Giant Out-of-Plane Spin Component and the Asymmetry of Spin Polarization in Surface Rashba States of Bismuth Thin Film

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We have performed high-resolution spin- and angle-resolved photoemission spectroscopy of bismuth thin film on Si(111) to investigate the spin structure of surface states. Unlike the conventional Rashba splitting, the magnitude of the in-plane spin polarization is asymmetric between the two elongated surface hole pockets across the zone center. Moreover, we uncovered a giant out-of-plane spin polarization as large as the in-plane counterpart which switches the sign across the $\bar{\Gamma}$-$\bar{M}$ line. We discuss the present finding in terms of the symmetry breaking and the many-body effects.

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One of the challenges in developing a new spintronic device is to generate spin-polarized electrons without applying a magnetic field. Spin-orbit coupling (SOC) enables the generation and manipulation of spin-polarized electrons solely by an electric field, since the electric field acts on a moving charge carrier as an effective magnetic field. In nonmagnetic solids, the electronic states with opposite spin have the same energy (Kramers' degeneracy) because of the time-reversal and the space-inversion symmetries (TRS and SIS). On the other hand, the spin degeneracy is lifted by the SOC in the structural-inversion asymmetric case, resulting in the splitting of energy bands (Rashba effect [1]). This Rashba effect leads to the vortical spin structure of surface bands where the spin vector points parallel to the surface and perpendicular to the measured momentum (k), as predicted by the theory [1] and also experimentally confirmed in Au(111) [2–4]. Angle-resolved photoemission spectroscopy (ARPES) has played a crucial role in establishing the Rashba effect, by directly observing the spin-split energy bands in noble metal surfaces [2–4], group-V semimetals and their alloy surfaces [5–13], as well as heavy-atom adsorbed semiconductor surfaces [14–18].

The Group-V semimetal bismuth (Bi) is a prime candidate to investigate the surface Rashba effect, since the splitting is fairly large owing to the heavy mass of the Bi atom. Ast and Höchst [7] reported the existence of two different surface-derived Fermi surfaces (FSs) in Bi(111), a small hexagonal electron pocket centered at the $\bar{\Gamma}$ point and six elongated hole pockets. Koroteev *et al.* [8] have concluded that these two different FSs originate in the spin-split bands due to the strong SOC. More recent spin-resolved (SR) ARPES of Bi [10,11] elucidated that the band splitting indeed derives from the Rashba splitting where the in-plane spin polarization (SP) vector is antisymmetric with respect to the zone center, as expected from the theory [1]. However, it is unclear to what extent the so-far believed simple vortical spin structure is adequate. A possible deviation would be crucial in the correct understanding of the surface properties of the Rashba system, and it would also open the way to realizing exotic quantum states in topological insulators.

In this Letter, we demonstrate that the surface spin states of Bi thin film exhibit unprecedented characters unlike the conventional Rashba splitting, by a SR-ARPES measurement with greatly improved resolution. Major findings of the present work are (i) the in-plane SP is remarkably suppressed on a half of six elongated hole pockets, and (ii) a giant out-of-plane SP is observed. These unconventional features are discussed in terms of the symmetry breaking and the many-body effects.

To prepare a Bi thin film, we cleaned a Si(111) substrate at 1000 °C to obtain the well-ordered 7×7 surface, then deposited Bi atoms at room temperature, and annealed the film at 150 °C. The 1×1 surface structure is confirmed by the low-energy electron diffraction (LEED) measurement and the film thickness is estimated to be 40 bilayers. ARPES measurements were performed using a SR-ARPES spectrometer at Tohoku University [19] equipped with a xenon discharge lamp [20]. We used one of the Xe I lines (8.437 eV) to excite photoelectrons. The energy resolutions during the SR- and regular ARPES measurements are 40 and 6 meV, respectively. We used the Sherman function value of 0.07 to obtain the SR-ARPES spectra.

Figure 1(a) shows the band dispersion and the FS of Bi/Si(111) around the $\bar{\Gamma}$-$\bar{M}$ line of the surface Brillouin zone (BZ). We identify a small FS (S_1) centered at the $\bar{\Gamma}$ point and surrounding elongated pockets (S_2), together with the ellipsoidal pocket (S_3) near the $\bar{M}$ point. Judging from the band dispersion in Figs. 1(a) and 1(b), the S_1 and S_3 FSs are ascribed to the electron pockets, while the S_2 FS to the hole pocket [5,7–10]. All of these bands and FSs are attributed to the surface states, while most of the bands located at the binding energy (E_B) higher than ~0.2 eV belong to the tail of the quantum well states (QWSs).

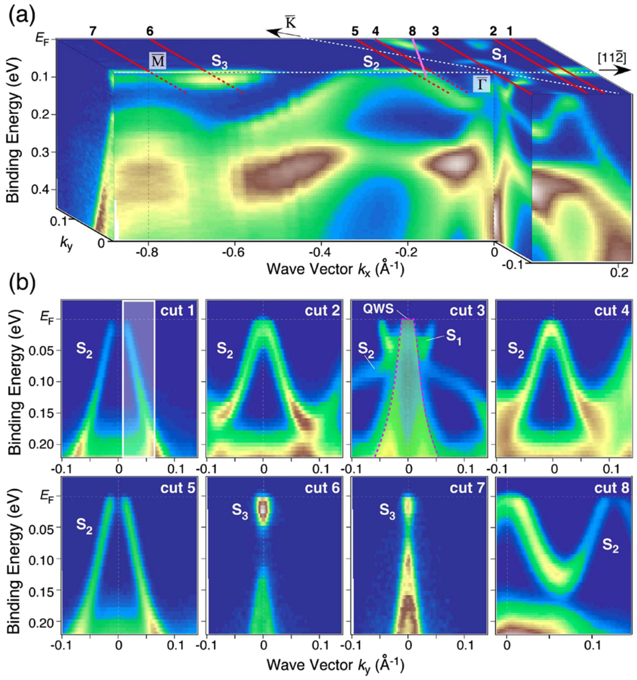

FIG. 1 (color online). (a) 3D plots of near-E_F ARPES intensity of Bi/Si(111) around the $\bar{\Gamma}$-$\bar{M}$ cut of the surface BZ as a function of the in-plane wave vector and E_B, measured at $T = 30$ K. The [11$\bar{2}$] direction of the silicon substrate is also indicated. (b) ARPES intensity as a function of E_B and k_y for several cuts indicated by red or pink lines (cuts 1–8) in (a). Area enclosed by the white rectangle in cut 1 is an example of the k integration window where the data in Fig. 2 are obtained.

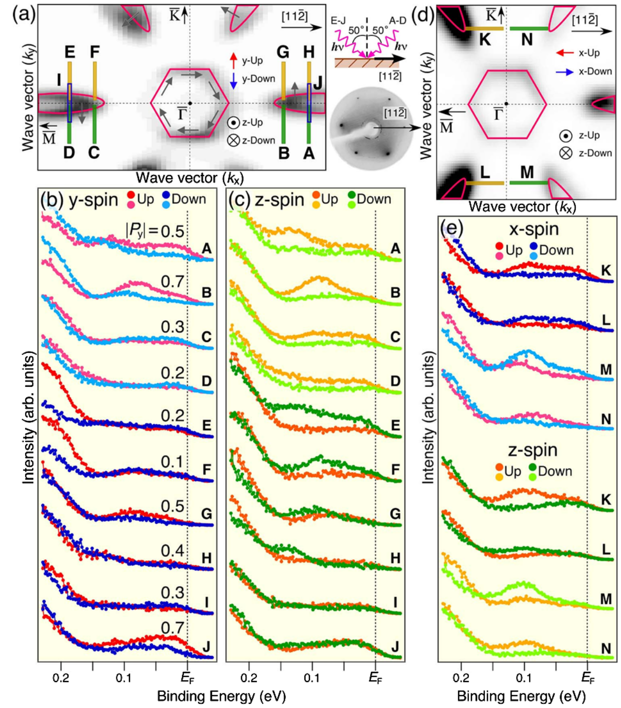

FIG. 2 (color online). (a) Near-E_F ARPES intensity of Bi/Si(111) as a function of k_x and k_y around the $\bar{\Gamma}$-$\bar{M}$ line. Red lines are guides for the FS of the surface bands. Lines A–J represent the k region where the spin-resolved EDCs in (b) and (c) were obtained. The [11$\bar{2}$] axis points to the positive x direction. The data in regions E–J were taken by rotating the sample by 180° with respect to those in regions A–D. The LEED pattern and geometry of the incident beam with respect to the [11$\bar{2}$] axis are indicated in the right panel. Expected spin configuration from the normal Rashba SOC is indicated by gray arrows. Definition of the spin vectors for y- and z-spin components is also indicated. (b), (c) SR-EDCs in k regions A–J, for y- and z-spin components, respectively. Maximum value of $|P_y|$ for the S_2 band is also indicated in (b). (d) ARPES intensity around the $\bar{\Gamma}$-$\bar{K}$ line together with the measured k regions K–N. (e) Corresponding SR-EDCs for both x- and z-spin components.

Now we turn to the SR-ARPES data. We focus on the S_2 band where a quite anomalous behavior is clearly observed. In Figs. 2(b) and 2(c), we display the near-E_F SR energy distribution curves (EDCs) for in-plane (y) and out-of-plane (z) spin components measured in various k regions, A–J shown in Fig. 2(a). When we discuss the complicated spin structure of the Rashba states which strongly depends on k, it is of particular importance to measure the SR-EDCs by specifying the absolute k location in the 2D BZ, since even a subtle misalignment of the sample orientation would cause a significant error in determining the spin polarization. In the present geometry of the ARPES spectrometer [19], we simultaneously collect the angular dependence of the ARPES intensity (non-SR) and a set of SR EDCs [see,, e.g., Fig. 1(b) and 2(b)], making it possible to specify the k region with higher accuracy than previous studies [10,11].

As displayed in Figs. 2(b) and 2(c), the EDC mainly consists of two components, a slopelike feature which rapidly increases its intensity at $E_B > 0.15$ eV, and a weaker broad feature at E_F-0.1 eV. The former corresponds to the tail of the QWS, while the latter is assigned as the S_2 band. The broad nature of the S_2 band is due to the k-integration effect of the highly dispersive S_2 band. In an ideal 2D Rashba picture, the in-plane spin has a vortical structure as denoted by gray arrows in Fig. 2(a). First we discuss the in-plane (y-axis) SP in regions A-D. In this sample geometry, the [11$\bar{2}$] axis of the silicon substrate points to the positive x direction and the angle between the incident beam direction and the [11$\bar{2}$] axis is about 40° (see right panel). As seen in Fig. 2(b), the SR-EDCs of the S_2 band in regions A and B are dominated by the up spin, while the down spin is slightly superior in regions C and D. This indicates that the in-plane spin direction is basically reversed in the two opposite S_2 pockets across the $\bar{\Gamma}$ point, qualitatively consistent with the Rashba picture [9–11]. However, a closer look also reveals that the SP is markedly suppressed in C and D. In fact, the magnitude of the SP along the y direction $|P_y|$, defined as $P = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$ where $N_\uparrow$ and $N_\downarrow$ are the spectral intensity of the up- and down-spin states, respectively, is 0.5–0.7 in regions A and B, while it is 0.2–0.3 in regions C and D. This is unexpected since $|P_y|$ should keep the same value across the $\bar{\Gamma}$ point in the normal Rashba picture. One may argue that the observed y-spin asymmetry could originate in the geometry of the experiment. To clarify this point, we rotated the sample by 180° so that the angle between the incident beam and the $[11\bar{2}]$ axis becomes $\sim$140°. The result is shown for regions E–H (also regions I and J). In this geometry, the overall intensity of the S_2 band is relatively suppressed, likely due to the photoexcitation selection rule, whereas the trend of y-spin asymmetry still holds. In fact, the estimated maximum $|P_y|$ of the S_2 band in regions E and F (0.1–0.2) is much smaller than that in regions G–H (0.4–0.5). A similar trend is also recognized by comparing the EDCs between regions I and J. These results strongly suggest that the observed y-spin asymmetry is robust to the variation of the sample geometry.

Besides the unusual asymmetry in the in-plane SP, we uncovered a sizable out-of-plane (z) spin component. Figure 2(c) plots the SR-EDCs for the z-spin component. We immediately notice that there exists a sizable difference between the up- and down-spin states [21]. Surprisingly, the magnitude of the z-axis SP $|P_z|$ (0.4–0.7) is as large as that of $|P_y|$, establishing that the spin of the S_2 band rotates out of the surface. In addition, P_z abruptly switches the sign even on a single FS sheet: the down-spin state is stronger in the positive k_y (regions E–H) while the up-spin state is stronger in the negative k_y (regions A–D). This suggests that the sign of the z-spin component changes across the $\bar{\Gamma}$-$\bar{M}$ line. The same trend is also confirmed by the data in regions I and J where the up- and down-spin EDCs almost overlap with each other because of the cancellation of two opposite spins. To see if a similar trend is observed along another high-symmetry line $\bar{\Gamma}$-$\bar{K}$, we also measured SR-EDCs and the result is shown in Fig. 2(e). It is apparent that the sign of P_z (also P_x) in region K (L) is the same as that in the region N (M), indicating that P_z (P_x) does not switch the sign across the $\bar{\Gamma}$-$\bar{K}$ line.

In Fig. 3(a) we highlight the main result of Fig. 2 by schematically illustrating the SP vectors of the S_2 band. The in-plane spin component has a vortical structure, but the magnitude of the SP perpendicular to k, called here P_θ, varies as a function of FS angle θ. P_z has a large component comparable to P_θ, and switches the sign by every 60° step of θ. As illustrated in Fig. 3(c), these features would lead to the periodic oscillation of P_θ and P_z, unlike the general Rashba SOC where $P_\theta = \text{const}$ and $P_z = 0$. The threefold symmetric variation of the z-spin component is naturally understood by considering the threefold crystal symmetry due to the presence of a second bismuth layer. Indeed, the sign-switching behavior of the z spin is consistent with the spin configuration in Au(111) [4] and Bi surface alloys [13], suggesting that the z-spin character is essentially governed by the crystal symmetry. We also note

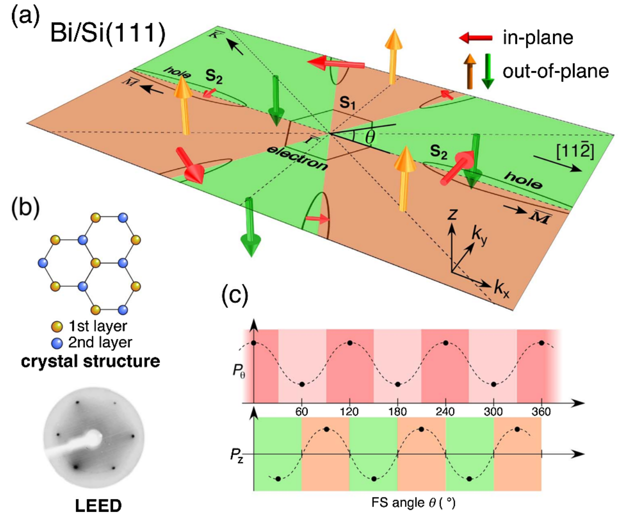

FIG. 3 (color online). (a) Schematic view of the spin structure of the S_2 hole pocket in Bi/Si(111). Size (length) of arrows roughly scales with the observed SP. Definition of the FS angle θ is also shown. We symmetrized the data by taking into account the crystal symmetry. (b) Structure of bismuth bilayer and the LEED pattern. (c) Schematic view of P_θ and P_z as a function of θ.

that the x and z components of the SP should vanish on the $\bar{\Gamma}$-$\bar{M}$ line due to the mirror symmetry. This means that the observed $|P_y|$ along the $\bar{\Gamma}$-$\bar{M}$ line would directly reflect the full SP of at most 0.7. This reduction of the full SP is also supported by recent first-principles calculations [22] which predict that the strong spin-orbit entanglement reduces the total SP of the surface states down to 0.5 in Bi_2Se_3 and Bi_2Te_3.

Now we discuss the origin of unconventional in-plane SP. The observed asymmetry with respect to the $\bar{\Gamma}$ point is not well understood by the general Rashba effect [1]. Moreover, the asymmetry might also break the TRS $[E(k,\uparrow) = E(-k,\downarrow)]$, since the SP between opposite k's is different. If the TRS breaking really takes place in Bi/Si(111), which only contains nonmagnetic elements, then this is quite intriguing since the TRS is usually broken by the magnetic order. While the origin of the in-plane spin asymmetry is unclear at the moment, one possible cause is the final-state effect [23,24] which does not break the TRS of the initial state. This effect depends on the vector potential of the incident light, and sometimes causes the observation of false SP for unpolarized bands. As we have shown in Fig. 1(b), this is not the case since the observed SP is essentially robust to the geometry change of the sample. Another cause for the TRS breaking is the peculiar surface conditions, such as various defects or steps on the surface. This could effectively reduce the symmetry of the SP, although the reproducible nature of the observed spin asymmetry, regardless of the types of Si substrate or the conditions of Bi deposition during the sample preparation, would not be reconciled with this picture. We think that the

TRS can be also broken at the surface by an electronic order which leads to the spin-density-wave (SDW) formation. In fact, possible SDW formation has been discussed in Bi(111) in terms of the nesting of an electron FS [8].

Next we briefly comment on the consequence of unusual in-plane spin states in relation to the spin Hall effect [25]. In the 2D Rashba system, the net surface SP vanishes through the integration of various spin states over the entire BZ, but the application of an in-plane electric field (along the x direction; E_x) causes a net SP along the y direction (S_y). Reversing the electric field (E_x) simply switches the sign of S_y with keeping the $|S_y|$ value constant. However, in the case of Bi thin film which possesses a threefold symmetric spin configuration, the $|S_y|$ value itself varies by reversing the electric field, suggesting that the spin current could be controlled not only by the strength of the electric field but also by the direction, resulting in the unusual spin Hall effect. Such a new concept of the tunable spin current via the field-direction control would be useful for developing novel functional spintronic devices.

Finally we discuss the out-of-plane SP in relation to other experiments and theories. It has been argued that in the surface alloy system of Bi and Pb on Ag(111) the in-plane potential gradient [12] causes the out-of-plane SP [13]. The distortion of surface wave function owing to the relaxation or the bucking of surface Bi atom may also enhance the in-plane potential gradient [26]. It has been also predicted by the $k \cdot p$ theory that the cubic Dresselhaus SOC in Bi_2Te_3, responsible for the hexagonal warping of the surface-Dirac-state FS, produces a sizable out-of-plane SP [27]. We thus speculate that a similar mechanism may be at work at the Bi surface. We would also like to remark here that the ARPES-determined out-of-plane SP and its sign-changing behavior (see Fig. 3) is in good agreement with the first-principles band calculations of $Bi_{1-x}Sb_x$ [28], whereas the calculated value of the out-of-plane SP (a few %) is much lower than the value obtained by the ARPES experiment (40–70%). It is thus necessary to develop a microscopic theory to unravel the observed giant P_z.

In conclusion, we revealed the asymmetry of the in-plane SP and the giant out-of-plane SP of the surface Rashba states of Bi(111) thin film, by means of SR-ARPES. The observed peculiar spin state is not explained in terms of the normal Rashba SOC, and invokes novel interpretations like TRS breaking and many-body effects. We conclude that the Bi thin film provides a precious opportunity to investigate the relationship between the spin texture of surface bands and the Rashba SOC that deviates from the model 2D system.

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