

Dirac Cone with Helical Spin Polarization in Ultrathin α -Sn(001) Films

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Spin-split two-dimensional electronic states have been observed on ultrathin Sn(001) films grown on InSb(001) substrates. Angle-resolved photoelectron spectroscopy (ARPES) performed on these films revealed Dirac-cone-like linear dispersion around the $\bar{\Gamma}$ point of the surface Brillouin zone, suggesting nearly massless electrons belonging to 2D surface states. The states disperse across a band gap between bulklike quantum well states in the films. Moreover, both circular dichroism of ARPES and spin-resolved ARPES studies show helical spin polarization of the Dirac-cone-like surface states, suggesting a topologically protected character as in a bulk topological insulator (TI). These results indicate that a quasi-3D TI phase can be realized in ultrathin films of zero-gap semiconductors.

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Topological insulators (TIs) are emerging as a new state of quantum matter with a bulk band gap and odd number of relativistic Dirac fermions, characterized by spin-polarized massless Dirac-cone (DC) dispersion of the edge or surface states [1–5]. The unique properties of surface electrons of TIs are an encouraging playground to realize new electronic phenomena, such as the quantum spin-Hall effect [1,5,6], and dissipationless electron or spin transport [5,7,8].

For an application of the exotic surface states of TI to electronic or spintronic devices, one of the most promising candidates are epitaxially grown films of TIs, such as Bi₂Se₃ on SiC(0001) [9] and Si(111) [10,11], HgTe on CdTe(001) [12–14], and α -Sn on InSb(001) [15]. The growth on semiconductor substrates makes them easy to combine with usual semiconductor electronic devices. Furthermore, the epitaxial growth itself enables to manipulate the electronic structure of grown TI films. Structural strain introduced from a lattice mismatch with the substrate opens a band gap in bulk bands of HgTe [12–14] or α -Sn [15] films for thicknesses between 0.1 to 1 μ m. While the size of the band gap is only a few tens of meV, it is very important for these films as a TI; neither α -Sn nor HgTe without any strain are TIs but zero-gap semimetal. Quantum-size effect (QSE) [16] from film thicknesses changes the electronic structure of TI even further. Once the electrons are confined in very thin thickness, the bulk-band dispersion perpendicular to the film is no longer continuous but discrete, forming quantum-well (QW) states. Such quantization of bulk bands enhances the bulk band gap, as observed in a Bi₂Se₃ film [9] and the layered compound (PbSe)₅ \times (Bi₂Se₃)_{3m} [17]. The thickness of ultrathin films also influences surface DCs to open a gap at the Dirac point, because of the hybridization between the top and bottom DCs [9,18]. Ultrathin films provide therefore a fertile ground to manipulate the electronic structure of materials concerning TI.

Zero-gap semimetal α -Sn (gray-Sn) is a good candidate to examine the influence of the QSE on the electronic structure of TI. Once a finite band gap is introduced in α -Sn, it is predicted to become a 3D TI from theoretical calculations of the bulk bands [2,19]. Although the α phase of bulk Sn is not stable at room temperature (RT), the epitaxial Sn films grown on lattice-matched substrates, such as InSb(001) [20–22], InSb(111) [23–25], and CdTe(001) [20,26], show the stable α phase even above RT. This is because the lattice-matched substrate stabilizes the α phase of the epitaxial Sn film. While the growth behavior of such α -Sn films is well known, the surface band structure, that would show DC with nonzero band gap from QSE, has never been studied so far.

In this Letter, we report the surface-state evolution of α -Sn(001) films grown on InSb(001) with various thickness of the films. In a certain range of thickness, the surface state showed DC-like dispersion, measured with angle-resolved photoelectron spectroscopy (ARPES). Both spin-resolved ARPES and circular dichroism of ARPES showed helical spin polarization of the DC-like surface state. With smaller thicknesses, we also observed the gap opening onto the DC-like surface states. Based on these results, we demonstrated that QSE can open a bulk band gap in zero-gap semimetal to realize an ultrathin quasi-3D TI.

We grew the α -Sn(001) films on InSb(001) substrates covered with 1 ML of Bi [1 ML is defined as the atom density of bulk-truncated InSb(001)]. With this procedure, Bi segregates at the surface during the Sn growth and forms the topmost atomic plane of the sample. Our Bi/Sn(001) films showed the low-background and sharp-spot low-energy electron diffraction (LEED) pattern as shown in Fig. 1(a), indicating the growth of a well-ordered Bi/Sn(001) film. Based on the double-domain (2×1) periodicity in the LEED pattern, Bi atoms possibly form a dimer row, terminating the dangling bonds on the surface. The detailed procedure of the sample growth, its

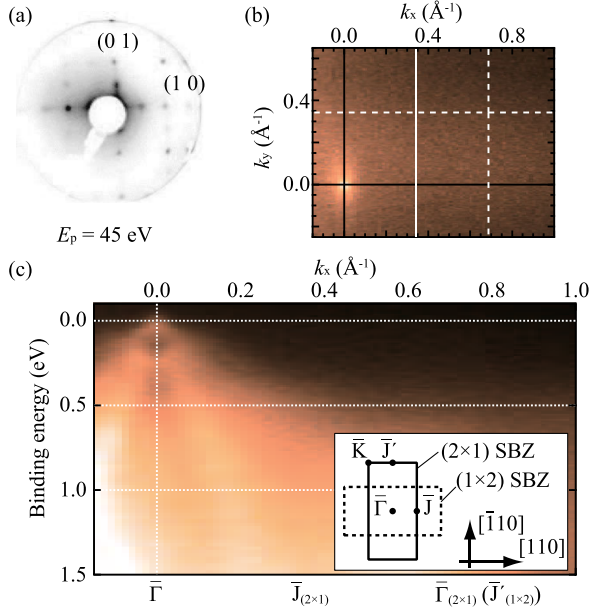


FIG. 1 (color online). (a) LEED pattern of the 12 ML Sn(001) film. (b),(c) Fermi contour (b) and the band dispersion along $[110]$ (c) measured by ARPES with $h\nu = 19$ eV. Solid and dashed lines in (b) correspond to (2×1) and (1×2) surface Brillouin zones depicted in the inset in (c), respectively. The inset also shows our definition of the coordinates. k_x (k_y) is defined as parallel to $[110]$ ($[\bar{1}\bar{1}0]$). All data were taken at room temperature (RT).

characterization, and the role of the surface Bi are shown in the Supplemental Material [27].

ARPES measurements were performed at the CASSIOPEE beam line (SOLEIL, France) with an energy

resolution of 20 meV, using linearly and left- or right-circularly polarized lights. The photon-incident plane is $(\bar{1}10)$ and the electric field of the linearly polarized photons lies in the incident plane. Figures 1(b) and 1(c) are the Fermi contour and the band dispersion along $[110]$ on a 30 ML Bi/Sn(001) film, respectively. There are no metallic electronic states crossing the Fermi level (E_F) except at $\bar{\Gamma}$. This state does not exhibit the (2×1) surface periodicity, suggesting that it originates from the subsurface Sn layers.

Figure 2 shows a series of ARPES intensity plots of the Bi/Sn(001) films from 12 to 34 ML taken along $[\bar{1}10]$ (a)–(e) and $[110]$ (f)–(j) with linearly polarized photons. At 12 ML, there are two bands S_1 and S_2 dispersing upwards and downwards from $\bar{\Gamma}$, respectively, as shown in Figs. 2(a) and 2(f). S_2 disperses almost linearly, showing quite a small effective mass. S_1 and S_2 show no energy shifts with different photon energies, indicating a 2D character. There is a finite gap of 150 meV between S_1 and S_2 . S_2 shifts upwards at 20 and 24 ML and S_1 is no longer observable below E_F for these thicknesses. A way to observe electronic states above E_F is presented in the following part. The dispersions of S_2 up to 24 ML are isotropic along $[110]$ and $[\bar{1}10]$. On the thicker films (30 and 34 ML), S_2 shifts downwards and S_1 appears again along $[\bar{1}10]$; the gap between S_1 and S_2 is now of 200 meV. However, the measurement along $[110]$ shows another surface state S'_2 [see Figs. 2(i) and 2(j)], dispersing between S_2 and S_1 , which degenerates with S_1 at $\bar{\Gamma}$. Hence, films thicker than 30 ML support metallic surface states which disperse across E_F continuously: this is a characteristic of topologically protected surface states of TIs. In addition, we observe another feature along $[110]$

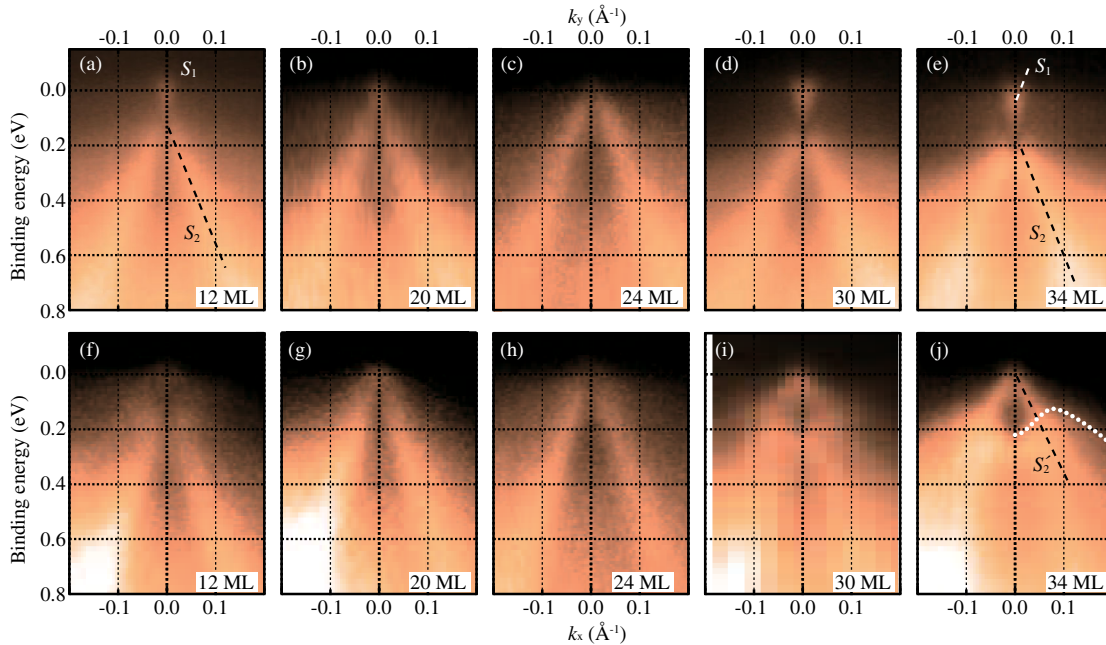


FIG. 2 (color online). (a)–(e) ARPES intensity plots of 12–34 ML films along $[\bar{1}10]$ measured with $h\nu = 19$ eV at RT. (f)–(j) The same as (a)–(e) but taken along $[110]$. Lines are guides for the eye.

whose upper edge is indicated by a dotted line in Fig. 2(j). It does not show any obvious peak, suggesting its origin from bulklike QW bands. Since the surface has two domains with 90° rotation, as shown by the LEED pattern, the dispersion of the initial states should be isotropic along these two directions. The differences between them are due to the parities of the surface states with respect to the measurement planes: (110) for (a)–(e) and $(\bar{1}\bar{1}0)$ for (f)–(j). Detailed discussion is provided in the Supplemental Material [27].

In order to obtain the surface-state band dispersion above E_F , we divided the ARPES spectra at 24 ML by Fermi-Dirac distribution function convolved with the instrumental resolution to take into account thermally populated electrons there. To increase the populations of thermally-excited electrons, the measurement was done at 450 K. The result, Fig. 3(a), shows a linear DC without any gap, with a Dirac point at ~ 20 meV above E_F . The velocity of electrons is 7.3×10^5 m/s, uniform from 0.6 to -0.15 eV. At the Dirac point, it is much larger than those

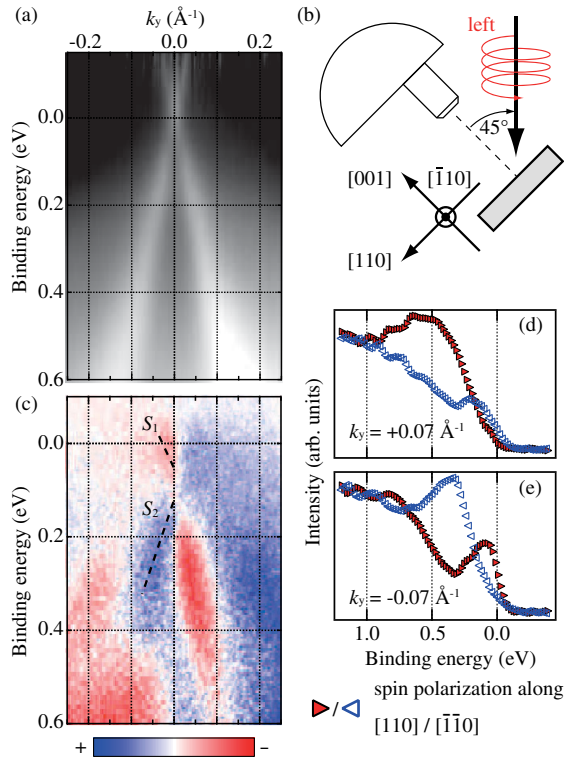


FIG. 3 (color online). (a) ARPES intensity plot of the 24 ML film along $[\bar{1}\bar{1}0]$ measured with $h\nu = 19$ eV, divided by the Fermi-Dirac distribution at 450 K function convolved with the instrumental resolution. (b) Experimental geometry in this work. (c) ARPES circular-dichroism plot of the 30 ML film taken with 19 eV photons at RT. Dichroism is obtained by subtracting the intensities of left-circularly polarized photons from those of right-circularly polarized ones. (d),(e) Spin-resolved ARPES spectra taken at RT with spin polarization toward $[110]/[\bar{1}\bar{1}0]$. The acceptance angle for the spin-resolved ARPES corresponds to $\Delta k_y = \pm 0.06 \text{ \AA}^{-1}$.

of typical 3D TIs, such as Bi_2Se_3 (2.9×10^5 m/s) and TlBiSe_2 (3.9×10^5 m/s) [28], and close to that of graphene (1×10^6 m/s) [29].

One of the most salient characteristics of DCs on TIs is the helical spin polarization. In other words, the electrons belonging to such states are spin polarized toward the direction perpendicular to both the wave vector k_{\parallel} and the surface normal. In order to evaluate the polarization of the surface state on the Bi/Sn(001) films, we measured both circular dichroism of ARPES and spin-resolved ARPES. As depicted schematically in Fig. 3(b), the incident circularly polarized photons were in the $(\bar{1}\bar{1}0)$ plane in our experimental geometry, and hence the helicity of the photons should probe the spin polarization along $[110]$ or $[001]$ [30]. Figure 3(c) is the circular dichroism map measured along $[\bar{1}\bar{1}0]$. To also observe the upper part of DC, we measured dichroism of ARPES in the 30 ML film, where both S_1 and S_2 are below E_F . They both show a clear dichroic effect. On S_1 , it is positive (negative) for $k_y > 0$ ($k_y < 0$); it is the opposite for S_2 . Such dichroic behavior is consistent with the helical spin polarizations of the non-trivial surface states on TI. In addition, there is another feature dispersing downwards from 0.2 to 0.6 eV with $|k_y| > 0.15 \text{ \AA}^{-1}$. It overlaps the peakless ARPES feature observed in Fig. 2(j).

Figures 3(d) and 3(e), are spin-resolved ARPES spectra measured at $k_y = 0.07$ and -0.07 \AA^{-1} , respectively, with linearly polarized photons at $h\nu = 19$ eV. The overall energy resolution was set to 120 meV and the angular acceptance of the detector was $\pm 1.8^\circ$ ($\pm 0.06 \text{ \AA}^{-1}$ with 19 eV photons). As shown in the spin-resolved spectra, S_1 is spin polarized towards $[\bar{1}\bar{1}]$ ($[110]$) at positive (negative) value of k_y , and those for S_2 are the opposite. They correspond to clockwise (CW) helicity for the lower cone S_2 and counter CW (CCW) for the upper cone S_1 . Simultaneously, we also measured the spin polarization along the surface normal. It shows almost negligible polarizations, indicating that the spin polarization of the DC on the Sn(001) films lies almost completely in the in-plane direction. It could be due to the absence of the C_3 symmetry on the (001) surface [31].

To obtain further insight into the electronic structure of the Bi/Sn(001) films, we performed density-functional-theory (DFT) calculations. We used the “augmented plane wave + local orbitals” method implemented in the WIEN2K code [32] taking spin-orbit interaction into account. We adopted the modified Becke and Johnson potential together with the exchange-correlation potential constructed by using the local density approximation [33,34]. The film was modeled by a symmetric slab of 32 Sn layers with the surface covered with (2×1) dimers of Bi, the structure of which was energetically optimized down to the 12th Sn layer.

Figure 4(a) shows the calculated states along $[110]$ and $[\bar{1}\bar{1}0]$. The contrasts (colors, online) of the circles represent

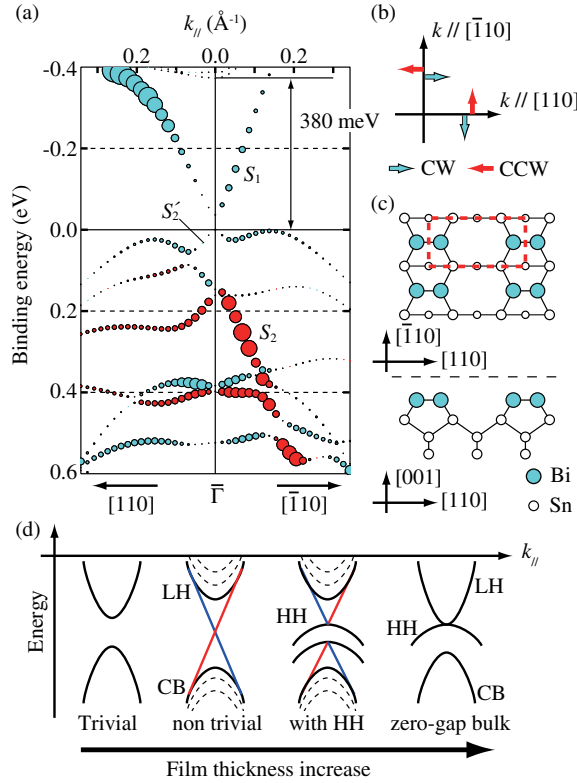


FIG. 4 (color online). (a) Calculated band structure along $[110]$ and $[\bar{1}10]$ for the slab of 32 Sn layers covered with Bi dimers. The radii of the circles are defined by the function in the text (1). The contrasts (colors) of the circles represent the spin polarization of each state. (b) Definition of the spin polarization directions. (c) Schematic picture of the assumed atomic structure for the DFT calculation. A dashed rectangle denotes the (2×1) unit cell. (d) Schematic drawings of the surface-state evolution on Sn(001) films with respect to light-hole (LH), heavy-hole (HH), and conduction-band (CB) bulklike QW states.

the spin polarization orientation of each state as defined in Fig. 4(b). The radii of the circles $R_{k_{\parallel}, E}$ are defined by the function

$$R_{k_{\parallel}, E} \propto \left| \sum_{i=1}^6 (|\langle \phi_{\text{CW}}^i | \Psi_{k_{\parallel}, E} \rangle|^2 - |\langle \phi_{\text{CCW}}^i | \Psi_{k_{\parallel}, E} \rangle|^2) \right|, \quad (1)$$

where $|\phi_{\text{CW}}^i\rangle$ ($|\phi_{\text{CCW}}^i\rangle$) represents the atomic orbital in the i th Sn layer with CW (CCW) spin polarization, and $|\Psi_{k_{\parallel}, E}\rangle$ is the eigenfunction of the calculated state at (k_{\parallel}, E) . Thus, the large circles in Fig. 4(a) represent the states which are spin polarized towards the CW or CCW directions and localized in the surface Sn layers.

As shown in Fig. 4(a), the calculated spin-polarized upper cone S_1 and lower cone S_2 agree with those experimentally observed. All states are calculated with smaller binding energies of ~ 80 meV than what are observed. Since the films we measured are double-domain ones, the overlap of the calculated states along $[110]$ and $[\bar{1}10]$ should be observed by ARPES. S_1 is isotropic along both

lines and the observed S_2 bands would originate from $[\bar{1}10]$. In addition, along $[110]$, there is another band S_2' which agrees with that observed along k_x on the 34 ML film [see Fig. 2(j)]. The upper edge of the heavy-hole-like QW states is also spin polarized around $\bar{\Gamma}$, possibly due to the hybridization with DCs. It could be the origin of the circular dichroism observed at $|k_y| > 0.15 \text{ \AA}^{-1}$. The band gap between bulklike QWs around $\bar{\Gamma}$ is 380 meV. Counting in whole SBZ, the gap is 230 meV: the conduction band minimum is around \bar{J}' . For thinner films, the agreement between experiment and calculation is rather poor since the substrate effect cannot be neglected.

In order to understand the role of surface Bi, we calculated Sn slabs with various surface structures without Bi. The slabs with dangling bonds [such as the (2×1) clean surface] made the other surface states dispersing around E_F which is not observed in this work. On the other hand, once the dangling bonds are saturated by adatoms, such as Bi and H, these artificial surface states disappear. Therefore, the main role of Bi on the Bi/Sn(001) films is probably to saturate the surface dangling bonds. The detailed results are in the Supplemental Material [27].

The spin polarization orientations calculated for S_1 (CW) and S_2 (CCW) are opposite to those observed by spin-resolved ARPES: CW (CCW) for S_2 (S_1). This is due to the photoelectron spin flipping due to the polarization of photons [35]. According to Ref. [35], the linearly polarized photons in our experimental geometry flip the spin polarization of the photoelectrons measured along $[110]$ with respect to the initial states.

In order to explain the surface-state band evolutions observed in this work, we propose the following scenario [see Fig. 4(d)]. (i) For very thin films (12 ML), the strong interference between the top and bottom surfaces opens the band gap on a DC [9,11,18]. (ii) By increasing the thickness, the topologically protected DC appears in the band gap because the interference between both faces become weak. It corresponds to thicknesses from 20 to 24 MLs in this work. (iii) At higher thicknesses, QW states with heavy-hole character appear in the gap and hybridize with DC. In this case, the pristine Dirac point lies below the topmost heavy-hole-QW state. Note that the upper part of the DC is still dispersing continuously in the gap between bulklike QW states. This case corresponds to the films with thicknesses above 30 ML and consistent with what is calculated. (iv) At infinite thickness, the gap between heavy-hole and light-hole QWs closes and the system becomes a 3D zero-gap semimetal. Based on this model, phase (ii) and (iii) can be regarded as TI with spin-polarized DC. Since such a TI phase can be achieved only for finite thicknesses, it could be categorized as “quasi-3D” TI. Moreover, since the QW states in (ii) and (iii) have the inverted band structure which is necessary for TI, it would also hold the 1D edge states at the edge of the QW, as in the case of HgTe QW [1,36].

In conclusion, we have reported Dirac-cone-like dispersion of surface states of α -Sn(001) films covered with 1 ML of Bi grown on InSb(001) substrates. Both the spin-resolved ARPES and circular dichroism of ARPES indicate helical spin polarization of the Dirac-cone-like surface states. A band gap in the film is estimated to be 230 meV showing that a new type of TI phase can be fabricated with ultrathin films of zero-gap semiconductors. Based on the evolution of Dirac-cone-like surface states with film thicknesses, we have demonstrated a new opportunity to fabricate ultrathin TI films with thicknesses down to few nm on conventional semiconductors. These results should offer new perspectives of applications in miniaturized electronic or spintronic devices.

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