Bi(111) thin film with insulating interior but metallic surfaces

Shunhao Xiao, Dahai Wei, and Xiaofeng Jin
State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China
(Dated: December 21, 2013)

The electrical conductance of molecular beam epitaxial Bi on BaF$_2$(111) was measured as a function of both film thickness (4-540 nm) and temperature (5-300 K). Unlike bulk Bi as a prototype semimetal, the Bi thin films up to 90 nm are found to be insulating in the interiors but metallic on the surfaces. This result has not only resolved unambiguously the long controversy about the existence of semimetal-semiconductor transition in Bi thin film but also provided a straightforward interpretation for the long-puzzled temperature dependence of the resistivity of Bi thin films, which in turn might suggest some potential applications in spintronics.

PACS numbers: 75.30.Et, 75.30.Gw

Bi is a pentavalent element in the periodic table with the atomic structure of [Xe]4f$^{14}$5d$^{10}$6s$^2$6p$^3$. It crystallizes in a rhombohedral (A15) structure with two ions and ten valence electrons per primitive cell. The even number of valence electrons makes it very close to being an insulator, but the very slight overlap between the conduction and valence bands eventually drives it to a prototype semimetal with a very small number of carriers ($3 \times 10^{17}$ cm$^{-3}$), therefore leading to an unusually long Fermi wavelength (30 nm) [1, 2].

It was predicted theoretically that due to the quantum size effect, Bi should undergo a semimetal to semiconductor transition in thin films when the thicknesses are comparable to the Fermi wavelength [3, 4]. However, the experimental identification is highly nontrivial and remains contradictory, although considerable effort has been made during the last fifty years [2, 5–8]. Especially, the experimentally observed non-monotonic temperature dependence of the electrical resistivity does not fit at all to the physical picture anticipated by the existence of a semiconductor phase [2, 12]. It was argued recently by Hirahara et al., by means of angle resolved photoemission (ARPES), that Bi(111) films should always be metallic because of the persistence of thickness-independent metallic surface states, in direct contrast to the semimetal-semiconductor transition [13, 14]. Therefore, the existence of semimetal-semiconductor transition in Bi films remains as a puzzle.

In this letter, we are going to demonstrate unambiguously that the interior of a Bi(111) film thinner than 90 nm prepared by molecular beam epitaxy on BaF$_2$(111) is indeed insulating or semiconducting while its surfaces are metallic. This result has finally clarified the long-standing issue of the semimetal-semiconductor transition in Bi films; in addition it might be related and even provide a new playground to explore the topological properties of Bi [15, 17] and Bi-based topological insulators [18–20].

Single crystalline Bi(111) films ranging from 4 to 540 nm thick were epitaxially grown on BaF$_2$(111) by molecular-beam epitaxy in an ultra high vacuum system equipped with reflection high energy electron diffraction (RHEED) and Auger electron spectroscopy (AES) [21]. Clean and ordered BaF$_2$(111) substrates were first prepared by annealing at 700 °C for 10 minutes then cooled down and kept at 70 °C, on which the epitaxial growth of Bi was followed while the evaporation rate was monitored by a quartz microbalance. To prevent oxidation in ambient air during the transport measurement, a 6 nm MgO capping layer was deposited on each sample before taken out from the UHV chamber. The grazing angle X-ray diffraction (XRD) experiment was performed at Beijing Synchrotron Radiation Facility [22]. The transport measurements were carried out on the samples patterned into standard Hall bars along the [112] direction, using Quantum Design physical property measurement system (PPMS-9T) [23].

Fig. 1 shows a set of representative RHEED and grazing angle XRD results for Bi/BaF$_2$(111) at different film thicknesses, which clearly indicates that the epitaxial growth of Bi on BaF$_2$(111) involves two stages. In the early stage below about 15 nm, the RHEED patterns (as for 6 nm thick film) are complicated, implying that the Bi films grow in polycrystal. This is confirmed by the XRD result which shows the coexistence of Bi pseudo-cubic phase ((100) peak at 27.1 degree) and Bi hexagonal phase ((1100) peak at 39.7 degree) in Fig. 1(b) and (c), respectively. In the later stage of film growth beyond 15 nm, the RHEED patterns (as for 25 nm thick film) become very simple, implying that the Bi films grow in single crystal. This is again revealed by XRD that the pseudocubic phase has disappeared and transformed completely to the hexagonal phase of Bi(111) as seen in Fig. 1(b) and (c). In fact, the overall growth behavior realized here in Bi/BaF$_2$(111) is quite similar to the previous observation of Bi on Si(111) 7×7 [24], although the structure transformation there happened at thinner film thickness. We there conclude that we can obtained experimentally pure Bi(111) single crystal films thicker than 15 nm on BaF$_2$(111).

Fig. 2(a) shows the electrical conductance of Bi as a function of film thickness measured at different tem-
temperatures, where three distinct regimes as marked can be realized. In regime (I) the conductance is extremely small reflecting the insulating nature of the pseudocubic phase of Bi. Regime (II) corresponds to the mixture of both pseudocubic and hexagonal phases of Bi, and the transformation from the former to the latter. The most interesting and surprising result lies in regime (III), where the conductance exhibits strong temperature dependence. It is noted that at 5 K the conductance remains almost unchanged with increasing Bi film thickness from 15 nm to 25 nm, i.e., the additional 10 nm Bi doesn’t contribute at all to the electrical conductance; this in turn strongly implies that the low temperature electrical transport in Bi films should be dominated by the metallic surface state while the corresponding film interiors are insulating. In contrast to the 5 K case the conductance at 300 K increases linearly as a function of film thickness, which suggests that besides the surface channel the electron transport in the film interior has also contributed to the conductance. However, this is possible only when the film interior is an insulator or a semiconductor with a very small energy gap about 10 meV, then it would behave like an insulator at low temperature (e.g., 5 K) because of the energy gap, but would become conducting at higher temperatures (e.g., 300 K) when the thermal excitation from the valence band to conduction band is no longer negligible. Therefore, this is the first direct experimental evidence for the existence of the long debated insulating or semiconducting phase in Bi films, although the physical picture turns out to be more complicated than what has been originally proposed. It is clearly now that Bi(111) thin films with thicknesses comparable the Fermi wavelength are indeed insulating or semiconducting but only in the film interiors yet their surfaces are always metallic.

Now we turn to estimate quantitatively the energy band gap of the Bi(111) film interior. Because of the two channels for the total conductance: the surface and interior contributions, we have:

$$G_{xx} = G_s + \sigma_{ixx} \frac{w}{l} d$$

$$G_s$$ and $$G_{xx}$$ are the total and surface conductances respectively, and $$\sigma_{ixx}$$ is the conductivity of the film interior; $$d, l, w$$ are the thickness, length, and width of the Bi(111) Hall bar respectively. It is immediately recog-
FIG. 3: (a) Resistance-temperature curves normalized with the value at 300 K. The inset is a zoom-in from 270 K to 300 K. (b) The temperature coefficients of resistivity between 270 K and 300 K as a function of sample thicknesses. The black curve is a guide to the eye.

FIG. 4: Temperature dependent conductivities of samples with different thickness. The inset shows ln($T_m^2d$) as a function of $1/T_m d^2$.

The appearance of the dip is in fact a result of the competition between the metallic surface and the semiconductor interior of Bi(111) thin film according to Eq. 1, as the relative weight of the former gradually increases and eventually dominates as the film thickness decreases.

With the new understanding on the Bi(111) thin film discussed above, we are going to demonstrate in the following that the longstanding puzzle about the non-monotonic behavior of the resistivity or conductivity versus temperature curve in Bi films can also be resolved. Similar to Eq. 1, the total conductivity $\sigma_{xx}$ from the two (surface and film interior) channels can be expressed as

$$\sigma_{xx} = \frac{\sigma_s}{d} + \alpha \cdot e^{-\frac{\Delta E}{kT}}$$  \hspace{1cm} (2)

Here $\sigma_s$ is the surface conductivity. According to the Matthiessen’s rule, it can be further expressed in resistivity as $\sigma_s = \frac{1}{(\rho_0 + \rho_T)}$, where $\rho_0$ and $\rho_T$ are the surface residual and electron-phonon induced resistivity. By adopting the results in literature for the surface electron-
phonon induced resistivity $\rho_T = sT \frac{2\hbar}{k}$, and the quantum size effect induced energy gap $\Delta E = \frac{b}{\sigma}$ ($b$ is a constant) [2, 4], then Eq. 2 turns into

$$\sigma_{xx} = \frac{1}{d(\rho_0 + sT)} + \alpha \cdot e^{-\frac{b}{kT_T d^2}}$$

(3)

For a given sample with fixed film thickness, it is obvious that the first term from the metallic surface would decrease as the sample temperature increases, while the second term from the semiconductor interior would increase. It is exactly this competition that caused the nonmonotonic behavior of the temperature dependent conductivity or resistivity. Depending on Bi film thickness, when the two terms are comparable in magnitude, a valley in conductivity should be expected in principle, which would qualitatively explain the experimentally observed phenomena in Fig. 4. This complicated behavior of conductivity versus temperature as well as film thickness has always made the electrical transport of Bi films puzzling and mysterious. Quantitatively, for each fixed film thickness the valley as a function of temperature can be determined by minimizing Eq. 3 while noticing the experimental fact that $\rho_T$ is smaller than $\rho_0$, therefore we reach to the following equation:

$$\ln(T_m^2 d) = -\frac{b}{kT_m d^2} + \ln\left(\frac{\alpha \rho_0^2}{sk}\right)$$

(4)

Clearly, as seen in the inset of Fig. 4, the experimental data of $\ln(T_m^2 d)$ vs $\frac{1}{T_m d^2}$ can be well fitted by a straight line with a slope of $-b/k \approx -6 \times 10^4$ K-nm$^2$, by which we can get the film thickness dependent energy gaps of the semiconducting interiors: 23 meV for 15 nm and 13 meV for 20 nm Bi films, respectively, which not only agree very well with the foregoing obtained result deduced from Fig. 2(b) but also provide the trend of thickness dependent energy gap of the film interiors in Bi.

In summary, we have demonstrated in this work that the long debated semimetal to semiconductor transition does happen in Bi(111) thin film when the film thickness is comparable to the Fermi wavelength of Bi; the problem had been controversial because of the subtle fact that the film interior is semiconducting while the surface is always metallic.

This work was supported by MSTC (No. 2009CB929203 and No. 2006CB921303), NSFC (No. 10834001), and SCST. The technical support from Beijing Synchrotron Radiation Facility (BSRF) for XRD measurements is also acknowledged.

* Corresponding author, E-mail: xfjin@fudan.edu.cn