

Softening versus hardening transition in surface bilayer bonding of bismuth nanofilm

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We have found that the surface bilayer of Bi(001) undergoes an unusual reversible transition at 350 K, well below the bulk melting temperature. Surface Debye temperature abruptly decreases without an anharmonic signature and the vertical-to-lateral ratio of surface thermal expansion increases in a critical manner, as revealed by high-resolution diffraction measurement. Because of the metallic-covalent bilayer structure of semi-metal Bi, the most feasible explanation for the result is that bond softening occurs between the first and second bilayers at 350 K. This softening transition leads to the simultaneous hardening of the topmost intrabilayer bonds.

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I. INTRODUCTION

Bismuth and Bi-based low-dimensional nanostructures are promising building blocks for next-generation thermoelectric and spintronic devices. They exhibit remarkable refrigeration and power generation due to large thermoelectric effects^{1,2} and surface spin polarization induced by strong spin-orbit interaction (the Rashba effect),³ with recent growing interest in topological surface states invoking the quantum Hall effect.⁴⁻⁶ A significant part of these functionalities, as well as the thermal stability of Bi-based nanostructured materials, is determined by the character of the outermost atomic layers, which becomes more pronounced as their size decreases. For example, the surface states affect their thermoelectric performance⁷ and give rise to spin currents.^{5,6} It is thus desirable to control heat, charge, and spin transports through the outermost atomic layers.⁸ In particular, a crucial contribution to reducing thermal conductivity arises from phonon scattering and reflection at surfaces/interfaces,^{1,2,9} and thermal transport is a key issue for practical device applications on the nanometer scale.¹⁰ Therefore, elucidating the lattice dynamics and thermal properties of the Bi surfaces is of both scientific and technological importance.

Over the past few years, it has been clarified that the surfaces of elemental Bi take the same atomic configurations as those of bulk.¹¹ Bulk Bi crystallizes in the A7 (or α -As) structure common to group-V semimetals, which is stabilized by Jones-Peierls mechanism¹² and is visualized as consisting of bilayers stacked along the trigonal [001] axis in an ABC fashion [Fig. 1(a)]. Each atom possesses three nearest-neighbor bonds as “intrabilayer” bonds and three next-nearest-neighbor bonds as “interbilayer” bonds. The short intrabilayer bonds are covalent and much stronger than the long interbilayer bonds. The most prominent feature of this highly anisotropic bilayer structure is *metallic-covalent duality*, which is known to bring about various phase-transition phenomena.¹³⁻¹⁶ Such bilayer stability is confirmed by natural cleavage along the (001) plane of Bi crystals¹⁷ in a way akin to graphite.¹⁸ The Bi(001) surface is thus terminated with the bilayer [Fig. 1(a)], which appears to be a unique “buckled graphene” structure.^{19,20} While the first interlayer spacing (d_{12}) shows no significant relaxation, the second in-

terlayer spacing (d_{23}) yields a slight expansion relative to its bulk value.²¹ Taking the rather low bulk melting temperature of Bi ($T_{m,bulk}=544$ K) into account, room temperature (RT) should already be sufficiently high for the open-packed Bi(001) surface to be destabilized. So far, most preceding works have focused on two extreme cases of the temperature dependence of this surface, i.e., a static structure well below $T_{m,bulk}$ ²¹ and phase transitions near $T_{m,bulk}$,²² accordingly, investigations into the thermal behaviors in the intermediate temperature range are lacking for both the bulk and nanoscale objects of Bi.

Here, we report our experimental findings on the unusual transition behavior of the (001) surface of Bi nanofilms at

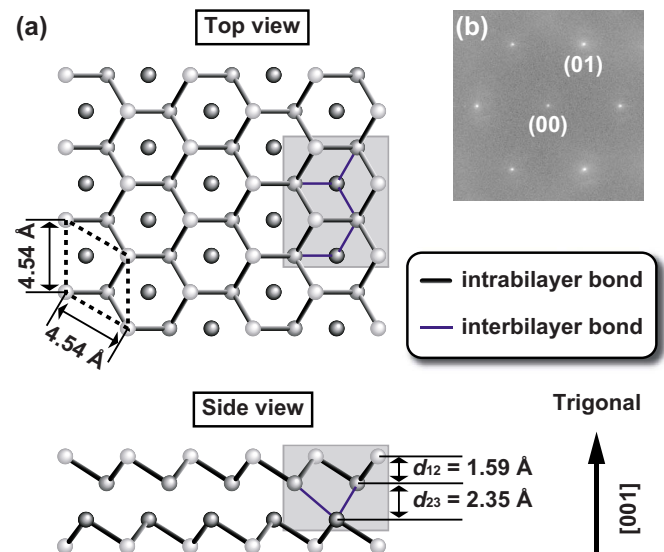


FIG. 1. (Color online) (a) Schematic illustration of the top and side views of the truncated-bulk crystal structure of Bi(001), showing the first three and four atomic layers, respectively. A two-dimensional unit cell with the lattice constant $a=4.54$ Å is indicated by the dotted lines. The first and second interlayer spacings at 140 K are $d_{12}=1.59$ Å and $d_{23}=2.35$ Å, respectively. The thick solid lines connecting pairs of Bi atoms denote the intrabilayer covalent bonds discussed in the text. The thin (blue) solid lines inside the shaded boxes denote the interbilayer bonds. (b) HRLEED pattern of a Bi(001) surface taken at primary energy $E=72.0$ eV.

moderate temperatures around RT. Debye temperature decreases and vertical-to-lateral thermal-expansion ratio increases above 350 K ($0.64T_{m,bulk}$), in a reversible and critical manner. The observed behavior is far from being explained by an ordinary premelting. After carefully inspecting the possible causes, we propose that the Bi(001) surface undergoes a softening transition of the outermost interlayer bonds accompanied by the hardening of the topmost intralayer bonds. The *softening vs hardening* transition is based on the metallic-covalent bilayer structure, thus providing an insight into the structural and dynamical properties of Bi-based nanomaterials.

II. EXPERIMENTAL METHOD

The experiments were carried out in an ultrahigh-vacuum ($<7 \times 10^{-11}$ Torr) permalloy chamber. The fabrication and growth mechanism of an atomically flat single-crystalline Bi nanofilm that provides a clean and ordered Bi(001) surface were described in detail elsewhere.^{23–25} The sample was cooled by a custom-made cryostat and heated by a tungsten resistive heater installed in a sample holder made of oxygen-free copper. The sample temperature was measured using a thermocouple attached to the end of the sample holder. The Bi(001) surfaces were characterized *in situ* by high-resolution low-energy electron diffraction (HRLEED). A sharp 1×1 LEED pattern was observed after annealing at 420 K [Fig. 1(b)]. All the measurements were performed under an isothermal condition with a temperature control of ± 1 K. This experimental scheme, combined with the well-defined material system, allows us to extract quantitative information about thermal behaviors in the topmost surface layer of Bi.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the peak intensities of the (00) spot measured during repetitive cycles of cooling and heating at the primary energy $E=72.0$ eV. In the Debye-Waller (D-W) model, the intensity attenuation is exponentially proportional to the scattering vector K^2 and mean-square oscillation amplitude $\langle u(T)^2 \rangle$ as follows: $-\ln(I/I_0) = \langle (\mathbf{K} \cdot \mathbf{u})^2 \rangle = K^2 \langle u^2 \rangle_K$. In the harmonic approximation, $\langle u^2 \rangle_K$ is proportional to T . It is apparent that the slope changes at 350 K, being steeper at higher temperatures. A similar additional intensity drop has been observed earlier on other metal surfaces and ascribed to premelting phenomena, such as thermal roughening and surface melting.²⁶ This is not the case, however, for the present Bi(001) surface, because no signature of surface disordering was detected throughout the temperature range considered. For example, the peak width of the (00) spot (i.e., surface step density) was proven to remain unchanged upon heating.²⁷ Furthermore, the ratio of the background-to-peak intensity stayed as low as ~ 0.02 at 400 K, which is well below the reported value for the creation and increased concentration of adatoms and/or vacancies.²⁸ Therefore, the change occurs just in the slope of the peak-intensity attenuation.

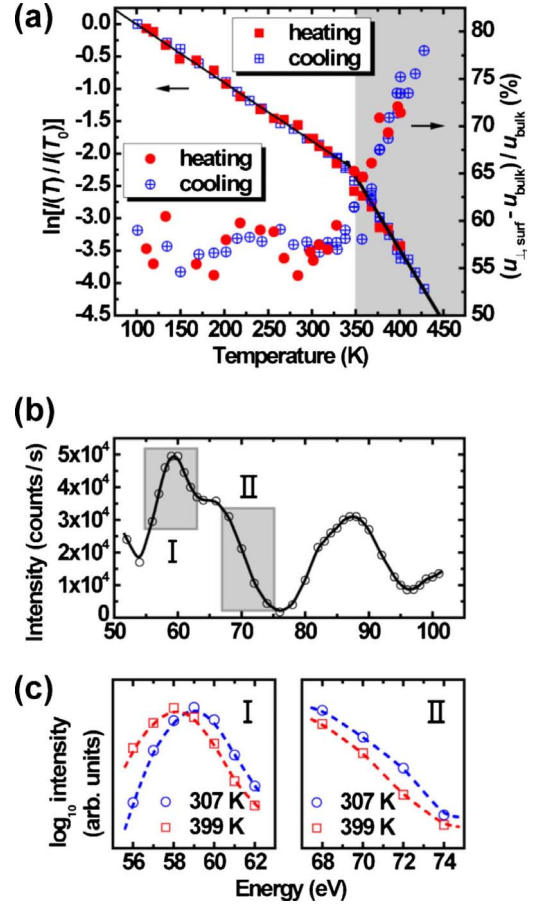


FIG. 2. (Color online) (a) Peak intensities of the (00) diffraction spot (squares) and the surface-to-bulk ratio of the normal component of atomic displacements u_{\perp} (circles) for a Bi(001) surface as a function of temperature with primary energy $E=72.0$ eV. The straight solid lines represent fits to $\ln[I(T)/I(T_0)]$ below (thin) and above (thick) 350 K, indicating the clear harmonic Debye-Waller behavior in each temperature regime but with different slopes. (b) (00) peak intensities as a function of the primary energy of the incident electron beam, $I(E)$ spectrum, taken at RT. The solid curves are guides to the eyes. (c) Comparison between the two temperatures of 307 K (blue circles) and 399 K (red squares) for each of the regions I (left) and II (right) designated in (b). The data are plotted on the logarithmic scale after normalization to the peak height at $E_p=58$ eV.

We also plotted surface-normal atomic displacements $(\langle u^2 \rangle_{\perp,surf})^{1/2} (\equiv u_{\perp,surf})$ normalized to the bulk value $u_{\perp,bulk}$ at the same temperature. Up to 350 K, $u_{\perp,surf}$ is larger than $u_{\perp,bulk}$ by 57%. Then, the surface-to-bulk ratio increases with temperature in a reversible and critical manner, reaching $\sim 80\%$ ($u_{\perp,surf}=0.26$ Å) at 430 K. We extracted an effective surface Debye temperature in two temperature regimes: $\theta_{D,surf}=76$ K ($T<350$ K) and 50 K ($T>350$ K). These two values are lower than $\theta_{D,bulk}=119$ K. Note that our result explains the discrepancy between two literature values, namely, $\theta_{D,surf}=71-88$ K obtained below 300 K²¹ and $\theta_{D,surf}=42$ and 48 K obtained above 300 K.²² The marked reduction in $\theta_{D,surf}$ above 350 K may have structural causes. However, we did not find obvious changes in LEED patterns or in intensity versus energy $I(E)$ spectra at different temperatures. There-

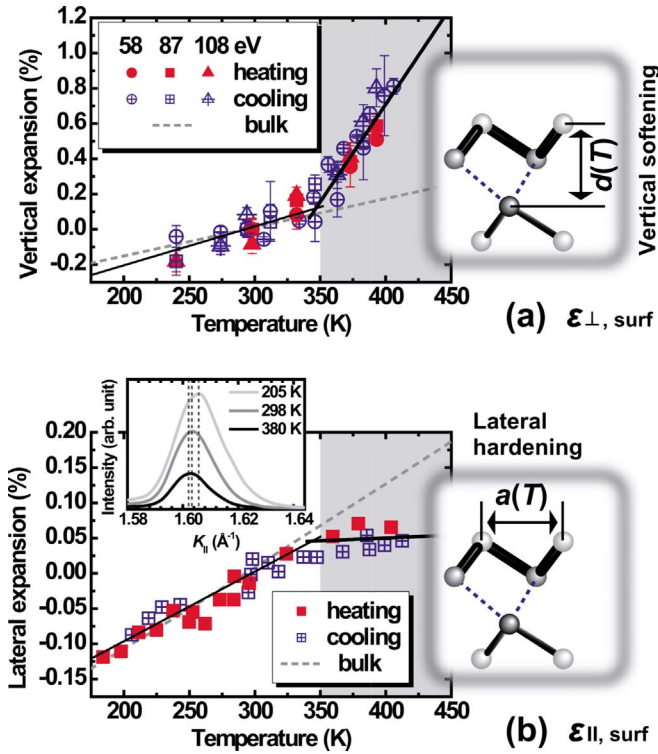


FIG. 3. (Color online) (a) Vertical and (b) lateral thermal expansions with respect to RT, deduced from the best-fit values for peak positions in $I(E)$ spectra [Fig. 2(c)] and (00)–(10) line scans, respectively. Standard deviation in the fits is indicated by the error bar, which is on the order of the symbol size in (b). The straight solid lines represent fits to the experimental data below (thin) and above (thick) 350 K. The corresponding bulk thermal expansions are also shown by dashed gray curves. $\varepsilon_{\perp,\text{surf}}$ in (a) indicates a marked increase in $d(T)$ above 350 K, possibly due to the softening of interbilayer bonds (inset). $\varepsilon_{\parallel,\text{surf}}$ in (b) indicates almost no change in $a(T)$ above 350 K, in accordance with the hardening of intralayer bonds (right inset). The left inset in (b) shows the (10) spot profiles at three different temperatures.

fore, there is no indication of a structural phase transition despite our naive expectation.

To gain deeper insight into this anomalous intensity drop, we closely examined the LEED $I(E)$ spectra of the (00) spot [Fig. 2(b)]. Regions I and II are magnified in Fig. 2(c) to directly compare two temperatures: 307 K (blue circles) and 399 K (red squares). We can see that the spectrum explicitly shifts toward lower energies (longer electron wavelengths) at higher temperatures. The shift of the $I(E)$ spectrum to lower energies manifests a surface vertical expansion, as demonstrated by Cao and Conrad.²⁸ In their peak-shift analysis, the vertical layer spacing is determined to be related to the peak position in the $I(E)$ spectrum, E_p , via the Bragg condition for a specular reflection. Since the bilayer spacing d is proportional to $E_p^{-1/2}$, the vertical thermal expansion is given by $\varepsilon_{\perp,\text{surf}} = [d(T) - d(\text{RT})]/d(\text{RT}) \approx [E_p(\text{RT})/E_p(T)]^{1/2} - 1$.

Figure 3(a) shows $\varepsilon_{\perp,\text{surf}}$ obtained during cooling and heating cycles for the three different energies $E_p = 58, 87,$ and 108 eV. $\varepsilon_{\perp,\text{surf}}$ increases with temperature. Up to 350 K, the fitted linear curve yields the coefficient of vertical thermal expansion $\alpha_{\perp,\text{surf}} = 23 \pm 4 (\times 10^{-6} \text{ K}^{-1})$ close to the

known value for bulk $\alpha_{\perp,\text{bulk}} = 16.8 (\times 10^{-6} \text{ K}^{-1})$.²⁹ However, $\varepsilon_{\perp,\text{surf}}$ increases more rapidly above 350 K, the same onset temperature as we found for the decrease in $\theta_{\text{D,surf}}$. We estimated $\varepsilon_{\perp,\text{surf}} = 0.8\%$ at 400 K, which is remarkably larger than the corresponding bulk value $\varepsilon_{\perp,\text{bulk}} = 0.17\%$. We thus conclude that the Bi(001) surface above 350 K exhibits an anomalous vertical expansion with $\alpha_{\perp,\text{surf}}$ that is six times as large as $\alpha_{\perp,\text{bulk}}$. Since thermal expansion is intimately related to the anharmonicity of interatomic forces in solids, the coincidence between the onset temperatures at which $\langle u^2 \rangle_{\perp,\text{surf}}$ and $\varepsilon_{\perp,\text{surf}}$ increase can be a signature of an enhanced anharmonicity.²⁶ Nevertheless, the steeper intensity drop above 350 K just stays harmonic ($\propto T$): it is far from being simply explained by the enhanced anharmonicity that should assume a gradual deviation from the D-W behavior (with T^2 and T^3 dependences).²⁸

We now discuss the observed unconventional thermal behaviors on the basis of the exotic bonding character of group-V semimetals. It is known that for the bulk A7 structure, the initial slopes of longitudinal-acoustic phonons are substantially smaller along the trigonal [001] direction than along in-plane directions.³⁰ Such elastic anisotropy is in agreement with the “weak” interbilayer bonding of the A7 structure, making its thermal expansion highly anisotropic ($\alpha_{\perp} > \alpha_{\parallel}$).²⁹ Bearing this in mind, one possible origin of the abrupt reduction in $\theta_{\text{D,surf}}$ is that the bonds between the first and second bilayers become sufficiently weak to soften the out-of-plane motion of atoms above 350 K. In turn, the softening transition of out-of-plane vibrations can drive the observed increase in $\varepsilon_{\perp,\text{surf}}$ [inset in Fig. 3(a)]. Our claim is further supported by recent arguments from first-principles calculations. According to Ref. 31, a negative, imaginary phonon mode appears at the T points of the A7 structure when volume increases by more than 10% of the equilibrium volume. Such a softening transition is unrealistic in bulk crystals (as melting already sets in prior to the 10% volume expansion upon heating) but it is still possible at free surfaces where phonons are generally softened compared with bulk ones.^{32,33} Indeed, a negligibly small difference in total energy for expanding surface interbilayer spacing (d_{23}) [see Fig. 1(a)] has been demonstrated by another calculation,²¹ indicating the inherent softness of the outermost interbilayer bonding and the tendency for the topmost bilayer to move toward the vacuum side.

The above phonon calculations have also predicted the decrease (increase) in phonon frequencies for the acoustic (optical) modes with increasing volume,³¹ which is quite consistent with experimental observations that the group-V semimetals enhance their structural anisotropy upon heating.³⁴ Thus, the softening of the outermost interbilayer bonds is suggested to be accompanied by the simultaneous hardening of the topmost intralayer bonds. The latter would be traceable from the lateral thermal expansion at the surface, $\varepsilon_{\parallel,\text{surf}} = [a(T) - a(\text{RT})]/a(\text{RT})$ [$a(T)$ being the lattice constant at a given temperature], which is directly derived from the distance between the (00) and (01) spots in line profiles during cooling and heating cycles. As can be seen from Fig. 3(b), the lateral thermal-expansion coefficient $\alpha_{\parallel,\text{surf}} = 9 \pm 2 (\times 10^{-6} \text{ K}^{-1})$ is in reasonable agreement with the bulk value $\alpha_{\parallel,\text{bulk}} = 11.4 (\times 10^{-6} \text{ K}^{-1})$.²⁹ Above 350 K,

however, $\epsilon_{\parallel,\text{surf}}$ seems indeed suppressed compared with its bulk counterpart, indicating the expected topmost-bilayer hardening [right inset in Fig. 3(b)]. Combining the effects shown in Figs. 3(a) and 3(b) produces a drastic enhancement of anisotropy in the surface expansion: the vertical-to-lateral ratio of the thermal-expansion coefficient $\alpha_{\perp,\text{surf}}/\alpha_{\parallel,\text{surf}}$ is increased from 2.5 ± 0.9 ($T < 350$ K) to roughly 130 ($T > 350$ K), which is much higher than the ratio of bulk As ($\alpha_{\perp,\text{bulk}}/\alpha_{\parallel,\text{bulk}} = 34$ at RT).²⁹

An additional argument in line with the *softening vs hardening* transition above 350 K is that it does not progress into further surface disordering, presumably owing to a reinforced covalent character in the topmost bilayer. It is likely that this transition involves the redistribution of the metallic and covalent bonding charges of the Bi(001) surface, most probably, involves charge transfer from the outermost interbilayer bonds to the topmost intrabilayer bonds. The topmost-bilayer hardening provides an additional atomistic explanation for the experimental observation and theoretical prediction that the surface melting of semimetal Bi remains blocked up to $T_{\text{m,bulk}}$.^{22,35,36}

IV. CONCLUDING REMARKS

In summary, we have found that, on the (001) surface of Bi nanofilms, $\theta_{\text{D,surf}}$ decreases and $\alpha_{\perp,\text{surf}}/\alpha_{\parallel,\text{surf}}$ increases dramatically at 350 K ($0.64T_{\text{m,bulk}}$) in a reversible and critical manner. Our findings are attributed to the softening transition of the outermost interbilayer bonds associated with the hardening of the topmost intrabilayer bonds, which is consistent with the metallic-covalent bilayer structure of Bi and the fact that the Bi(001) surface does not melt. The electronic origin of this new transition, such as the role of the huge spin-orbit interaction of Bi, has not yet been unveiled and should be addressed in the future.³⁷

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