^{(2)}$; both are in between Bi layers. The Debye temperatures of $Bi^{(3)}$ and $Bi^{(4)}$ are both 70 K, which were lower than that of $Bi^{(1)}$. It is notable that these values are consistent with the results of the preceding experiments on the single-crystal Bi (111) surface.[10]

The Bi 1BL on Bi_2Te_3 is commensurate to the Bi_2Te_3 surface, meaning that the parallel lattice constant of Bi_2Te_3 is smaller than that of bulk Bi by 3.5%. As a result, Bi1BL is elongated to the surface normal by $7 \pm 3\%$ so that the volume will be conserved. The calculated Poisson's ratio is 0.5 ± 0.1. This value exceeds the Poisson's ratio of bulk Bi (0.33) and is almost the maximum of the theoretically possible Poisson's ratio 0.5 for an elastic material. Therefore we can say that Bi1BL is strongly distorted. Such distortion (in-plane lattice contraction and out-of-plane lattice expansion) is also qualitatively consistent with the actual structure used to calculate the band dispersion shown in Ref. 14.[22]

In order to understand the influences of the Bi lattice distortion on the electronic structure, we performed first-principles calculations for the single bilayer Bi. Figures 5(a) and 5(b) show the band structures of a freestanding Bi bilayer along the high symmetry lines in the surface Brillouin zone [inset in Fig. 5(a)]. The distance between Bi layers is determined by minimizing the total energy, while the in-plane lattice constant is fixed. The optimized distances are close to the experimental values of 1.59 and 1.71 Å for the bulk Bi and the 1 BL Bi on the Bi_2Te_3 substrate in this work, respectively. The band gap is 0.1 and 0.4 eV for the former

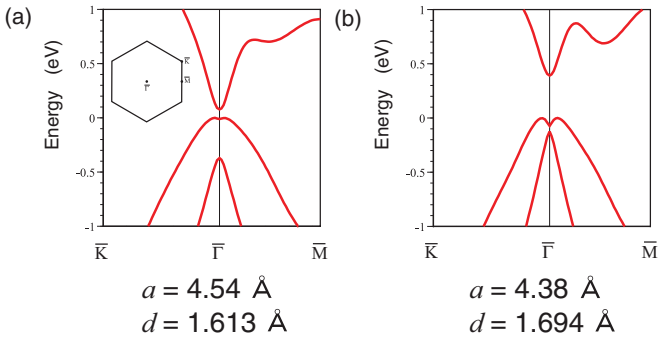

FIG. 5. (Color online) Calculated band structures of the single bilayer Bi with various lattice constants. a is the in-plane lattice constant and d is the distance between the two bismuth layers. The inset in (a) shows the Brillouin zone with high symmetry points.

(a) and latter (b) case, respectively. It can be easily recognized that the in-plane distortion has a great influence on the band structure. A wide energy gap of a TI film makes it easier to control the characteristics of the electrical conductivity of the edge states by electron or hole doping. Therefore, it seems like a good idea to grow a bilayer Bi on a substrate with a smaller in-plane lattice constant such as Bi_2Te_3 because the horizontal contraction and vertical expansion will be achieved in a natural way and thus result in the larger band gap, although the effects of the substrate itself also need to be taken into account.[14]

In summary, we have investigated the surface atomic structure of Bi_2Te_3 and Bi1BL by LEED IV analysis. It revealed a slight contraction of the surface of Bi_2Te_3 along the surface normal and the significant contraction (expansion) for the in-plane (out-of-plane) lattice parameters of bilayer Bi. Our *ab initio* calculations suggested that the strong distortion of the Bi bilayer helps obtain a wider energy gap, which is an advantage in easily tuning the properties of a topological insulator.

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