

STM driven modification of bismuth nanostructures

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ABSTRACT

The tip of a scanning tunneling microscope (STM) gently interacting with the substrate is used to modify (110) bismuth islands deposited on highly oriented pyrolytic graphite (HOPG), and hence to investigate the atomic and electronic structure of the islands. The tip interaction leads to the evolution of metastable 3 ML thick regions into structures of higher thermodynamic stability, which in the case of bismuth on graphite are rods (typically ≥ 5 ML high) and stripes. The formation of trenches that extend along the stripes is observed which is related to the presence of kinks and weak bonds at the 3–5 ML interface. Migration of whole islands along particular substrate directions is evidence for superlubricity due to the misfit between Bi and HOPG unit cells. Perimeter diffusion through atoms and not vacancies is a driving force of all observed modifications. The Bi islands are found to be able to deform and their decay is not governed by Ostwald ripening (which is absent in this system). Instead quantum size effects play a major role in the evolution of the islands, as evidenced by the observation of preferred widths. Density functional theory calculations reveal an oval Fermi surface with de Broglie wavelength corresponding to observed width of islands. These results are all consistent with a thin film Bi allotrope which has both paired atomic layers on the surface and bulk-like chains of bonds vertically through the structure.

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1. Introduction

The study of the dynamics of atoms on surfaces provides insight into the nanoscopic world where diffusion and surface energies dramatically affect the growth of thin films [1–9]. Processes like diffusion or film growth are usually very fast and as a consequence difficult to observe. One of the solutions is to use scanning tunneling microscopy (STM) operating at reduced temperature which results in slowing down dynamic processes occurring on the surface (see Refs. [2,5] and references therein). An alternative approach is to use STM at room or elevated substrate temperature and record images with higher frequency which results in so called Video-STM (see [8] and references therein). In both cases it is important to avoid unwanted perturbations due to the tip–sample interaction [8], but those interactions can be employed to control manipulation of single atoms [10–14], molecules [15] or small islands [16]. Similar experiments allow measurement of friction on the nanoscale and observations of superlubricity — as a consequence of incommensurate contact between two surfaces the friction nearly completely disappears [17–19].

It was recently shown by Blunt et al. [20] that it is possible to observe coarsening of films of metallic nanoparticles driven by an AFM tip. Blunt et al. showed that the interaction of the SPM probe with the sample is equivalent to an increase in sample temperature. In consequence,

diffusion is activated leading to morphological changes (similar to Ostwald ripening [2,5]). It is therefore well-established that tip–surface interactions can be used for both modification, and exploration of the properties, of nanostructured surfaces.

We show here that the structural and electronic properties of Bi islands can be explored through mechanical coarsening driven by a STM tip. We observe superlubricity [17–19,21] in the motion of entire islands as well as the effects of perimeter diffusion (PD) of atoms, which result in restructuring of our nanostructures, and a preference for well-defined nanostructure dimensions, suggesting the existence of quantum size effects (QSE). These QSEs are confirmed by density functional theory (DFT) calculations. These results are consistent with certain [22,23] thin film allotropes of bismuth (see Discussion below).

1.1. Bismuth and film morphology

Bismuth is characterized by a small density of states at the Fermi level which makes the bulk semi-metallic [24]. The surface is more metallic due to formation of surface states [24]. Bi has a low concentration of charge carriers, small effective masses, and de Broglie wavelengths much larger than for other metals [24–26]. All these properties make Bi a very promising candidate to explore novel quantum electronic effects, and especially to search for quantum size effects (QSE) [23,27–33].

Bismuth is located in group 15 of the periodic table. It crystallizes in the A7 structure, with a two atom basis, that can be described using rhombohedral (see Fig. 1(a)), hexagonal or cubic primitive cells [24]. In this paper we refer to the Bi crystal structure using the rhombohedral

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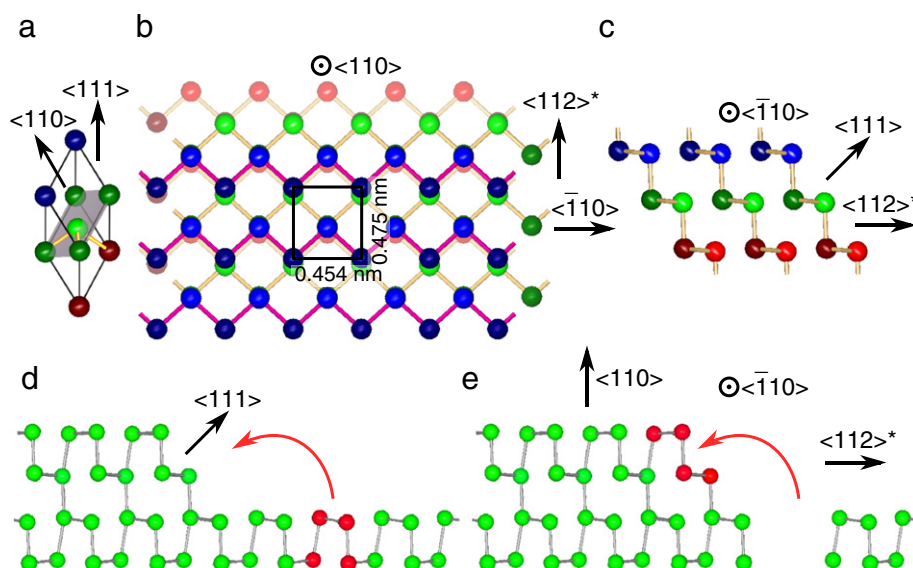


Fig. 1. Crystallographic structure of bulk and thin film bismuth. (a) Rhombohedral unit cell, shaded rectangle corresponds to (110) plane. (b) Top view of the (110) surface plane of a Bi crystal (along $\langle 110 \rangle$ direction) and (c) side view (along $\langle \bar{1}10 \rangle$ direction). Atoms forming different Bi(110) layers are indicated using different colors — blue, green and red for 1st, 2nd and 3rd bilayer. (d) and (e) Ball models showing a hybrid bulk/BP structure with 2 ML base and 2 ML stripe. The “dead” wetting layer is not shown. The group of four atoms indicated using red color initially located in the base (d) can be transferred to the stripe forming the trench (e).

notation. The most stable crystallographic orientation for thin films is usually Bi(110) [22,34–45] which is also the case for Bi on HOPG [22,35–37].

This system has been characterized in a series of previous reports [22,23,34–41] and typically consists of 3 ML thick islands with the (110) plane parallel to the surface and a preferred elongation direction along $\langle \bar{1}10 \rangle$ (see island B2 Fig. 2(a)). 2 ML thick stripes are formed on top of these bases. Further 2 ML stripes grow on top, resulting in islands with a step-like structure with heights in the sequence of 3, 5, 7, ... ML [35]. Annealing of these islands results in formation of rods a few μm long and up to 30 nm tall [37].

The surface of Bi(110) bulk is characterized by a rectangular unit cell with a two atom basis and one dangling bond per unit cell (i.e. the box in Fig. 1(b)), atoms indicated with darker colors have dangling bonds directed “up”. Each atom is covalently bonded with three nearest neighbors where two of these bonds lie nearly in plane forming characteristic zig-zags along $\langle \bar{1}10 \rangle$. Three second nearest neighbors are bonded through weaker bonds.

Thin films of Bi growing on Si(111) [42] and quasicrystals [44] are observed to have a paired layer structure and it has been proposed that this is evidence for a black phosphorus (BP) like allotrope with A17 structure. The BP structure is characterized by paired covalently bonded layers without the surface dangling bonds of the bulk structure. Our previous experiments showed evidence both for and against the BP structure for Bi on HOPG [22,35] and allowed us to propose a variety of possible alternative allotrope structures [22]. We have suggested that a BP-like surface reconstruction is possible while the interior maintains the bulk structure, leading to hybrid structures of the kind shown in Fig. 1(d) [22]. These islands grow on top of a “dead” wetting layer which does not contribute to the electronic structure [23,34].

2. Experimental

Commercially available HOPG substrates (SPI-2) were used in all experiments. After cleaving in air, they were loaded into the UHV system and annealed at 900 K for 16 h to remove contaminants. After cooling down the substrate to room temperature high purity bismuth (99.999%) was evaporated from a ceramic crucible and deposited onto the substrates at rate 0.01 Å/s.

STM measurements were carried out using an Omicron UHV STM at a base pressure of 10^{-8} Pa and at room temperature. The STM tips used in the experiments were cut Pt90%–Ir10% ones. Typical scanning parameters used during measurements were $V_{\text{bias}} = -0.8$ V and $I = 10$ pA.

The film thickness was monitored with a calibrated quartz crystal, and was measured in units of monolayers (ML). Here we define 1 ML as the thickness equivalent to that of a single rhombohedral Bi(110) plane i.e. 3.3 Å.

The electronic structure for a 2 ML film was obtained from first-principles calculations using HGH-type pseudopotentials and a plane-wave basis set [23,46]. The main program employed was developed by the ABINIT group; spin–orbit coupling was included using the relativistic LDA approximation.

3. Results and discussion

3.1. Morphological changes

In a typical experiment bismuth islands are stable for weeks in UHV at room temperature [35]. However, during STM investigations the tip interacts with the film [35,37] and as a result it is relatively easy to modify or even destroy deposited islands. In some cases this interaction was very gentle resulting only in small modifications of the morphology. We can see this process as one in which the presence of the tip gives additional energy to the atoms allowing them to move much more easily. In this sense, such modifications can be seen as the acceleration of the natural tendency for the as-grown islands to relax to equilibrium structures (as observed at elevated temperatures [37]). We performed a series of experiments in which we observed Bi islands for a long time while recording subsequent images. A typical sequence is shown in Fig. 2. In this, set scanning parameters (set point current and bias voltage) were kept constant (other experiments showed that reduction of the tip–sample distance can increase rate of modification).

3.1.1. Initial configuration

In Fig. 2(a) the initial situation is that there are four islands denoted A, B and C where island B comprises two parts (B1 and B2) which are connected by the stripe (#1). All islands (A, B1, B2 and C) are elongated in the same direction as the stripes on their top. This direction

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