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Investigation of quantum confinement within the tunneling-percolation transition for ultrathin bismuth films

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ABSTRACT

We investigate conduction phenomena in ultrathin bismuth (Bi) films that are thermally evaporated onto flat quartz. Critical points in the conductance as a function of deposition time are identified and used to scale the data from time dependence to coverage dependence. The resulting nonlinear coverage scaling equation is verified independently via analysis done on transmission electron microscope images of the evaporated films. The scaled data yields critical exponents in very good agreement with classical percolation theory, and clearly shows the transition from the tunneling regime into percolation. Surprisingly, no noticeable signatures of size-quantization effects in the nucleation sites as a function of deposition time is observed in either regime. We discuss our findings in light of Boltzmann transport modeling of 1D conduction as an approximation to the narrow percolative paths that form at the onset of percolation. Our results suggest that lack of a preferred crystallite orientation in the nucleation process may indeed cause quantum-confinement to be too smeared out to be observable in the tunneling to percolation transition.

1. Introduction

Ultrathin Bi films (i.e. a few tens of atoms thick) offer a host of opportunities to investigate interesting quantum phenomena not commonly observed in thicker films or in bulk. These include density of states quantization [1], mean-free path suppression in the direction perpendicular to film growth [2], pronounced surface scattering of electrons and phonons which can lead, e.g., to enhanced thermoelectric figures of merit [3], quantum-plasmons arising from the interaction of the carriers with photons [4], and abnormal optical constants [5]. Bi is particularly interesting in this context because it has many unique properties not observed in other materials: it can achieve a negative refractive index in the far infrared range [6], it has a very small effective mass ($\sim 0.001 m_e$) which gives rise to quantum confinement effects at sizes comparatively much larger and achievable via commonly available lithography techniques than required for most materials, and because it is a semimetal, Bi undergoes a semimetal to semiconductor transition as a function of size-confinement [7]. In addition, thin films of Bi excited by an electron beam have been proposed as a candidate system for generating terahertz radiation [8].

Many previous studies have presented evidence of quantum effects in Bi. Magnetoresistance measurements have shown evidence of quantum confinement effects in thin nanopatterned antidot Bi films as well, exemplifying the interesting effect that confinement to various morphologies and "in-between" dimensions can give rise to in Bi [9]. Bi nanowires have been used extensively to demonstrate quantum effects because of their confinement in two directions [10]. Additionally, a critical transition between superconducting and insulating phases has been observed in thin Bi films [11].

In practice, the evolution from a barren substrate to a continuous Bi film begins with the formation of individual nucleation sites ("islands") that are randomly scattered over the substrate surface. As more material is added, the islands eventually merge to form a continuous film [12]. This structural evolution triggers a host of fundamental changes in the dominant underlying transport mechanisms in the structure. Early on, when only separate islands exist, the dominant transport of electrical current is the tunneling of electrons across the dielectric (or vacuum) barriers that exist between the conductive islands. This regime is accurately described in the framework of the Simmons model [13] and/or variable-range hopping [14]. These tunneling models predict an exponential increase in the conductance as the island-to-island distances decrease.

Percolation theory is needed to effectively describe the conductivity as the Bi film evolves from individual islands to a continuous film. When the areal material coverage reaches a critical amount, several different properties related to the 'connectedness'

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of the material across the substrate show divergent and critical behavior that are not well captured in by the tunneling models. These divergences at the critical point have interesting implications, such as a proposed "dielectric anomaly" in the far infrared [5], as well as marked changes in the behavior of the DC conductivity as a function of added material. While percolating systems are well understood theoretically, experimental evidence rigorously corroborating the theory remains scarce. The case for Bi is particularly cumbersome because the material readily oxidizes with exposure to air, requiring measurements to be performed in situ in the vacuum deposition chamber, or the use of passivation layers which can distort results [15–17].

In this paper, we study conductance phenomena in ultrathin Bi films in order to attempt to answer the question as to whether quantum confinement can be observed at some point along the tunneling to percolation transition. Our measurements reveal a consistent transition from tunneling to percolation to bulk conductivity. In the percolation region, critical exponents are found to agree very well with those predicted by percolation theory. However, no clear signatures of a quantization transition are observed. To elucidate our results, we model the effects of quantization on the island conductivity within the percolation regime using Boltzmann transport theory and find it to generally support our experimental findings, provided that certain assumptions are made. We propose that quantization is not observed in the percolation regime because the connected islands that contribute to conduction are necessarily far reaching in the in-plane directions, causing electrons to be mostly confined in the out-of-plane direction. This constraint demands very high confinement and the right crystal orientation to change the conductivity, conditions which are generally not met in the case of an amorphous and polycrystalline film, such as ours.

2. Experiment

The substrates used were quartz (Chemglass Life Sciences). The substrate dimensions were 1 mm × 6 mm × 13 mm. Electrical contact pads were fabricated by evaporation of ~50 nm Au atop a ~5 nm Cr adhesion layer through a shadow mask and covered the entire substrate top surface except for a ~500 μm rectangular strip of width 4 mm that separated the two contact pads where the relevant percolation effects were to be investigated (see section 2a of the Supplementary information). Electrical measurements were conducted in situ inside the thermal evaporator's steel vacuum chamber using a semiconductor parameter analyzer (Agilent 4156C), as described in section 2b of the Supplementary information. Thermal evaporation of Bi (5N, Kurt J. Lesker) was carried out at a fixed deposition rate of 0.2 Å/s, as measured by an Inficon XTM/2 quartz crystal monitor with a rate resolution of 0.1 Å/s. This slow rate allowed for better resolution in the measurements and control of the final thickness if it was desired to stop evaporation at a given measured current or thickness. The evaporation was done with the substrate at room temperature. The vacuum typically operated in the range of 10^{-6} Torr. The semiconductor parameter analyzer was configured to measure current at a constant applied voltage of 1 V and at 100 ms intervals. At the applied voltage, the measured current would typically fluctuate ~1 pA around a base value of ~1 pA for a bare substrate. Samples were imaged using a transmission electron microscope (TEM, Philips CM20). TEM measurements were performed on samples that were necessarily removed from vacuum after having deposition stopped at the desired point and thus experienced rapid oxidation in the atmosphere. However, the oxidation would not affect the morphology of the deposited film. For TEM analysis the evaporation substrate was a copper TEM grid with a SiO membrane (Ted Pella, Inc.).

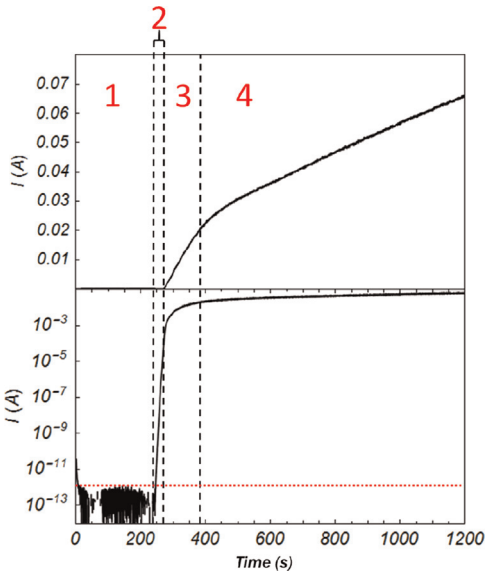

Fig. 1. Linear (top) and log (bottom) plots of raw data collected with horizontal axes aligned. Vertical dotted lines indicate different regimes; horizontal line in log plot indicates baseline noise level.

3. Results and analysis

Fig. 1 shows a typical conductance vs time measurement result plotted in both log and linear plots so that each regime is illustrated. Regime 1 is the region in which tunneling exists but is below the noise level of the system. Regime 2 is the brief period in which tunneling current is measurable but the percolation threshold p_c has not yet been reached; though brief in time it covers 8 orders of magnitude in current. Regime 3 is the percolation regime, which will be described in more detail. Regime 4 is the bulk regime in which the substrate area is sufficiently covered and most of the additional material added contributes only to an increase in film thickness. It is easily characterized by its linear nature. We begin by fitting an exponential relation to the tunneling regime to identify the end of this regime which coincides with the beginning of the percolation regime. The fitted curves and equations can be seen in section 4 of the Supplementary information; they all exhibit unambiguous exponential behavior. Once the end of the tunneling regime is determined, the data for the percolation regime can be fitted. The raw data consists of current measured at a constant voltage with respect to time. As discussed in section 3 of the Supplementary information, to fit the data to the canonical percolation equation, the data's time variable, t, must be transformed into surface coverage of the form $p = 1 - e^{-Rt}$, where R is a constant related to the deposition rate. To first verify this relation, we deposited nominal thicknesses (i.e., as reported by the crystal thickness monitor, as if the deposited material formed a complete uniform film immediately) in the range 3–200 Å on SiO membrane TEM grids. High contrast and resolution TEM images shown in Fig. 2 of different amounts of deposited material were then collected and the surface coverage as a function of time was measured by performing image analysis, as detailed in section 7a of the Supplementary information. These coverages are plotted with respect to their deposition times, as shown in Fig. 2. The multiple points at each time correspond to the same sample, but with the image analysis performed on images of different magnifications.

Once the time to surface coverage transformation has been