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# The growth of bismuth on $Bi_2Se_3$ and the stability of the first bilayer

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ABSTRACT

Bi(0001) films with thicknesses up to several bilayers (BLs) are grown on Se-terminated $Bi_2Se_3$(0001) surfaces, and low energy electron diffraction (LEED), low energy ion scattering (LEIS) and atomic force microscopy (AFM) are used to investigate the surface composition, topography and atomic structure. For a single deposited Bi BL, the lattice constant matches that of the substrate and the Bi atoms adjacent to the uppermost Se atoms are located at fcc-like sites. When a 2nd Bi bilayer is deposited, it is incommensurate with the substrate. As the thickness of the deposited Bi film increases further, the lattice parameter evolves to that of bulk Bi(0001). After annealing a multiple BL film at 120 °C, the first commensurate Bi BL remains intact, but the additional BLs aggregate to form thicker islands of Bi. These results show that a single Bi BL on $Bi_2Se_3$ is a particularly stable structure. After annealing to 490 °C, all of the excess Bi desorbs and the Se-terminated $Bi_2Se_3$ surface is restored.

## 1. Introduction

Topological Insulators (TIs) are promising materials for superconductor, spintronics and quantum computing applications because of their intrinsic topological surface states (TSS) that are protected by time-reversal symmetry [1–3]. $Bi_2Se_3$ is one of the most well-known TIs due to its comparatively large, and thus practical, bulk band gap of 0.35 eV [2] and it's simple surface band structure in which the TSS form a Dirac cone [4]. $Bi_2Se_3$ has a rhombohedral structure belonging to the $R\bar{3}m$ space group. Five two-dimensional (2D) hexagonal lattices of Bi and Se are stacked together along the [0001] direction in the sequence of Se-Bi-Se-Bi-Se to form a quintuple layer (QL). Adjacent QLs are connected to each other by weak van der Waals forces. When a high quality pure $Bi_2Se_3$ single crystal is cleaved in ultra-high vacuum (UHV) or subjected to ion bombardment and annealing (IBA) in UHV, the resulting surface is highly ordered and terminated by Se at the top of a complete QL [5].

Bulk Bi is also a 2D material that is composed of bilayers (BLs) bonded to each other by van der Waals forces [6]. A single Bi(0001) BL is also reported to be a 2D topological insulator [7, 8]. Ultrathin Bi films of only a few BLs are attracting more interest for their nontrivial properties such as a large magnetoresistance and topological edge states [9, 10]. Hetero-structure engineering with Bi BLs and other materials, including 3D TIs, are becoming popular because of the ability to control their electronic properties and fabricate unique device structures [11–13]. Recent studies show giant Rashba-split states in Bi BL-terminated $Bi_2Se_3$ surfaces prepared by both epitaxial growth [14–16] and hydrogen etching methods [17, 18].

Deposited Bi grows on TI surfaces at room temperature along the [0001] direction in a quasi bilayer-by-bilayer mode, and has the same hexagonal lattice symmetry as $Bi_2Se_3$ [19, 20]. Previous STM work shows that the first Bi bilayer is strongly compressed on $Bi_2Se_3$(0001) substrate so that it matches the lattice parameter of the substrate. Further Bi deposition forms BL islands that eventually coalesce to complete bilayers with sufficient coverage. A periodic buckling of the lattice is found beginning from deposition of the 2nd BL and lasting until the 5th BL is deposited. The Bi BL lattice gradually relaxes to become bulk-like at a coverage of 24 BLs.

An interesting aspect of the Bi/$Bi_2Se_3$ system is the unique stability of a single deposited BL. Density functional theory (DFT) calculations show that the single BL-terminated structure has a lower surface energy than the bare Se-terminated surface [21, 22] and there is a stronger bonding between a QL and a Bi BL than there is between QLs [23, 24]. In support of this notion, $Bi_2Se_3$ surfaces terminated with a single Bi BL have been found to spontaneously form on *in-situ* [22] and *ex-situ* [25] cleaved samples. In addition, there is a report that exposing a Se-terminated surface to air for 5 min can form a stable Bi BL on the surface, presumably through a (still-unidentified) surface chemical reaction [26].

The present paper presents a low energy electron diffraction (LEED), low energy ion scattering (LEIS) and atomic force microscopy (AFM) study of Bi BLs grown on $Bi_2Se_3$(0001) by molecular beam epitaxy (MBE). It is confirmed that the first deposited BL grows epitaxially, and it is further shown that the Bi atoms in this first BL sit in fcc-like sites. As shown previously, subsequent layers grow as islands, since they are

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affected by the strain resulting from the differences in the lattice constants of $Bi_2Se_3$ and Bi, until the film is thick enough to form what is essentially bulk single crystal Bi. A relatively low temperature annealing of the thicker films shows that the first BL remains in place as the rest of the deposited Bi coalesces into islands, which is another sign of the unique stability of the 1st BL.

## 2. Experimental procedure

Single crystal $Bi_2Se_3$(0001) is used as the substrate. Bulk $Bi_2Se_3$ was prepared by melting stoichiometric mixtures of Bi (99.999%, Alfa Aesar) and Se shot (99.999 + %, Alfa Aesar) in an evacuated quartz ampule ($2 \times 10^{-6}$ Torr) with an inner diameter of 17 mm, and then following a slow-cooling procedure [5]. Approximately 1 cm × 1 cm × 2 mm single crystal $Bi_2Se_3$ plaques are cleaved from the bulk $Bi_2Se_3$ crystals and attached to a transferable tantalum (Ta) sample holder (Thermionics) using spot-welded Ta strips.

Most of the measurements are performed in an ultra-high vacuum (UHV) main chamber that has a base pressure better than $2 \times 10^{-10}$ Torr. There is a load-lock chamber that enables the sample holders to be inserted without the need to vent and re-bake the main chamber. The samples are transferred onto an x-y-z manipulator that allows for rotation about both the polar and azimuthal axes and includes an electron-beam heater. For the measurements performed here, the samples are heated radiatively without applying a bias voltage to the filament, as the annealing temperature needed to prepare $Bi_2Se_3$ is rather low. This main chamber contains a sputter gun (Physical Electronics) for sample cleaning, optics for LEED (Princeton Research), and the equipment needed for LEIS that is described below. The sample is held at room temperature during the collection of LEED images and LEIS spectra.

A Se-terminated $Bi_2Se_3$(0001) surface is prepared in the main UHV chamber by ion bombardment and annealing (IBA), which involves 30 min of 500 eV $Ar^+$ ion bombardment at a current density of $2.5 \times 10^{12}\,cm^{-2}\,s^{-1}$ with the sample at room temperature followed by annealing at 490 °C for 30 min. This IBA procedure produces high quality clean and well-ordered surfaces, as described elsewhere [27]. The annealing temperature is calibrated by a thermocouple attached to the Ta sample holder, but the actual temperature of the surface can vary from −50 °C to +20 °C from the reported value as the thermocouples are not attached directly to the samples. Also, thicker samples require more annealing time to allow the surface to reach the desired temperature.

Bi(0001) BLs are grown on $Bi_2Se_3$(0001) surfaces at room temperature using a molecular beam epitaxy (MBE) system that is attached to the main chamber such that samples can be transferred under UHV. Bi is evaporated at a rate of 1.45 Å $min^{-1}$, as calibrated by a quartz crystal microbalance (QCM), from a Knudsen cell heated to 530 °C. The amount of Bi deposited is also confirmed using AFM images, as discussed below.

The rear-view LEED system (Princeton Research Instruments) is used to ascertain the sample cleanness, crystallinity and orientation of the surface unit cell, and to monitor how the lattice parameter changes with the growth of Bi films. The sample position is kept the same with respect to the LEED optics for each measurement. The electron beam is normally incident onto the surface with the beam energy fixed at 21.8 eV.

Low energy ion scattering (LEIS) time-of-flight (TOF) spectra are used to identify the surface elemental composition [28] and measure the neutral fraction (NF) of scattered $Na^+$ [29]. A 3.0 keV $Na^+$ ion beam (Kimball Physics IGS-4) pulsed at 100 kHz is normally incident onto the sample surface and the scattered projectiles are collected at a scattering angle of 125° by a microchannel plate (MCP) detector located at the end of a 0.57 m long flight tube. A bias voltage of 400 V is applied to deflection plates in the flight tube to separate scattered ions from neutrals, allowing for independent collection of spectra for the total scattered yield and the scattered neutrals. The bias voltage is periodically turned on and off every 60 s while both spectra are collected simultaneously to avoid any effects of long term drift in the incident ion beam current. The front of the MCP is held at ground potential so that the scattered neutrals and ions impact the detector with the same kinetic energy.

Impact collision ion scattering spectrometry (ICISS) is used to probe the surface atomic structure [30]. ICISS is performed using a 3.0 keV $Na^+$ ion beam and a Comstock electrostatic analyzer (ESA), which measures only scattered ions, by fixing the scattering angle at 161° and rotating the sample about the polar axis. An energy spectrum is first collected to locate the positions of the Bi single scattering peak (SSP) and the Se SSP. The detection energy is then fixed at one SSP energy and the intensity of that SSP is monitored with respect to the incident polar angle as the sample is rotated. The energy is then set to the other SSP energy, and the ICISS data collection procedure is repeated. The sample manipulator has a computer-controlled stepper motor that automatically rotates the sample to enable quick and reproducible collection of the ICISS angular distributions.

AFM images are collected using a separate Dimension 3000 (Digital Instruments) apparatus. The samples used for AFM are cleaved *in situ* under UHV, as this produces larger terraces that are better suited for AFM than IBA-prepared samples [25, 31]. Bi is deposited in UHV using the MBE system, and the samples are then removed from vacuum and transported to the AFM instrument. The tapping mode images are collected in air at room temperature using TESPA-V2 silicon tips (Bruker).

## 3. Results

AFM measurements are conducted to both calibrate the coverage of the Bi BLs and to monitor changes of the surface topography. Fig. 1 shows AFM images collected after various treatments. Fig. 1(a) shows the surface of $Bi_2Se_3$ following *in situ* cleaving in UHV, although the sample was removed from vacuum to collect the image. The IBA-prepared samples are essentially atomically flat, but they contain QL-high steps that separate terraces with widths of approximately 200 nm [27]. In contrast, *in-situ* cleaved samples contain wider terraces, which makes them more suitable for calibrating the Bi coverage with AFM. Figs. 1(b)–(e) show images collected from Bi films grown on $Bi_2Se_3$. The green curve labeled A in Fig. 1(g) shows the profile of the line shown in the 1.0 BL image (Fig. 1(c)). The heights of the features seen in Fig. 1(g) are all about 0.5 nm, which corresponds to that of a single Bi BL, and this value is indicative of all of the features observed in the AFM images. The Bi coverage is calculated from the ratios of the accumulated area of the Bi islands or films to the area of the entire substrate. Analysis of the areas measured for Bi evaporation times of 2.5, 3.5 and 5.5 min indicate that these substrates are covered with 0.7, 1.0 and 1.5 BL, respectively. This implies that the Bi evaporation rate is about 1.4 Å $min^{-1}$ on average, which is consistent with the value determined using the QCM (1.45 Å $min^{-1}$). A 6 Bi BL covered surface is also examined, as shown in Fig. 1(e), in which the surface is fairly flat with a height variance of ± 0.5 nm, as shown by line profile B in Fig. 1(g), but it still has features with heights that are integral numbers of Bi BLs. The AFM images confirm that Bi grows in quasi bilayer-by-bilayer mode at high coverages and there's no evidence of tall islands for a 6 BL coverage at room temperature.

LEED is used to monitor the surface symmetry and determine how the lattice parameter changes with Bi deposition. Fig. 2 shows LEED patterns collected for different coverages of Bi. Note that the LEED image and background appear dimmer on the right half of the screen due to a degradation of the screen coating. A pristine Se-terminated $Bi_2Se_3$ substrate displays a 1 × 1 hexagonal pattern, as seen in Fig. 2(a). Three-fold LEED spots that are observed at higher beam energies are not shown here. When a single Bi BL is deposited onto the substrate, the LEED spots shift slightly towards the center and get much brighter, as seen in Fig. 2(b) [16]. Three-fold higher-order satellite spots start to