Impurity effect on surface states of Bi (111) ultrathin films*

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The surface impurity effect on the surface-state conductivity and weak antilocalization (WAL) effect has been investigated in epitaxial Bi (111) films by magnetotransport measurements at low temperatures. The surface-state conductivity is significantly reduced by the surface impurities of Cu, Fe, and Co. The magnetotransport data demonstrate that the observed WAL is robust against deposition of nonmagnetic impurities, but it is quenched by the deposition of magnetic impurities which break the time reversal symmetry. Our results help to shed light on the effect of surface impurities on the electron and spin transport properties of a 2D surface electron systems.

Keywords: bismuth, weak antilocalization, surface states

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1. Introduction

Spin-polarized two-dimensional (2D) surface states arising from the Bi or Bi-based topological insulators are of large potential interest for the next generation of magnetic memory and logic devices.[1–3] Recently in particular, it has been shown that the Rashba–Edelstein effect and the inverse Rashba–Edelstein effect can be regarded as a counterpart of the spin Hall effect and inverse spin Hall effect for spin-charge interconversion.[4–8] When an in-plane current flows through a surface state, due to the spin momentum locking nature resulted from the Rashba effect, the charge flow is accompanied by a non-equilibrium spin polarization with direction perpendicular to both the current direction and the surface normal. By coupling this spin polarized current to an adjacent magnetic layer, an efficient spin–orbit induced torque will act on the magnet as shown by Mellnik *et al.* in a bilayer system Bi_2Se_3/permalloy.[6] By using spin pumping, Rojas Sanchez *et al.* successfully injected a spin current from an NiFe layer into a Bi/Ag bilayer and detected the resulting charge current in the 2D interface. Usually, these kinds of devices consist of a thin film that host the 2D surface states and a magnetic layer. The direct contact between these two would introduce impurities into the 2D surface states, which are in general very sensitive to surface adsorption atoms. Thus, it is important to know how the magnetic or nonmagnetic impurities that come from the magnetic layer would affect the electron and spin transport in the 2D surface electron systems.

Angle-resolved photoemission spectroscopy (ARPES) measurements have shown that the surface states of Bi are highly metallic in contrast to the semimetallic nature of bulk Bi.[9–11] Especially, by reducing thickness, the Bi film interior can be transformed into semiconductor.[12–14] These make the strong spin splitting surface state of Bi ultrathin film one of the most promising platforms for application. By combining scanning tunneling microscopy with density functional theory, Klein *et al.* has shown that the Bi (111) surface provides a well-defined incorporation site in the first bilayer that traps highly coordinating atoms such as transition metals or noble metals.[15] However, the transport study of the impurities effect on surface states are mainly in poly crystalline Bi films,[16–18] in which the surface has no well defined orientation. It is still not clear how the impurities would affect the surface conductivity and the phase coherence length in the Bi (111) surface states. On the other hand, as for application in real devices, it is also important to know whether the surface states are robust in air conditions, and show up in the physical properties of the Bi (111) films.

In this work, we introduce magnetic (Fe, Co) and nonmagnetic (Cu) impurities onto the surface of single-crystalline Bi (111) films and performed magnetotransport measurements. A significant reduction of surface conductivity is found for 0.5 monolayer (ML) of Cu, Fe and Co impurities on 5-nm Bi (111) film. The magnetotransport data demonstrate that the observed WAL is robust against deposition of nonmagnetic impurities, but it is quenched by the deposition of magnetic impurities which breaks locally the time reversal symmetry. More surprisingly, the Bi (111) surface state is found to be very robust against oxidation, even with the fact that Bi is believed to be a prototypical semimetal with topologically trivial electronic band structure.[19] Our results help to shed light on the effect of surface impurities on the electron and spin transport properties of a 2D surface electron system.

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2. Experimental details

The Bismuth films were grown by molecular beam epitaxy on a semi-insulating (111)-oriented Si substrate and characterized in situ using reflection high energy electron diffraction (RHEED). A clean Si (111)-7×7 surface was obtained by a cycle of e-beam heat treating as shown by the RHEED pattern in Fig. 1(a). High-purity Bi was deposited onto the substrate at room temperature by thermal evaporation from a directly heated ceramic crucible. The deposition rate is calibrated *in situ* by a quartz microbalance. The layered Bi (111) film has a bulk single-crystal rhombohedral phase with thickness more than 6 bilayers (BL).[20] The observed sharp streaks in the RHEED pattern for a 5-nm film as shown in Fig. 1(b) demonstrate the high crystal quality of the film. The impurities are introduced by using the shadow mask technique.[21] This enables us to have the epitaxial Bi (111) film on Si (111) with half of the surface covered *in situ* by 0.5-ML Cu, Fe or Co before the MgO capping. The side by side samples thus have half a pristine surface and half the surface covered by impurities on top. The film was capped with 5-nm MgO to protect it from oxidation before being taken out of the ultrahigh vacuum (UHV) and then patterned into a Hall bar by photolithography. Transport measurements were mainly performed in an Oxford Instruments cryostat with temperature down to 1.4 K and magnetic field up to 9 T.

3. Results and discussion

The red curve in Figs. 1(c), 1(d), and 1(e) shows the temperature dependence of square resistivity ρ_{xx} of the pristine 5.0-nm Bi (111) film. Two characteristic behaviors can be observed from the non-monotonic curve: a low temperature metallic behavior ($\mathrm{d}\rho_{xx}/\mathrm{d}T > 0$) and a higher temperature semiconducting behavior ($\mathrm{d}\rho_{xx}/\mathrm{d}T < 0$). This is consistent with the notion that the former is due to surface conduction and the latter is caused by thermally activated conduction through the semiconducting interior.[12–14] The semiconducting film interior will guarantee that the low temperature transport explored will all be originated from the surface states. Thus, we can take the value of ρ_{xx} at 5.0 K as the surface resistivity ρ_{xx0}, which corresponds to a surface conductivity $\sigma_{xx0} = 1/\rho_{xx0}$. It should be mentioned that, even the films in Fig. 1(c), 1(d), and 1(e) are with the same nominal thickness, there is a small difference in the surface conductivity. The reason behind this is that the surface states conductivity is very sensitive to the unintentional defects such as step edges or impurities, and this is why we design the special side by side sample as described in the experimental part to quantitively estimate the influence of surface impurities.

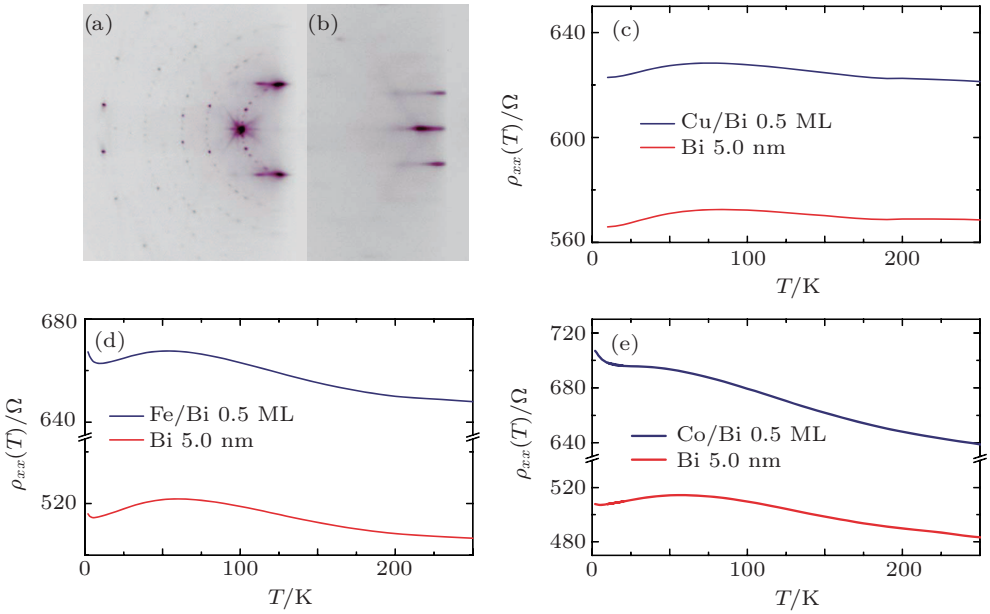


Fig. 1. (color online) Representative RHEED pattern of the Si (111)-7×7 surface (a) and a 5.0-nm Bi (111) films (b). The temperature dependence of the square resistivity ρ_{xx} of a 5.0-nm pristine Bi (111) film and with 0.5-ML Cu, Fe, and Co impurities on top is shown in panels (c), (d), and (e), respectively.

We first show how the surface impurities would affect the surface conductivity. It can be clearly seen from the blue curve in Figs. 1(c), 1(d), and 1(e) that the overall temperature dependent behavior of square resistivity ρ_{xx} remains almost the same to the corresponding pristine film after the 0.5-ML Cu, Fe, and Co impurities are introduced on top of the 5.0-nm Bi (111) film. However, as is clearly visible, the square resistivity ρ_{xx} increases (or conductivity decreases) significantly when adatoms are adsorbed onto the Bi (111) surfaces. The increase of resistivity of these films with impurities indicates that the adatoms deposited at the surface can be reasonably assumed to be well separated clusters, otherwise the shunting effect from these noble metal films, which usually have higher conductivity than the Bi films, will reduce the total resistiv-

ity. The sensitivity of surface conductivity to surface impurities here again gives strong support to the recent finding that the surface states contribute to a large extent of the total conductance of the Bi (111) films. Moreover, the relative change in the surface conductivity depends on the deposited material. For instance, with the same impurities coverage of 0.5 ML, the relative change in surface conductivity is 9%, 23%, and 28% for Cu, Fe, and Co, respectively. It can be seen that the magnetic impurities (Fe and Co) would have stronger influence on the surface conductivity than the nonmagnetic impurities (Cu). Our results are consistent with earlier reports in topological insulator Bi_2Te_3 films[22] and poly crystalline Bi films.[16–18]

In fact, the different influence for the nonmagnetic and magnetic impurities is reasonable considering the special electronic band structure of the surface states. It has been shown by (spin- and) angle-resolved photoemission spectroscopy (ARPES) that the surfaces of Bi (111) films are characterized by a quasi-two-dimensional metallic surface states with strong spin-splitting.[9–11] Due to time reversal symmetry, the spin-conserving backscattering from $+k$ to $-k$ states of propagating electrons near the Fermi level E_F is strongly suppressed, which is confirmed by scanning tunneling microscopy (STM) experiment.[23] Then, when the adatoms with magnetic moments are introduced on to the surface, the local time-reversal symmetry will be broken; hence the direct (spin-conserving) backscattering channel for electrons and holes is now activated. This increasing scattering probability will lead to a reduction of the electron mean free path. This is why the Fe and Co impurities on Bi (111) will lead to a more significant reduction of the surface conductivity compared to Cu impurities, which can be regarded as simple scattering centers. Additionally, no anomalous Hall effect is observed in Fe and Co deposited samples, which seems to suggest that the magnetizations of the Fe and Co clusters are random in direction.

We now concentrate on the impurity effect on the coherent transport of electrons in the surface states. The red curve in Fig. 2 shows the magnetoresistivity of the 5-nm pristine film at 1.5 K. The cusp around the zero magnetic field (perpendicular to the film plane) shows typical weak antilocalization behavior.[16,24–27] The effect of weak antilocalization in weakly disordered two dimensional systems with very strong spin orbital coupling can be understood in terms of the quantum scattering along the same path but in opposite directions. When a magnetic field is applied, the phase pickups along the two paths have opposite signs, and as a consequence, a positive magnetoresistance is observed.[26] However, after the introduction of impurities on to the surface, distinct magnetoresistivity behaviors can be resolved from the blue curve in Fig. 2. The WAL cusp becomes broadened after the nonmagnetic Cu impurities are deposited. For the magnetic impurities Fe, the WAL cusp is almost gone. Even more dramatically, the WAL is completely suppressed for the Co impurities.

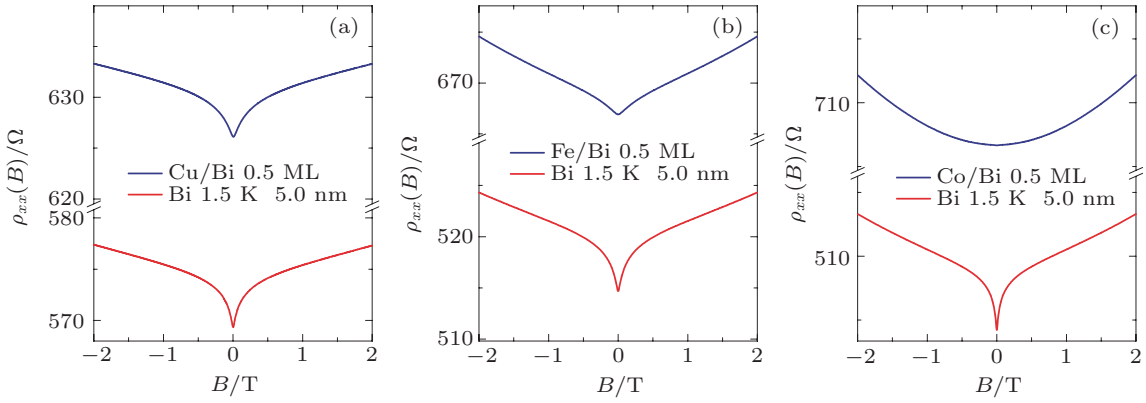


Fig. 2. (color online) The influence of nonmagnetic (Cu in panel (a)) and magnetic (Fe in panel (b) and Co in panel (c)) impurities on the WAL in Bi (111) films.

The broadening of the magnetoresistivity curve for the Cu impurities could be understood as the reduced phase coherence length l_φ induced by the additional Cu surface scattering centers (which will be discussed in detail in the following). While the magnetic impurities, which would form clusters on the Bi (111) surface, will break the locally time-reversal symmetry and will lead to a crossover from the symplectic to unitary classes.[28] The magnetoresistivity of the 5-nm sample with 0.5-ML Fe deposition shows the intermediate regime in this crossover process. For the Co impurities, the magnetoresistivity shows an almost B^2 dependence on the magnetic field, which means the WAL is completely suppressed. The very different effect of magnetic and nonmagnetic impurities in our data clearly associates the WAL effect we observed with the surface states. Otherwise it should not be so sensitive to the surface modification, if the WAL originates from the Bi film bulk states. It should be mentioned that even with 1 ML of Fe impurities on top, the WAL also cannot be completely suppressed, while 0.25-ML Co impurities are enough to kill the WAL behavior. A plausible explanation for this could be that the exchange coupling in Co is much stronger than that in Fe. Nevertheless, these results demonstrate that the Bi (111) sur-

face states are robust against nonmagnetic disorder perturbation, while quite sensitive to the surface magnetic impurities.

Next, we will go into details of how different impurities will affect the phase coherence length l_φ as mentioned before. In fact, detailed knowledge in the quantum corrections to magnetoconductivity may provide an alternative technique for identifying the surface states. As for a 2D electronic system, the magnetoconductivity data can be described by the two dimensional Hikami–Larkin–Nagaoka (HLN) theory in the presence of strong spin–orbit coupling:[28]

$$\Delta\sigma_{xx}(B) = \alpha\frac{e^2}{2\pi^2\hbar}\left[\Psi\left(1/2+\frac{\hbar}{4eBl_\varphi^2}\right)-\ln\left(\frac{\hbar}{4eBl_\varphi^2}\right)\right], \quad (1)$$

where $\Delta\sigma_{xx}(B) = \sigma_{xx}(B) - \sigma_{xx}(0)$, e is the electronic charge, $\hbar$ is the Planck constant, l_φ is the phase coherence length, Ψ is the digamma function, and α should be equal to 1, 0, and $-1/2$ for the orthogonal, unitary, and symplectic cases, respectively. When turning into the magnetoconductivity description, the data plotted in Fig. 2(a) is now shown in Fig. 3. It can be seen from the black curve that equation (1) gives reasonable good fitting to the low field data. It is interesting to find out that for both the pristine Bi (111) films and the one with Cu impurities on top, the extracted α is consistently around $-1/2$, which is as expected for a 2D strong spin orbital coupling surface states. However, the Cu impurities will significantly reduce the phase coherence length l_φ of the system from 182 nm to 114 nm at 1.5 K. In fact, for both cases the low temperature transport is through the 2D surface states with very strong spin orbital coupling. Thus the magneto transport in it can be described by the HLN theory, which will give a constant $\alpha = -1/2$ in symplectic cases. While due to the increasing scattering center from the Cu surface impurities, it could be anticipated that the phase coherence will become shorter. This is consistent with the conclusion that we draw from the influence of Cu impurities on the surface states conductivity.

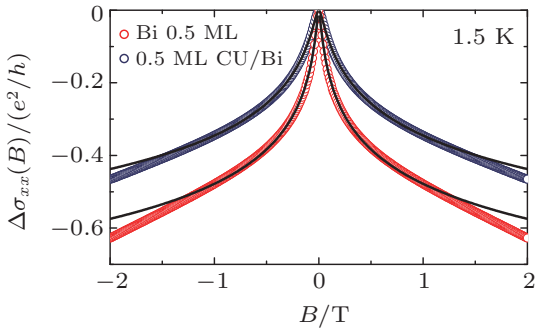


Fig. 3. (color online) Magnetoconductivity curves for the 5.0-nm Bi film with (blue) and without (red) Cu surface impurities. The black line shows the low magnetic field data fits reasonably good to Eq. (1).

By applying this fitting procedure to the curves at different temperature, we can extract the temperature dependence of the α and the phase coherence length l_φ. The detailed results are shown in Fig. 4(a). The extracted α value is found consistently to be around $-1/2$ for both cases, while the phase coherence length l_φ shows dramatic temperature dependence. For the films with Cu impurities l_φ is systematically smaller than the pristine Bi (111) film in the considered temperature regime. Theoretically, the phase coherence length is defined as $l_\phi = (D\tau_\phi)^{1/2}$, where D is the diffusion constant and τ_ϕ is the inelastic scattering time. The inelastic scattering time depends on temperature, which usually increases as temperature decreases. Thus the temperature dependence observed here is as anticipated.

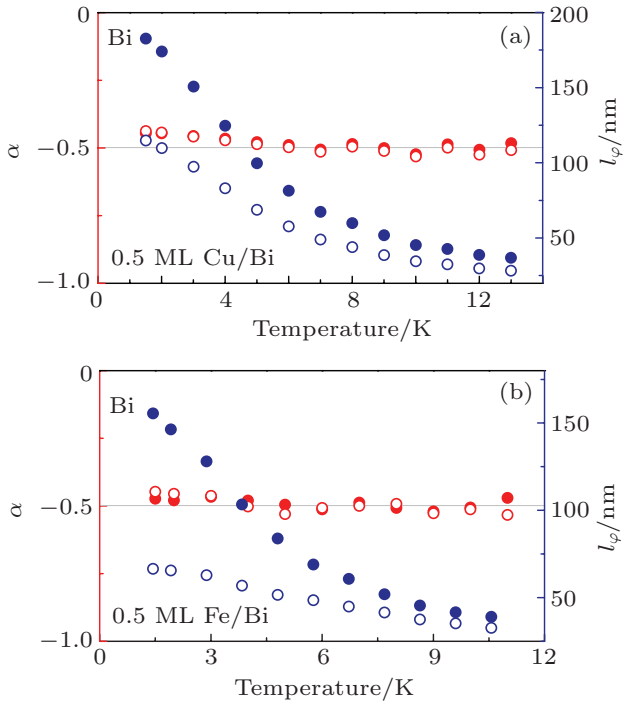


Fig. 4. (color online) The extracted α value and phase coherence length l_φ as a function of temperature for both the pristine Bi (111) films and the films with surface impurities. (a) Solid dots for the pristine Bi films and open circles for the Bi films with Cu impurities. (b) Solid dots for the pristine Bi films and open circles for the Bi films with Fe impurities.

The influence of the 0.5-ML Fe impurities is also considered here. The result is summarized in Fig. 4(b). Without exception, the α value is also consistently around $-1/2$. But, it should be noted that the phase coherence length l_φ is reduced from 155 nm to 66 nm. This corresponds to a reduction of 57%, which is larger compared to the 37% reduction induced by Cu impurities. This is reasonable as the Fe impurities break the locally time-reversal symmetry and activate the direct backscattering channel, while the Cu impurities simply serve as the surface defect scattering center. This is consistent with their difference in affecting the surface conductivity.

Finally we show that the metallic surface states of Bi (111) thin films are very robust against surface oxidation. The experiment is specially designed in the following way: after an 8.0-nm thick Bi (111) thin film was epitaxially grown on

Si (111), only half of the sample was covered in-situ by the 4-nm MgO capping layer, then the whole sample was taken out of the UHV chamber to be exposed in air for 1 hour at 300 K. After this process, the uncovered Bi (111) surface will be oxidized while the other should be protected because of the MgO capping layer. Then the sample was put back into the UHV chamber and the oxidized Bi (111) part was capped by 4-nm MgO. Figure 5(a) shows the resistivity as a function of temperature for the 8-nm Bi (111) thin film with and without the foregoing surface oxidation. Quite unexpectedly, compared to the Bi (111) film without oxidation, the resistivity on the oxidized Bi (111) part is only slightly increased, and the overall temperature dependence behavior is not changed. This result indicates unambiguously that the interface between the surface Bi-oxide and the Bi film inside remains metallic just as without the surface oxide. More surprisingly, the WAL for the 8-nm Bi (111) thin film with and without the surface oxidation looks very similar as shown in Fig. 5(b), which implies again that the metallic surface of the Bi (111) thin film survived after the surface oxidation. A plausible understanding could be that the surface oxidation simply displaces the metallic surface toward the film interior. These findings are quite unexpected when considering the fact that Bi is a prototypical semimetal with topologically trivial electronic band structure.

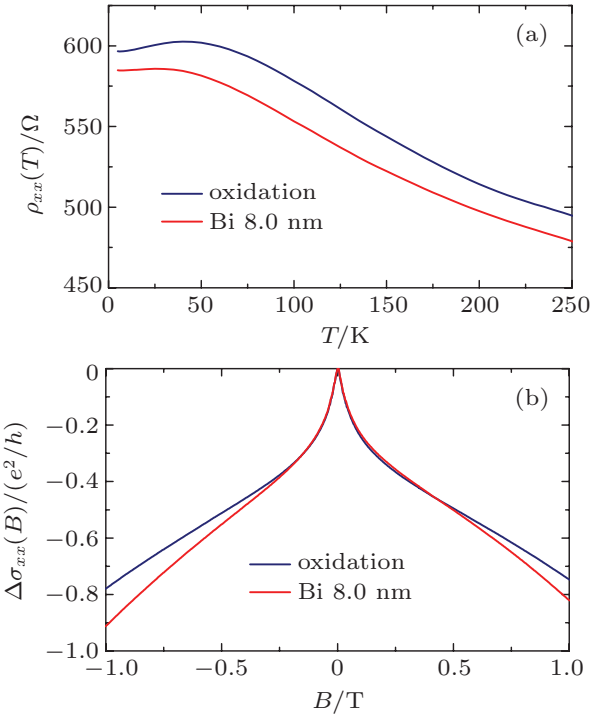


Fig. 5. (color online) The influence of surface oxidation on an 8.0-nm Bi (111) film. Temperature dependence of the film resistivity with and without oxidation is shown in panel (a), while the corresponding magnetoconductivity is plotted in panel (b).

4. Conclusion

In conclusion, we show that the surface states conductivity of Bi (111) films are very sensitive to surface impurities modification. The WAL effect, which arises from the 2D strong spin orbital coupling surface states, is suppressed by magnetic impurities, but it is quite robust against nonmagnetic impurities. Even more dramatically, the surface states are very robust against the surface oxidation. We believe these unique properties could possibly make the Bi surface states useful in future spintronics devices.

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