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# Semimetal-to-semiconductor transition in bismuth thin films

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Field- and temperature-dependent magnetotransport measurements on Bi layers grown by molecular-beam epitaxy have been analyzed by mixed-conduction techniques. In the thin-film limit, the net hole density scales inversely with layer thickness while the mobility scales linearly. By studying the minority electron concentration as a function of temperature in the range 100–300 K, we have unambiguously confirmed the long-standing theoretical prediction that quantum confinement should convert Bi from a semimetal to a semiconductor at a critical thickness on the order of 300 Å.

We have studied dependences of the electron and hole concentrations and mobilities on layer thickness and temperature for Bi thin films in much more detail than has been reported previously. From these results, we are able to construct a coherent picture of the free-carrier statistical properties, which are key to any comprehensive understanding of electronic phenomena in this material. It will be seen that the data provide clear evidence for a confinement-induced energy gap in the thinnest film studied ($d$ = 200 Å). This confirmation of the long-standing prediction of a semimetal-to-semiconductor (SMSC) transition is based not on data from the low-temperature region which has received the most attention previously (only majority holes are observed at low $T$), but on the concentration of thermally generated minority electrons in the range 100 K $< T <$ 300 K.

Bismuth is in many respects an ideal material for probing quantum confinement phenomena. The electron effective mass along certain axes is quite small[1] ($< 0.003m_0$) and the mean free path in bulk can be extremely long ($\mu_n$ and $\mu_p$, the electron and hole mobilities, can both exceed[2] $10^6$ cm$^2$/V s at low temperatures). In fact, a 1965 magnetotransport study of bismuth thin films by Ogrin, Lutskii, and Elinson[3] produced the first clear experimental evidence for the quantum size effect in any solid. When the film thickness $d$ was varied, both the resistivity $\rho$ and the Hall coefficient $R_H$ displayed oscillations as the Fermi energy passed into and out of resonance with the quasi-two-dimensional (2D) subbands. That work was the forerunner to all subsequent research into the physics of heterostructure quantum wells.

Bulk Bi is a semimetal, since the three conduction-band minima at the $L$ points lie $\approx$ 40 meV lower than the single valence-band maximum at the $T$ point.[1] However, Lutskii[4] and Sandomirskii[5] pointed out quite early the possibility of using quantum confinement to convert the material into a semiconductor. The SMSC transition should occur when the energy shift due to confinement, scaling as $d^{-2}$, becomes great enough to raise the lowest electron subband to an energy higher than that of the uppermost hole subband. The critical thickness $d_T$ for this transition is predicted by most calculations to fall somewhere in the range 230–320 Å.[6–10]

However, despite numerous transport and optical investigations of quantum size phenomena in bismuth thin films,[8,11–13] and despite several early claims that the SMSC transition had been observed,[3,14–16] it is now generally agreed that those studies produced no convincing experimental confirmation for the existence of the semiconducting phase at small $d$.[6,10,11,13,17] Although they stop short of claiming that the evidence is conclusive, Chu and co-workers have even suggested in recent discussions of this issue that the available data argue *against* the occurrence of a SMSC transition.[8,10] The absence of a transition becomes understandable theoretically if one replaces the usual condition that the electron wave function should vanish at the boundaries of the Bi film by the alternative condition that the gradient of the wave function vanishes. The ground-state electron and hole subband energies then depend only weakly on layer thickness, and the energy gap $E_g$ would remain negative for all $d$.[8,10,13]

Arguments for and against the existence of a semiconducting phase have focused primarily on the presence or absence of sudden changes in the resistivity, Hall coefficient, and magnetoresistance as functions of layer thickness.[3,5,6,8,13–15,18] It was expected that if the energy overlap of the conduction and valence bands could be eliminated and the material converted into a semiconductor, the equilibrium electron and hole concentrations ($n$ and $p$) would abruptly decrease. Such conclusions were either explicitly or implicitly based on the assumption that, as in bulk Bi, the statistical properties of the thin films are governed by intrinsic considerations. Similarly, virtually all theoretical analyses of Fermi energies and carrier concentrations for $d$ spanning the transition region[6,8–10,19] have taken the electron and hole densities to be equal. However, in the only previous experimental work to directly determine the dependences of $n$ and $p$ on $d$, Komnik *et al.*[12,20] demonstrated that this assumption is strongly violated. Those authors found that due to band bending related to impurity states either at the surface or at the interface with the substrate, the low-temperature electron concentrations in a series of films varied as

$$n \approx n_i + n_s/d, \qquad (1)$$

where $n_i \approx 2.5 \times 10^{17}$ cm$^{-3}$ is the bulk intrinsic concentration resulting from energy overlap of the conduction and valence bands, and $n_s \approx 2.75 \times 10^{12}$ cm$^{-2}$ is the sheet density associated with surface states. This relation clearly yields $n \gg p$ in the thin-film limit, in violation of most previous assumptions. It will be seen below that the present investigation yields a very similar result, except that in our case the majority carriers are holes rather than electrons. Although it has naturally not been confirmed that $|n-p| \gg n_i$ in the thin Bi films studied by other workers, we are aware of no data which are inconsistent with this hypothesis.[12] Furthermore, such a result seems likely (except in special cases of compensation), due to the small energy gap and the inevitable presence of defect states at the surface.

From the experimental dependences of $n$ and $p$ on $d$, it is clear that at thicknesses small enough for the SMSC transition to occur, the Fermi energy at low temperature will lie either high in the conduction band or low in the valence band. Since the majority carrier concentration then becomes insensitive to the introduction of an energy gap, one should expect no abrupt changes in the resistivity or Hall coefficient at the transition point.[12] Although the results of Komnik *et al.* have been known since 1971, a surprising number of subsequent analyses have failed to account for the implications of Eq. (1). For example, in addition to the transport investigations cited above, the plasma reflectivity measurements of Takaoka and Murase[21] were undoubtedly influenced by the large net carrier concentrations at small $d$. In summary, we are aware of no previous study which provides compelling evidence either for or against the occurrence of a SMSC transition in thin Bi films.

The growth of Bi-CdTe heterostructures by molecular-beam epitaxy (MBE) has been described in detail elsewhere.[22] Substrates were (111)B CdTe purchased from II-VI, Inc. Following deposition of a 3000-Å CdTe buffer layer at 250°, the substrate temperature was lowered to 150 °C and the Bi film was grown at a rate of 0.2–0.5 Å/s. The structure was then covered with a 100-Å CdTe cap. Reflection high-energy electron diffraction (RHEED) was used to examine the specific surface reconstruction of the deposited layers. While the CdTe buffer layer exhibited reconstruction associated with the (111)B surface of CdTe, the Bi films displayed no reconstruction. The diffraction streaks were sharp and Kikuchi lines were present, providing *in situ* evidence for the uniform two-dimensional growth of Bi. In this work we report measurements on four films, having thicknesses of 200 Å, 300 Å, 400 Å, and 5000 Å. These $d$ were confirmed using a mechanical step profiler.

For each sample, the resistivity and Hall coefficient were measured as a function of magnetic field ($0 \leq B \leq 7$ T) and temperature ($4.2 < T < 300$ K) by the van der Pauw technique. In all measurements, $B$ was aligned with the trigonal axis and the current flow was in the plane normal to that axis. While the holes are essentially isotropic in that plane, the anisotropy of the electron mass is quite large ($m_2/m_1 \approx 200$),[1] so we have employed the relation $\mu_n \approx 2\mu_1$ for the effective electron mobility obtained from the van der Pauw measurements. Only a few previous investigators have attempted to extract electron and hole densities and mobilities in thin Bi films from the field-dependent transport coefficients.[12,23,24] We have employed a hybrid mixed-conduction procedure,[25] which combines the conventional multicarrier fits with "mobility spectra" from the formalism of Beck and Anderson.[26]

Figure 1 illustrates experimental mobilities for electrons (filled points) and holes (open points) in three of the four films. While both $\mu_n$ and $\mu_p$ could be determined at all temperatures in the 5000-Å film, data for the thinner samples showed no clear evidence for electrons in the low-$T$ limit. Note that the electron and hole mobilities for a given film at a given temperature tend to be comparable, and that the low-temperature $\mu_p$ scale almost linearly with $d$ (presumably due to boundary scattering[17]). For comparison, Fig. 1 also shows curves corresponding to $\mu_p$ (solid) and $\mu_n$ (dashed, representing $\mu_1/2$) in bulk Bi.[27] We find that whereas the hole mobility in the 5000-Å film approaches the bulk dependence at the highest temperatures, $\mu_n$ in that sample remains a factor of 5 below the bulk curve. In previous studies of thin films, Jin *et al.* also reported $\mu_n \approx \mu_p$,[23] while Partin *et al.* obtained a mobility ratio $\mu_n/\mu_p$ closer to that in bulk.[24] This qualitative difference is probably related to the two-step growth process employed by the latter authors, which allowed them to produce films in which boundary scattering did not dominate the electron mobility when $d \geq 2000$ Å. Calculations to be published elsewhere show that one expects $\mu_n/\mu_p$ in thin films to be much smaller for boundary scattering than for phonon processes. It is significant that the Hall coefficient in our 5000-Å film is positive at higher temperatures and low magnetic fields, whereas in bulk Bi it is negative for the relevant geometry.[27]

Dependences of the electron and hole concentrations

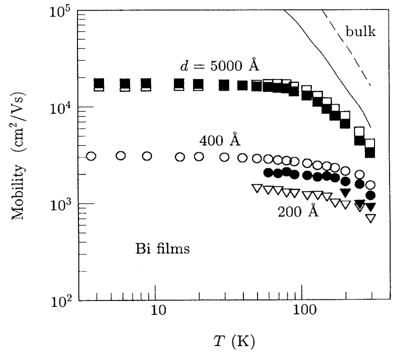

FIG. 1. Experimental mobilities for electrons (filled points) and holes (open points) vs temperature in three of the films. The curves represent bulk dependences (Ref. 27) for electrons (dashed) and holes (solid).

on temperature are shown in Fig. 2 for all four samples. Note that in the 5000-Å film, $n \approx p$ over the entire temperature range, as should be expected when there is an energy overlap between the conduction and valence bands and the net doping density is significantly smaller than the intrinsic concentration. That sample is slightly $n$ type, with $N_D - N_A \approx 7 \times 10^{16}$ cm$^{-3}$. At $T = 4.2$ K, the electron and hole concentrations of $\approx 4 \times 10^{17}$ cm$^{-3}$ are roughly a factor of 1.5 larger than the values usually reported for bulk Bi.[1,28] Similarly, the 300-K densities $n \approx p \approx 5 \times 10^{18}$ cm$^{-3}$ in that film are about a factor of 2 larger than the bulk results[27–29] [in previous studies of Bi thin films, both Komnik *et al.*[12] and Partin *et al.*[24] also obtained $n$(300 K) exceeding typical bulk values]. However, despite the slightly larger densities at both low and high temperatures, our data preserve the bulk variation $n_i \propto T^{3/2}$ for $T$ in the range 100–300 K.[20,28,29]

Also apparent from Fig. 2 is that in contrast to the nearly equal electron and hole concentrations in the 5000-Å sample, the three thinner films are strongly $p$ type at low temperatures. The net concentrations are found to follow quite closely the thickness dependence of Eq. (1), with $p_s \approx 8 \times 10^{12}$ cm$^{-2}$. For these $p$-doping levels and the energy overlap appropriate to bulk Bi, one predicts that the low-temperature electron concentration should be slightly less than $10^{17}$ cm$^{-3}$ in the 400-Å film and that the Fermi level should be below the bottom of the conduction band in the two thinner films. Accounting for the uncertainty in the mixed-conduction analysis of the data, we find that all three samples have low-temperature electron concentrations less than $(1-2) \times 10^{17}$ cm$^{-3}$. With increasing temperature, however, the $n(T)$ dependences for the films with thicknesses of 300 Å and 400 Å indicate strong thermal activation. By the time $T$ reaches 300 K, $p/n$ is rapidly approaching unity and both $n$ and $p$ are comparable to values observed in the 5000-Å film. On the other hand, the 200-Å sample displays no significant minority-carrier generation until the temperature approaches ambient. Electrons are not observable at all until $T$ reaches 200 K, and at 300 K their density remains at least a factor of 5 lower than $n$ in any of the other films even though the hole concentrations are essentially equal at that temperature. These features strongly suggest that the conduction-band minimum and valence-band maximum in the thinnest film are separated by an energy gap, which considerably reduces the thermal activation of minority electrons.

It is well known that the concentration of thermally generated intrinsic carriers in a semiconductor is quite sensitive to the magnitude of $E_g$. If we approximate in lowest order by assuming parabolic bands and nondegenerate statistics, the "law of mass action" yields[25]

$$n_i \equiv (np)^{1/2}$$
$$\approx 2\nu_n^{1/2} \left(k_B T/2\pi\hbar^2\right)^{3/2} \left(m_n^{\rm DS} m_p^{\rm DS}\right)^{3/4} e^{-E_g/2k_B T}, \quad (2)$$

where $\nu_n = 3$ is the number of equivalent electron valleys and $m_n^{\rm DS}$ and $m_p^{\rm DS}$ are the density-of-states effective masses. Since the energy gap may generally be taken to have a linear dependence on temperature: $E_g \approx E_g^0 + \gamma T$, it is evident from Eq. (2) that if $n_i/T^{3/2}$ is plotted against inverse temperature on a semilogarithmic scale, the slope of the curve should be directly proportional to the zero-temperature extrapolation $E_g^0$. Figure 3 illustrates the carrier concentration data for all four samples plotted in this way. Note that even though $n \approx p$ in the 5000-Å sample at all temperatures while the 300-Å and 400-Å films have relatively large net hole concentrations, the intrinsic concentrations for all three are in excellent agreement. The slopes vanish to within experimental uncertainty, indicating $E_g^0 \approx 0$ for $d \geq 300$ Å. However, $n_i$ for the 200-Å sample lies significantly below the other results, and displays a clear activation behavior corresponding to an energy gap of $\approx 40$ meV. We consider this to be unambiguous experimental evidence for the occurrence of a semiconducting phase in thin Bi films. It should be emphasized that $E_g^0$ is a zero-temperature extrapolation and does not necessarily represent the actual gap in the neighborhood of 300 K. To our knowledge, the temperature coefficient for the indirect gap in Bi has never been determined, although it is believed to be small.[29]

The results in Fig. 3 imply that the critical thickness for the SMSC transition falls somewhere between 200 Å and 300 Å. If the confinement energy is taken to scale as $d^{-2}$ and it is specified that the band edges shift from an overlap of $-40$ meV in the thick-film limit[1] to an energy gap of 40 meV at $d = 200$ Å, we obtain the rough estimate that the SMSC transition occurs at $d_T \approx 280$. This agrees quite well with most theoretical predictions, which tend to fall in the range 230–320 Å.[6–10]

Summarizing, we have studied the magnetotransport

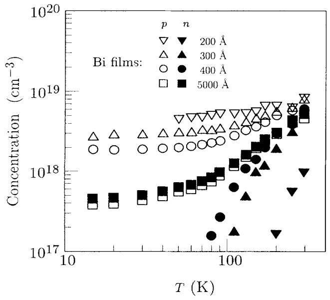

FIG. 2. Experimental electron and hole concentrations vs temperature in four Bi films with thicknesses between 200 and 5000 Å.

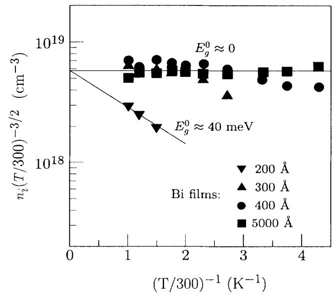

FIG. 3. Intrinsic carrier concentration (normalized to $T^{3/2}$) vs inverse temperature in four Bi films with thicknesses between 200 and 5000 Å.

properties of MBE-grown Bi thin films on CdTe substrates. A hybrid mixed-conduction analysis of the field-dependent resistivity and Hall coefficient has enabled us to obtain accurate temperature dependences for the electron and hole densities and mobilities in each sample. A detailed consideration of the intrinsic carrier concentrations in the temperature range 100–300 K demonstrates that while the samples with thickness $\geq$ 300 Å are semimetallic, quantum confinement has induced an energy gap of $\approx$ 40 meV in the film with $d$ = 200 Å. This represents an unambiguous confirmation that a semimetal-to-semiconductor transition occurs in Bi thin films, at a critical thickness on the order of 280 Å. While the possibility of a SMSC transition was theoretically predicted nearly 30 years ago,[4,5] the semiconducting phase had never been positively identified despite numerous attempts, and more recent calculations based on alternative boundary conditions have suggested that the transition may not occur at all.[8,10,13] We point out that due to an inverse scaling of the net background carrier concentration with layer thickness [Eq. (1)], most of the previous data should not have been expected to display any abrupt changes at the transition point, because the quantities studied depended primarily on *majority*-carrier properties. The present approach is far more sensitive because it is based on the dependence of the *minority*-carrier concentration to the presence or absence of an energy gap.

It has recently been suggested that a narrow-gap semiconductor whose band alignment is indirect in momentum space[30] would have highly attractive properties in certain optical and electro-optical device applications.[31,32] Indirect narrow-gap superlattices (INGS) such as Bi-CdTe (Refs. 33 and 22) could potentially provide the unique combination of a small $E_g$, weak optical absorption, and a long electron-hole recombination lifetime. As a result of the finding that quantum-confined Bi can be converted into a variable-gap semiconductor with an indirect band alignment in momentum space, initial work on MBE-grown Bi-CdTe superlattices is now under way.[22]

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