Large surface-state conductivity in ultrathin Bi films

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In situ microscopic-four-point probe conductivity measurements were performed for ultrathin Bi films on Si(111)-7×7. From the extrapolation of thickness-dependent conductivity and decrease in conductivity through surface oxidization, we found clear evidence of large surface-state conductivity ($\sigma_{SS} \sim 1.5 \times 10^{-3}\ \Omega^{-1}/\square$ at room temperature) in Bi(001) films. For the thinnest films (~25 Å), the transport properties are dominated by the highly inert surface states that are Rashba spin-split, and this suggests the possibility of using these Bi surface states for spintronics device application. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2813613]

Historically, semimetal bismuth (Bi) has been examined extensively to study the quantum size effect (QSE) due to its extremely long Fermi wavelength λ_F (~30 nm). Back in the 1960s, Ogrin *et al.* reported the oscillation of the Bi film resistance as a function of the film thickness d (Ref. 1), and Sandomirskii predicted a semimetal-to-semiconductor (SMSC) transition caused by the QSE.[2] However, whether such intriguing phenomena can really be observed has been debated and there is still no definite conclusion.[3–5] In the above works, the film thickness was mainly in the order of a few hundreds of angstrom, $d \sim \lambda_F$, or thicker. Recently, Nagao *et al.* showed that epitaxial Bi(001) films can grow on the Si(111)-7×7 surface in the thickness range of several tens angstrom, $d \ll \lambda_F$.[6] In our previous photoemission study on such ultrathin Bi(001) films, we found that the density of state (DOS) near the Fermi level (E_F) is dominated by the highly metallic surface states, and the SMSC transition does not occur due to these states. Figure 1 shows the measured Fermi surface and most of it is composed of the surface states that show large Rashba spin splitting.[7] Illustrated together is the projected bulk Fermi surface in white lines [a tiny hole pocket is located at $\bar{\Gamma}$ (0, 0) and a small electron pocket at $\bar{M}$ (0.8, 0)]. From a simple estimation of the area inside the Fermi surface in Fig. 1, there are $\sim 10^{13}$ carriers/cm^2 for the surface states, whereas only $\sim 10^{11}$ carriers/cm^2 are present inside the film assuming the bulk carrier density for films of $d \ll \lambda_F$, which is two orders of magnitude smaller. Of course, the mobility of bulk Bi is known to be very high, but it can be expected that the surface states should play an important role in determining the physical properties of these films. Indeed, one of the reasons for the absence of clear detection of the above-mentioned QSE-related phenomena was that the presence of surface or interface states may hide away such behaviors based only on the bulk band structure.[3]

In this letter, we explicitly show from micro-four-point-probe (MFPP) measurements that the surface-state conductivity of Bi(001) is large compared to the bulk. From the thickness dependence and surface oxidization measurements, the surface-state conductivity σ_{SS} is revealed as $1.5 \times 10^{-3}\ \Omega^{-1}/\square$ at room temperature. Our results show that the properties of the thinnest films (~25 Å) are dominated by the surface states and not by the states inside the film.

The experiments were performed using a custom-made ultrahigh vacuum chamber for *in situ* MFPP measurement equipped with a reflection-high-energy electron diffraction (RHEED) system.[8] The probe spacing was 20 μm. Bi was deposited on the Si(111)-7×7 surface (n type, 1–10 Ω cm) at room temperature and postannealed at ~350 K, which makes the films atomically flat.[6] In this paper, we use the hexagonal indexing in which the trigonal axis corresponds to [001]. One bilayer (BL) is defined as the atom density in the covalently bonded Bi(001) plane (1 BL $= 1.14 \times 10^{15}$ atoms/cm^2 and 3.9 Å thick). The thickness has been calibrated *in situ* with RHEED by the completion of the Si(111)β-$\sqrt{3} \times \sqrt{3}$-Bi phase[9] which was also confirmed by the allotropic transformation from the Bi{012} phase into the Bi(001) phase.[6,10]

Figure 2(a) shows the measured resistance R as a function of the film thickness. The inset shows the enlarged view for films with large thickness. The resistance decreases monotonically as the film thickness increases. Figure 2(b) shows the two-dimensional (2D) conductivity σ obtained from R through the relation $\sigma = \ln 2/\pi R$. The conductivity is

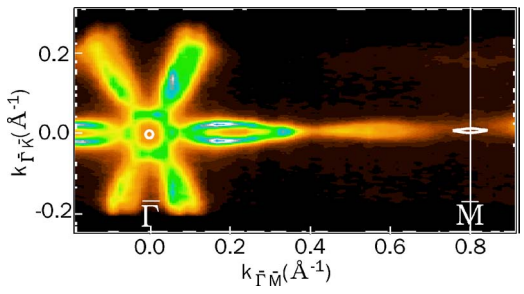

FIG. 1. (Color online) The Fermi surface of a 6.8 BL Bi(001) film measured by photoemission spectroscopy (Ref. 7). The projected bulk Fermi surface (a tiny hole pocket at $\bar{\Gamma}$ and a small electron pocket at $\bar{M}$) is also shown by white lines.

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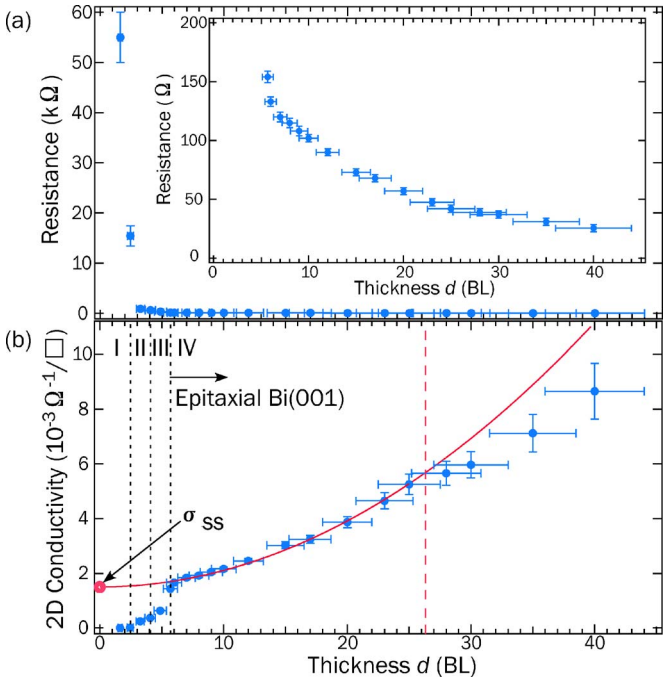

FIG. 2. (Color online) (a) Measured resistance as a function of the film thickness. The inset shows the close-up by changing the vertical scale. (b) The 2D conductivity obtained by $\sigma = \ln 2/\pi R$ from the data of (a). The solid line shows the parabolic fit for $6 \leqslant d \leqslant 25$ BL. The horizontal error bars show the uncertainty in the film thickness, and the vertical error bars represent the data spread by measuring different parts of the sample. The numbers I–IV in (b) correspond to the different stages of Bi growth on Si(111)-7×7 reported in Ref. 6.

assumed 2D because the probe spacing (20 μm) is much larger than the film thickness ($d \leqslant 156$ Å). In this conductivity, we think that the contribution from the Si substrate is negligible because σ is almost zero ($\sim 10^{-6}\ \Omega^{-1}/\square$) at $d \sim 0$. This is also supported by the fact that the interaction at the Bi–Si interface is very weak.[7,10] Also shown in Fig. 2(b) are the numbers I–IV representing different stages of Bi growth on Si(111)-7×7.[6] It should be noted that the conductivity increases drastically at stage III where the allotropic transformation from Bi{012} to Bi(001) takes place.[10]

We now discuss the thickness dependence of the conductivity in stage IV ($d \geqslant 6$ BL), where high-quality single crystalline flat Bi(001) films are formed. As shown in Fig. 1, this phase has highly metallic surface states.[7] For simplicity, the measured conductivity is divided into two parts, the contribution from the surface state and that from the carriers inside the film, $\sigma(d) = \sigma_{SS} + \sigma_{film}(d)$. We assume no thickness dependence for σ_{SS} because hardly any thickness dependence was found in its band structure.[7] Looking at Fig. 2(b), the data of $6 \leqslant d \leqslant 25$ BL can be well fitted with a parabola shown as the solid curve, whereas above 25 BL, the data points deviate from the parabola. This initial quadratic dependence on the film thickness can be understood as follows. In general, the 2D conductivity is expressed in the Drude model as the product of elemental charge (e), 2D carrier concentration (n_{2D}), and mobility (μ), $\sigma = e n_{2D} \mu$. The 2D density of the carriers inside the film can be expressed as $n_{2D} = n_{3D} d$, where n_{3D} is the carrier density of bulk Bi, meaning that n_{2D} is proportional to d. Furthermore, we believe that for $6 \leqslant d \leqslant 25$ BL, the mean free path l for the carriers inside the film is determined by the film thickness d, as depicted in Figs. 3(a) and 3(b). The interface scattering at the Bi/Si and Bi/vacuum

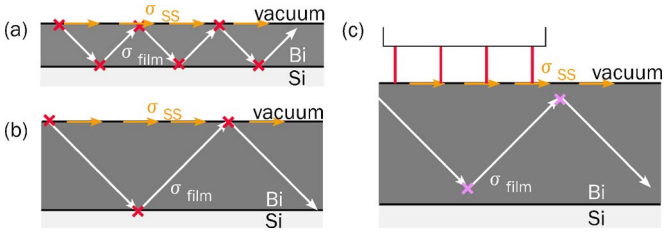

FIG. 3. (Color online) The schematic drawing of carrier flow inside the film for $6 \leqslant d \leqslant 25$ BL where the scattering is mainly at the interfaces [(a) and (b)], and that for $d \geqslant 25$ BL where it is due to phonons and defects (c). The measurement configuration with the four probes is also shown in (c) (the length does not scale).

interfaces is dominant in this thickness range, and when the thickness is doubled, the probability of scattering becomes half. As μ is proportional to l, this means that μ is also proportional to d. As a consequence, σ_{2D}, the product of n_{2D} and μ, has a d^2 dependence. For $d \geqslant 25$ BL, the interface scattering is no longer dominant and the film carriers presumably undergo phonon or impurity scattering inside the film [Fig. 3(c)], showing the deviation from the parabolic dependence and close to the expected linear dependence. The mean free path l of the film carriers is estimated to be ~ 100 Å, which is quite short considering that l of bulk Bi is very long.[11] This is presumably due to the poorer crystalline quality of the films compared to bulk single crystals and scattering into surface states.[12]

By extrapolating the parabolic curve in Fig. 2(b) to $d = 0$, a finite value remains (red circle). If there were only film carriers and no contribution from the surface states, it should be zero at $d = 0$. We therefore believe that this unambiguously represents the surface-state conductivity of Bi(001) and the obtained value is $\sigma_{SS} \sim 1.5 \times 10^{-3}\ \Omega^{-1}/\square$.

To confirm the above finding, we have tried to oxidize and destroy the surface states and see how the conductivity of the films changes. Namely, σ_{SS} can be estimated from the decrease of the conductivity $\sigma_{SS} = |\Delta\sigma|$. Figure 4(a) shows the RHEED pattern of the clean Bi(001) surface. The 1×1 periodicity can be seen clearly with Kikuchi patterns representing the good crystalline quality of the films. We observed

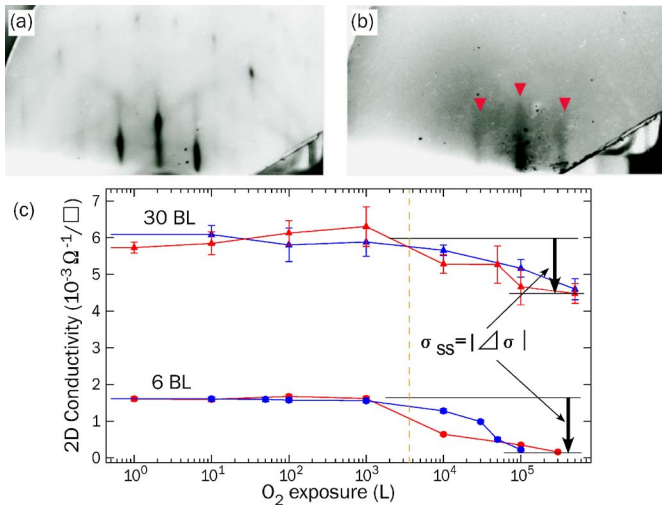

FIG. 4. (Color online) RHEED patterns of a clean Bi(001) surface (a), and that after 10^4 L of O_2 exposure (b). The triangles in (b) show the spots at the zeroth Laue zone. (c) The conductivity change for the 6 and 30 BL Bi films after O_2 exposure.

no change in the RHEED pattern until we exposed more than 10^4 L (Langmuir) of O_2, which shows that it is highly inert to oxidization at room temperature, consistent with Refs. 13 and 14. Figure 4(b) shows the RHEED pattern after 10^4 L O_2 exposure. The spots at the first Laue zone disappear with the background becoming quite high. The spots at the zeroth Laue zone can be seen (triangles), although they become very weak and broad. Since transmission-type diffraction spots cannot be observed, this indicates that we have not destroyed the whole film, but have only damaged the surface. The basic feature of the RHEED patterns is the same even after exposure to 5×10^5 L.

Figure 4(c) shows the change of the 2D conductivity after O_2 exposure for 6 and 30 BL Bi films. The red and blue markers represent two different samples. The conductivity shows virtually no change until 10^4 L of O_2 exposure, consistent with the RHEED observation. It starts to decrease gradually, and with more than 10^6 L, we could not obtain a linear *I-V* curve. As the current first needs to flow into the surface states and then inside the film in our measurement geometry [Fig. 3(c)], this shows that the surface is oxidized completely and the decrease has most probably saturated, consistent with Ref. 14. The difference of conductivity $|\Delta\sigma|$ which is equal to σ_{SS} before and after the surface-state destruction is $|\Delta\sigma|\sim1.4\times10^{-3}$ (1.5×10^{-3}) $\Omega^{-1}/\square$ for the 6 (30) BL film, in good agreement with that estimated in Fig. 2(b). It should be noted that this is the highest conductivity value reported for a metallic surface state at room temperature. From the bulk resistivity, 1 BL of Bi film would only have a 2D conductivity of 3.4×10^{-4} $\Omega^{-1}/\square$,[15] showing that σ_{SS} is indeed very large. Estimation of the conductivity from the band structure using the Boltzmann equation shows that this is due to the large Fermi surface and the Fermi velocity arising from the steep band dispersion.[7] The mean free path of the surface states derived from σ_{SS} is 20–50 Å, similar to that reported for other surfaces.[16]

Furthermore, we notice from Fig. 4(c) that after destroying the surface state for the 6 BL (~25 Å) film, the conductivity is less than 10^{-4} $\Omega^{-1}/\square$. This means that the film contribution is almost negligible compared to σ_{SS} and the current mainly flows through the surface state. Moreover, as is well known, the surface states of Bi(001) are spin-orbit split due to the Rashba effect.[17,7] The magnitude of the spin splitting is much larger than the Rashba-split 2D electron gases formed at semiconductor heterostructure quantum wells. This indicates that for very thin Bi films, the current is highly spin polarized and they may be good candidates to realize the spin field-effect transistors[18] or experimentally observe the quantum spin Hall phase.[19] It would also be interesting to explore the relation between these surface states and the superconductivity found in granular Bi films.[20]

In conclusion, we have shown that the conductivity in ultrathin Bi(001) films (~25 Å) is dominated by the surface states from thickness dependent and oxidization measurements using the MFPP method. The present result suggests that these ultrathin Bi films may be promising materials for spintronics device applications.

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