Comment on "Quantum transport in the surface states of epitaxial Bi(111) thin films"

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Zhu *et al.* [Phys. Rev. B **94**, 121401(R) (2016)] recently reported an experimental work that claims that epitaxial Bi(111) films grown on Si(111) are (1) topologically nontrivial, and (2) metallic only at the surface and insulating in the interior bulk, consistent with the old prediction of a semimetal-to-semiconductor (SMSC) transition. Here we point out that although Bi can be nontrivial, the SMSC transition does not happen at the same time. Through the comparison of the thickness and temperature dependence of the film conductivity of Bi with $Bi_{0.9}Sb_{0.1}$ performed *in situ*, we find no evidence of the insulating bulk states of Bi when the thickness is less than 240 Å, which is in accordance with our angle-resolved photoemission spectroscopy measurements and density functional theory calculations.

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Semimetal bismuth (Bi) has been one of the most intensively studied materials in the history of condensed-matter physics. Recently, there have been two controversial issues about the intriguing physical properties of Bi. The first one is concerning the old prediction of a semimetal-to-semiconductor (SMSC) transition [1]. Xiao *et al.* showed that for Bi films whose thickness d is thinner than 900 Å, the SMSC transition does actually take place [2]. However Aitani *et al.* reported that Bi films in the thickness range of 25–60 Å show bulk-surface coherent transport; the bulk and the surface states form a single transport channel that shows quantum behavior at low temperature [3]. These two apparently contradicting results were reasonably explained by high-resolution angle-resolved photoemission spectroscopy (ARPES) measurements in which a clear Fermi-level crossing was detected for the holelike bulk band for films thinner than $d \sim 120$ Å, whereas it became insulating at $d \sim 700$ Å [4]. However, Zhu *et al.* claimed that bulk is insulating even at $d \sim 40$–160 Å in Ref. [5].

The other issue is about the topological properties of Bi. Bi was believed to be topologically trivial from theory [6], but several groups claimed that the surface-bulk connection of the Bi electronic structure shows that Bi is nontrivial [7–9]. Furthermore, Ref. [5] reported that Bi is indeed topologically nontrivial by detecting quantum oscillations in Bi(111) ribbons from transport measurements. There are no serious attempts to explain this apparent inconsistency between theory and experiment. However, a sophisticated *ab initio* calculation showed that the topological properties of Bi (as well as the occurrence of a SMSC transition) is highly sensitive to the lattice constant of Bi and only a slight change of 0.01–0.02 Å in the in-plane lattice constant can indeed change the topology and the electronic structure of Bi [10].

To summarize, the claim of Zhu *et al.* about these two controversies is that (1) the Bi films are topologically nontrivial and (2) the bulk states of Bi films at $d \sim 40$–160 Å are insulating [5]. In this Comment, we would like to point out that although it is possible to say that the experimentally studied Bi films up to now are topologically nontrivial due to lattice strain, it is unlikely that the bulk is insulating. Our systematic *in situ* transport measurements clearly show that bulk Bi is still metallic below $d \sim 240$ Å by comparing the results of Bi and $Bi_{0.9}Sb_{0.1}$, a true topological insulator. This result is consistent with our ARPES measurements [4] and also supported by density functional calculations [11].

Figure 1 shows the temperature dependence of the film resistivity for Bi (a) and $Bi_{0.9}Sb_{0.1}$ (b) films at various film thicknesses grown on Si(111)-7×7 [12,13]. The measurements were performed in a custom-made *in situ* micro-four-point-probe surface-state transport measurement system equipped with sample preparation tools such as reflection high-energy electron diffraction (RHEED) and sample annealing capabilities [14]. In Fig. 1(a), one can see that all the Bi films with different film thickness of 24, 48, and 239 Å show metallic behavior from 20 to 300 K. This is clearly in contrast to what is shown in Ref. [5] (where a change from a semiconducting to a metallic behavior at 120 K was found). However, from these data alone, we cannot say whether this is due to the fact that (i) the surface is metallic while the bulk is insulating, or (ii) both the surface and the bulk are metallic. This is because our measurements are done without any capping layers which means that much more care has been taken not to contaminate the sample surface and the film itself compared to Ref. [5].

Let us now turn to the data for $Bi_{0.9}Sb_{0.1}$ in Fig. 1(b), which is the first example of a three-dimensional topological insulator. One can notice a semiconducting behavior for the 239-Å-thick film, while the 98-Å-thick film shows a semiconductor-to-metal transition at ∼150 K. For the 29-Å-thick film, a metallic behavior is found already from room temperature. So a transition from a semiconducting to a metallic behavior in the temperature dependence of the film resistivity is found here by reducing the film thickness and enhancing the surface/volume ratio. The complete different behavior between Bi and $Bi_{0.9}Sb_{0.1}$ for the films with the

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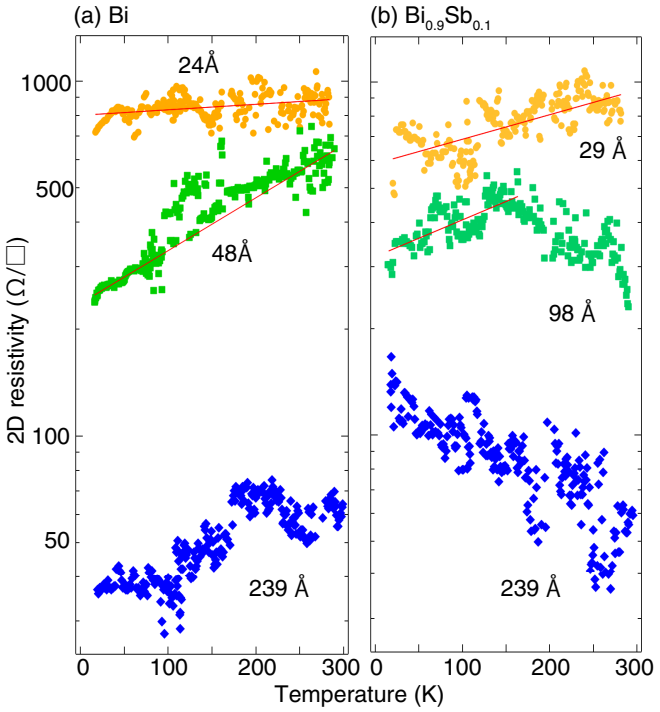

FIG. 1. (a) Temperature dependence of the film resistivity for a 24-, 48-, and 239-Å-thick Bi(111) film. (b) Temperature dependence of the film resistivity for a 29-, 98-, and 239-Å-thick $Bi_{0.9}Sb_{0.1}$(111) film. The red solid lines are linear fits to the data.

same thickness of 239 Å shown in Figs. 1(a) and 1(b) is a strong evidence that bulk Bi is not insulating at this film thickness. The Fermi surface of Bi and $Bi_{0.9}Sb_{0.1}$ has only a slight difference and thus it is difficult to say that only the surface states are contributing to the film conductivity for the 239-Å-thick Bi film. Concerning the 24- and 48-Å thick Bi films, a decrease in resistivity which is linear with temperature is found which can be attributed to the reduced electron-phonon scattering by lowering the temperature as typically found in metals. However, the slope is clearly different between the two ($0.31 \pm 0.06\ \Omega/\mathrm{K}$ and $1.42 \pm 0.05\ \Omega/\mathrm{K}$ for the 24- and 48-Å-thick film, respectively). In contrast, for the 29- and 98-Å-thick $Bi_{0.9}Sb_{0.1}$ films, the slope below 150 K is nearly the same ($1.20 \pm 0.10\ \Omega/\mathrm{K}$ and $0.97 \pm 0.10\ \Omega/\mathrm{K}$ for the 29- and 98-Å-thick film, respectively), which means that the surface states are actually dominant in the case of $Bi_{0.9}Sb_{0.1}$. Furthermore, information on the electron-phonon coupling of the surface states of Bi can be inferred from the peak width of the ARPES spectra which do not show significant thickness dependence in our ARPES measurement [4]. So these facts clearly show that the bulk states should also be involved in this metallic transport in Bi at least for the 48-Å-thick film. It is rather difficult to make a definite conclusion for the 24-Å-thick film only from these data. But as far as we judge in combination with our previous low-temperature quantum transport [3] and ARPES [4] data, it is likely that the bulk is still metallic even at this thickness. This is also supported by *ab initio* calculations reported in Ref. [11], which clearly show that the bulk hole band has a higher energy than the Fermi level at the $\bar{\Gamma}$ point. So we think bulk Bi cannot be insulating even for a very thin film, which is in contrast to the SMSC prediction [1] and Ref. [5].

The data shown in Ref. [5] can be interpreted in the following way even when not assuming a bulk insulator. The authors have claimed that the film conductivity becomes constant for films thicker than 150 Å at 5 K in Fig. 3 in Ref. [5]. However, a careful inspection shows that the conductivity is still increasing at $150 < d < 275$ Å and not constant when grown on Si. This increase of the film conductivity as a function of film thickness is direct evidence that the bulk is still contributing to the film transport. The conductivity should increase as the film becomes thicker due to a larger contribution from the bulk states, clearly meaning that the bulk is metallic for all the films studied in Ref. [5]. And the reason why the authors could only obtain $\alpha \sim -0.5$ in the weak antilocalization analysis [Fig. 4(c) in Ref. [5]] is also because the bulk states are metallic and the surface and the bulk form a single channel in the coherent transport. If the bulk was insulating and the coupling of the top and bottom surfaces was the reason for this behavior, a transition to two separate transport channels ($\alpha = -1$) would have been observed by increasing the film thickness. The authors should have at least observed a gradual change from $\alpha \sim -0.5$ to $\alpha = -1$ since the coupling should become weaker for thicker films. Thus these data are clearly not consistent with a semiconducting bulk picture as the authors insist.

The authors furthermore claim that the observation of the Aharanov-Bohm (AB) or Altshuler-Aronov-Spivak (AAS) effects for the films fabricated into nanowires [Fig. 2(a) in Ref. [5]] is more clear evidence of the insulating bulk of Bi, in addition to the temperature dependence of the resistance. However, we think this is not an intrinsic property of the film itself since it is clear that the bulk hole band is still metallic if one performs *in situ* ARPES measurements without any sample fabrication [4]. Thus the capping layer or the fabrication process is definitely influencing the transport properties of Bi in Ref. [5].

Now let us discuss the topological properties of the Bi films. The in-plane lattice constant of these Bi films on the Si(111)-7×7 surface was determined as 4.50 ± 0.02 Å from x-ray-diffraction measurements for 60-Å-thick film at room temperature [15]. This is smaller than the one used in the theoretical calculations that concludes Bi to be a trivial material (4.54 Å) by 0.44%. Bi will likely be more contracted when cooled down and recalling that a compressive strain of 0.3% can drive Bi into a topologically nontrivial state [10], the fact that evidence of nontrivial topology was found in nanoribbons fabricated from the Bi(111)/Si film in Ref. [5] is reasonable and supported by theoretical calculations. It is also not surprising that Bi was claimed nontrivial for Bi films grown on Ge(111) [9] from ARPES studies, since the lattice constant in this system was determined as 4.45 Å, which is 2% compressed from 4.54 Å [16]. A puzzling case is the claim that single-crystal Bi also shows a surface-state band dispersion consistent with nontrivial topology [7,8], since it should not be strained at all. While we cannot explain the reason for this, a detailed structure determination should be performed for single-crystal Bi samples to confirm if the lattice constant used in the calculation is consistent with the experimentally determined one.

The authors in Ref. [5] have stated that since Bi is topologically nontrivial, the surface state should be robust against

oxidation which is in contradiction to our previous results [17]. We believe there is a serious misunderstanding here. The first point is that not all the surface states are of topological origin in strained Bi. Namely, only the band that constitutes the two electron pockets at $\bar{\Gamma}$ and $\bar{M}$ is the topological state judging from how the surface states and the bulk connect with each other. Second, the existence of the topological surface states of topological materials are guaranteed as long as the perturbation is weak enough not to change the bulk band topology. Even if the bulk band topology is unchanged, the surface-state dispersion can alter drastically, which has actually been shown for oxidation of Bi_2Se_3 [18]. Information concerning the interface between oxygen and Bi is crucial to understand what has happened when we oxidize Bi. Thus the fact that the surface-state conductivity disappeared completely by heavy oxidation does not necessarily contradict the fact that Bi is topological. Judging from RHEED, the whole film was not oxidized since at least some of the diffraction spots were observed (Fig. 4 of Ref. [17]). Thus one would naively think that the surface states at the interface to the substrate should survive and contribute to the transport, which was actually not observed in Ref. [17]. But this is consistent with the observation in Ref. [5] that a 0.5-monolayer Co deposition on the Bi surface completely destroyed the weak antilocalization behavior of the whole film. The origin of these peculiar behaviors is an open question.

Another important point which should be mentioned is that Ref. [10] claims that Bi undergoes a SMSC transition when the in-plane lattice constant is expanded by 0.4%. This was initially proposed in Ref. [19]. On the other hand when the lattice is compressed, the overlap between the bulk electron and hole pockets increases, making the bulk Fermi surface larger. Thus we think that bulk states of Bi films with compressed in-plane lattice constants are more metallic compared to the unstrained case and unlikely to undergo a SMSC transition even when the bands become discrete due to the quantum size effect.

As a final remark, we would like to mention that the terms "surface" and "bulk" may not be appropriate when discussing ultrathin Bi films. Since it has been shown that the top and the bottom surface states couple due to the overlap of the respective wave functions from ARPES [4] and transport measurements [5], the "surface states" discussed are no longer surface states in the usual sense that are localized at one side of the film, especially the states near $\bar{M}$. Instead the wave function spreads out across the whole film with more weight at the surface and interface, and in this context it is difficult to distinguish them from the usual bulk states. So the system should be regarded as a pure two-dimensional system without clear distinction between the surface and bulk states. As a result, irrespective of whether the bulk is insulating or not, Bi films can exhibit quantum transport behavior expected for a low-dimensional system.

Note added in proof. We recently became aware of a paper stating that Bi is a second order topological material in three dimensions [20]. The signature of quantum oscillations in Bi nanoribbons shown in Ref. [5] may be related to the presence of one-dimensional hinge states that are expected to exist from the bulk-edge correspondence for a second order topological material.

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