Rashba effect in antimony and bismuth studied by spin-resolved ARPES

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Abstract
We have performed spin- and angle-resolved photoemission spectroscopy of antimony (Sb) and bismuth (Bi) thin films grown on Si(111) to elucidate the nature of the Rashba effect in the spin-split surface bands. In Sb, we revealed spin polarization with the in-plane vortical texture on an elongated hole-like Fermi surface. The spin polarization is strongly momentum-dependent, almost vanishing at the region away from the Brillouin zone center. Such unusual suppression of the spin polarization is not observed in Bi, pointing to a strong influence from the quantized bulk bands on the surface spin polarization in Sb. The present result strongly suggests that bulk-surface interband scattering should be properly taken into account to understand the Rashba surface states in group-V semimetals.

Keywords: Rashba effect, photoemission, group-V semimetal

1. Introduction

The Rashba effect [1] caused by strong spin–orbit coupling is one of the most important and useful physical phenomena for developing next-generation spintronics devices, since it enables the generation and manipulation of spin-polarized electrons without a magnetic field. Intensive investigations have been carried out for two-dimensional surfaces or interfaces of non-magnetic
solids, where the time-reversal symmetry is held but the space-inversion symmetry is lost. Rashba spin–orbit coupling is known to have a vortical spin structure in the surface bands with the spin vector parallel to the surface and perpendicular to the measured momentum ($k$). Spin- and angle-resolved photoemission spectroscopy (spin-resolved ARPES) is a powerful technique to elucidate the characteristics of the Rashba effect, since it directly observes the spin-split energy bands, as demonstrated in semiconductor heterostructure interfaces [2], noble metal surfaces [3–5], group-V semimetals [6–18], their alloy surfaces [19, 20] and heavy-atom adsorbed semiconductor surfaces [21–25]. Furthermore, the Rashba effect has been reported in a variety of systems such as one-dimensional metal nanowires [26] and three-dimensional materials with the inversion asymmetry of bulk crystal [27].

Generally, Rashba spin–orbit coupling becomes larger in materials with heavier atoms due to the larger atomic spin–orbit coupling. The group-V semimetal bismuth (Bi) has provided an excellent platform for investigating the Rashba effect, and the characteristics of the spin structure have been intensively studied using state-of-the-art spin-resolved ARPES spectrometers [28–30]. The isostructural group-V semimetal antimony (Sb) is also an interesting target for studying the nature of the Rashba effect, although the Rashba effect may be smaller than that of Bi due to the smaller atomic number. It is theoretically proposed that bulk Sb is a topological semimetal [31, 32], and its thin film exhibits a topological phase transition as a function of film thickness [32]. A few ARPES studies have been reported for Sb thin films [9, 10]. By using non-spin-resolved ARPES and band structure calculations, Bian et al [9] have proposed that the spin polarization of the surface state is reduced when the surface state hybridizes with the bulk or quantum well states (QWSs). However, the proposal has not been experimentally validated.

In this paper we report the spin structure of Sb thin film revealed by spin-resolved ARPES. We uncovered that the in-plane spin polarization strongly depends on the momentum, even in a single Fermi surface sheet. We have compared the observed spin polarization between isostructural Sb and Bi, and found a marked difference in the momentum dependence. We discuss the implications of this difference in terms of the hybridization between the surface bands and the QWSs.

2. Experimental methods

To fabricate a Sb thin film we cleaned a Si(111) substrate at 1150 °C and deposited Bi atoms at room temperature. After annealing the film at 150 °C, we deposited Sb atoms at room temperature. Since both Sb and Bi films grow in a bilayer (BL) structure as shown in figure 1(a), we used a Bi thin film as a buffer layer for growing a Sb thin film (see figure 1(b)). This method is different from the previous study where a Bi-terminated Si(111) $\sqrt{3}\times\sqrt{3}$ R30° substrate prepared at low temperature was used [9]. It is noted that there is a finite lattice mismatch between Sb and Bi films (cf: the bulk lattice constants for Sb and Bi are 4.31 Å and 4.54 Å, respectively), which would cause a finite lattice strain to the Sb thin film. We have estimated the thickness of the Sb thin film and Bi buffer layer to be 18 and 10 BL, respectively, by the quartz oscillator thickness monitor and the energy position of the QWSs in the ARPES spectra. The 1×1 surface structure of Sb thin film was confirmed by the low-energy electron diffraction (LEED) measurement as shown in figure 1(c). The successful growth of a Sb thin film is also demonstrated by the ARPES-determined band dispersions consistent with the previously reported band dispersions for Sb [6, 7, 9].
The regular (non-spin-resolved) ARPES and spin-resolved ARPES measurements were performed using a spin-resolved ARPES spectrometer based on the MBS A-1 analyzer [30], and we used one of the Xe I lines (8.437 eV) to excite photoelectrons [33]. We set the energy resolution during the regular and spin-resolved ARPES measurements at 8 and 40 meV, respectively. To obtain the spin-resolved ARPES spectrum, we used the Sherman function value of 0.07 as estimated by the Rashba-split surface state of Au(111) single crystal [34]. We set the sample geometry to predominantly observe the $\bar{\Gamma} \bar{M}$ direction of the surface Brillouin zone (see figure 1(d)) where the bulk $\bar{\Gamma}$ and T points are projected onto the $\bar{\Gamma}$ point, while the bulk X and L points are projected onto the $\bar{M}$ point. We set the temperature of measurement at 30 K or 375 K. We used the experimental results at 375 K to determine the states above $E_F$ by utilizing the finite distribution of the Fermi–Dirac distribution (FD) function. We have confirmed that the observed overall band dispersions and the Fermi surface topology are essentially the same between 30 K and 375 K.

3. Results and discussion

Figure 2(a) shows the plot of ARPES intensity at the Fermi level ($E_F$) around the $\bar{\Gamma} \bar{M}$ line in the Brillouin zone measured at $T=375$ K. We observe a ring-like Fermi surface (FS1) centered at the $\bar{\Gamma}$ point and surrounding Fermi surfaces (FS2) elongated in the $\bar{\Gamma} \bar{M}$ direction. This Fermi surface topology is similar to that for a cleaved surface of bulk single crystal [6, 8]. Figures 2(b) and (c) display the ARPES intensity divided by the FD function at $T=375$ K convoluted with an instrumental resolution, plotted for the $k_x$ direction at $k_y=0.00$ Å$^{-1}$ (left panel) and $k_y=0.03$ Å$^{-1}$ (right panel), respectively. The electron-like FS1 is attributed to the surface states,
because it is well separated from the QWSs. On the other hand, the hole-like FS$_2$ is caused by both the surface states and the QWSs, and interestingly the spectral weight shows a marked momentum dependence. It is inferred that a part of this hole pocket in the region of $\sim -0.2$ Å$^{-1} < k_x < \sim 0.2$ Å$^{-1}$ originates predominantly from the surface state, because the surface state is well separated from the QWSs (figures 2(b) and (c)), while the remaining part of $k_x < \sim -0.2$ Å$^{-1}$ is composed of both the surface state and the QWSs since they are indistinguishable at $k_y = 0.03$ Å$^{-1}$ (see figure 2(c)). As seen in figure 2(b), the surface bands degenerate at the Kramers point owing to the time-reversal symmetry. This Kramers point is located at the binding energy of $\sim 0.16$ eV, which is closer to $E_F$ by $\sim 60$ meV than that of Sb thin film on Bi-terminated Si (111) [9] and bulk Sb crystal [6], suggesting that our Sb thin film is slightly hole-doped. The overall band dispersion of the QWSs is also shifted upwards by $\sim 60$ meV, consistent with the hole-doped nature.

Next we discuss the spin polarization of the elongated hole pocket FS$_2$ in comparison with previous spin-resolved ARPES results for Bi thin film [15, 17]. We have chosen four momentum cuts (A–D) for the spin-resolved ARPES measurement (see the yellow rectangles in figure 3(a)), which are located near the Fermi vector ($k_F$) points of FS$_2$ and thus suitable to trace the near-$E_F$ components of the hole-like bands (figure 3(b)). Figure 3(c) shows spin-resolved ARPES spectra for the in-plane ($y$) components measured in regions A–D. The spectra mainly

![Figure 2](image_url)
Figure 3. (a) ARPES intensity at $E_F$ around the $\bar{\Gamma}$ point as a function of the two-dimensional wave vector for Sb thin film measured at $T = 30$ K. (b) ARPES intensity as a function of binding energy and $k_y$ for cuts A–D as indicated in (a). Areas enclosed by the yellow rectangle in (a) and (b) represent the momentum window of the spin-resolved ARPES measurement. (c) Spin-resolved EDCs for the in-plane spin component in regions A–D, and (d) corresponding energy dependence of the spin polarization. Note that the rather broad and asymmetric peak seen in the down-spin EDCs for regions C and D in (c) is due to the momentum integration effect arising from the wider momentum window of the spin-resolved ARPES measurements. (e) Spin-resolved EDCs and corresponding spin polarizations for the out-of-plane spin component in regions A and D.
consist of two components (see the spectra for region D as an example), located at $E_F - 0.15$ eV and 0.15–0.25 eV, respectively. First we focus on the near-$E_F$ feature. In region D, which is closest to the $\bar{\Gamma}$ point, the down-spin spectra is dominant, suggesting a vortical spin texture with a counter-clockwise rotation, consistent with the reported spin polarization vector of the elongated hole pocket in Bi [15, 17]. In region C, we again find dominant down-spin spectra, whereas the weight is obviously reduced. In regions A and B, the reduction of down-spin weight is more prominent, and the up- and down-spin spectra are no more distinguishable in region A. This systematic reduction of the relative down-spin weight is reflected in the spin polarization in figure 3(d), where the spin polarization varies systematically from $-0.9$ (region D) to 0 (region A). One may think that the observed suppression in the in-plane spin polarization in regions A and B is simply a consequence of the change in the spin-vector direction. To clarify this point, we plot in figure 3(e) the spin-resolved energy distribution curves (EDCs) and the corresponding spin polarization in Sb thin film for the out-of-plane spin component at two representative momentum regions A and D. Obviously, the up- and down-spin EDCs clearly overlap each other, and no meaningful out-of-plane spin polarization is observed. This signifies that the observed suppression of the in-plane spin polarization in figures 3(c) and (d) indeed originates from the intrinsic suppression of the total spin polarization. It is also worth noting that our previous study on Bi thin film [17] has clarified a large out-of-plane spin component in contrast to Sb. While the origin of such a difference is unclear at present, we speculate that it can be explained either by (i) the intrinsic difference in the spin-vector direction between Sb and Bi or (ii) the difference in the amount of domain mixture at the surface between Sb and Bi, which needs to be clarified in future by surface structure experiments such as scanning tunneling microscopy.

Another interesting aspect in figures 3(c) and (d) is that the QWSs also have a finite spin polarization and the spin vector points in the opposite direction to that of the near-$E_F$ state. Generally, the QWS is expected to be spin-degenerated as long as the system maintains space inversion symmetry. In the thin-film case, however, the space-inversion symmetry is naturally broken due to the difference in the boundary condition between the vacuum-side surface and interface, leading to the spin splitting of bands due to the Rashba effect. In our experiment, we did not find any signature for the band splitting of the QWSs, although a finite spin polarization was observed. It is thus inferred that the space-inversion symmetry breaking would be weak in Sb thin film, and the initial states of the QWSs are spin polarized around the topmost surface due to the reflection of the wave function by the surface barrier, and such a polarization of spins is detected by the surface-sensitive ARPES technique as in the case of bulk Bi crystal [16] and Bi thin film [18].

To clarify whether the observed unusual suppression of the spin polarization is unique for Sb, we have also performed a spin-resolved ARPES measurement for Bi thin film on Si(111), and the result is shown in figure 4. As is clearly visible in figure 4(a), Bi(111) shows a Fermi surface topology quite similar to Sb(111); i.e., a ring-like electron pocket and elongated hole pockets. As seen from the spin-resolved ARPES spectra for the four regions A–D (figure 4(b)), the down-spin component is always superior to the up-spin counterpart irrespective of the momentum location on the hole pocket, in sharp contrast to the case of Sb, where the spin polarization almost vanishes in regions A and B. In fact, as shown in figure 4(c), the absolute spin polarization is ~0.6–0.8 in Bi, distinctly different from Sb where the absolute spin polarization varies from zero to nearly full value (0.9) in the similar momentum region, as
is clearly seen from the direct comparison of the momentum dependence of spin polarization in figure 5(a).

Now we discuss the physical mechanism behind the unusual suppression of the spin polarization in Sb. The first possibility is the extrinsic final-state effects which are categorized into two cases; (i) the spin-dependent matrix element effect, and (ii) the difference in the final-state band structure. For (i), it has been recently reported based on the laser-based spin-resolved ARPES experiments on topological insulators [35] that the spin polarization of photoelectrons is sensitive to the polarization of incident light; the spin orientation of photoelectrons emitted

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from the spin-polarized surface is modified from the original spin texture of the initial state owing to the interaction between the photoelectrons and the incident light. Such an effect strongly depends on the electric field vector (in linearly polarized cases) or the angular momentum (in circularly polarized cases) of the incident light. In the present study, we used a Xe discharge lamp which emits essentially unpolarized light, and hence the modification of spin orientation during the photo-excitation process is small and would not account for the observed suppression of the spin polarization in Sb. As for (ii), the small difference in the film thickness between Sb and Bi films (18 and 15 BL, respectively) may cause the observed difference in the spin polarization due to the difference in the final-state band structure. While such an effect may not be completely excluded, it is hard to attribute the observed contrasted spin polarization behavior between Sb and Bi to the thickness difference, since the momentum dependence of the spin polarization in the 18-BL Bi film is essentially the same as that of the 40-BL film in our previous report [17], which suggests that the film thickness is not sensitive to the spin polarization for the elongated hole pockets.

From the above discussions, it is thus strongly suggested that the suppression of spin polarization in Sb is an intrinsic feature related to the detailed characteristics of the band structure. According to the band structure calculations by Bian et al [9], the spin polarization of the surface state is reduced when the surface state is close to or overlaps with the bulk band projection (or QWSs). We immediately recognize from figure 5(b) that the bulk band projection is totally different between Sb and Bi. In Sb, it overlaps with the surface state in the region away from the $\Gamma$ point ($k_x < -0.2 \text{ Å}^{-1}$), while the bulk band projection is substantially away from the surface state in Bi and as a result no overlap is seen. Intriguingly, the sudden reduction of the spin polarization value at $k_x \sim -0.15 \text{ Å}^{-1}$ in Sb roughly coincides with the momentum point where the bulk band projection starts to overlap with the surface band. We thus conclude that the hybridization between the surface and bulk bands reduces the spin polarization through the

![Figure 5.](image)

Figure 5. (a) Comparison of the momentum dependence of spin polarization for the near-$E_F$ states between Sb and Bi thin films. (b) Comparison of the ARPES intensity along the $\Gamma M$ cut and the bulk band projection (hatched area) [9, 12] between Sb and Bi thin films.
enhanced electron scattering (interband scattering) between the spin polarized surface states and the non-polarized bulk bands (or QWSs). It is also noted here that the reduction of the surface spin polarization through the hybridization with bulk has also been reported in other Rashba systems such as hydrogen-covered W(110) [36], suggesting that it is a generic feature of various Rashba systems. We also emphasize that the direct comparison of electronic states between Bi and Sb thin films provides a precious opportunity for effectively distinguishing the bulk influence of the spin polarization in the Rashba surface states, because Sb has a surface state very similar to that of Bi, while the energy position of the bulk band is very different between the two. The present result thus indicates that the hybridization between the QWSs and the surface states should be properly taken into account to understand Rashba Spin–orbit coupling in group-V semimetals.

4. Summary

We have performed spin-resolved ARPES measurements of a Sb thin film grown on Bi/Si(111), and found that the in-plane spin polarization of the Rashba-spilt surface states is highly dependent on the momentum location in the elongated hole pocket, unlike in the case of Bi thin film where the spin polarization keeps a nearly constant value. We have concluded that the hybridization between the bulk band (or QWSs) and the surface band is responsible for the suppression of the spin polarization in Sb, indicating an important role of the bulk-surface interband scattering to the spin polarization of the Rashba surface states.

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