Epitaxial Growth of Bi(111) on Si(001)*

G. Juwadi, † H. Hattab, C. A. Bobisch, A. Bernhart, and E. Zubkov
Fachbereich Physik, Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany

C. Deiter, T. Weisemoeller, F. Bertram, and J. Wollschläger
Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany

R. Möller and M. Horn-von Hoegen
Fachbereich Physik, Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany
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Despite the large lattice mismatch and different lattice symmetry, it is possible to grow smooth and almost defect-free bismuth (Bi) films on a Si(001) substrate. High resolution low-energy electron diffraction measurements have confirmed that the (111) orientation is the preferred direction of the growth. However, at low temperature and low coverage regime, rotationally disordered crystallites of (110) orientation are also observed. After the formation of a continuous layer at 5.6 bilayer (2.2 nm), the growth occurs in a bilayer-by-bilayer fashion at 150 K. The remaining lattice mismatch of 2.3% is accommodated by a periodic array of interfacial misfit dislocations, which gives rise to a periodic surface height undulation with sub-Ångström amplitude. Additional growth to the desired thickness caps the height undulation resulting in an atomically smooth surface (terrace size > 100 nm). The Bi(111) film is relaxed to bulk lattice constant and shows excellent crystalline quality with an abrupt interface to the Si substrate.

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I. INTRODUCTION

The fabrication of smooth thin films on silicon (Si) is of great interest for both basic research and technological applications. The ultimate goal of obtaining single crystalline films of an atomically flat surface, an abrupt interface and a relaxed bulk structure is always a challenge to researchers. Such films are well-suited to explore transport behavior in an ultrathin medium as well as at the surfaces.

As a material, semi-metallic bismuth (Bi) has unique electronic properties such as a long Fermi wavelength [1], a large carrier mean free path [2], and a small carrier effective mass [3]. Because of these attributes, Bi is an attractive medium to study finite size effects and quantum transport phenomena. In 1998, Yang et al. [4] have observed a very large magnetoresistance effect in the single crystalline Bi films prepared by electrodeposition method. This has opened up the possibility of Bi films to be used for spin based electronic devices. In the late 90’s, Kammler [5] and Tanaka et al. [6] have first attempted to study Bi films and later on Nagao et al. [7, 8] and Kammler et al. [9] have shown a method of preparing high quality Bi(111) films on Si(111) at room temperature. These films were intensively studied and found various interesting phenomena such as the spin-orbit coupling effect [10–12], highly metallic surface states near the Fermi level [11, 13], and quantum-well states [14]. These exciting results have further stimulated researchers to go deep into the fundamental properties and realize potential applications in the spintronic devices. Besides that, our earlier results have shown, despite of having a large lattice mismatch (∼18%), that Bi can be grown epitaxially on Si(001) [15, 16].

Here, in this paper, we report on the growth behavior of Bi on Si(001) and characterize the surface morphology at different coverages. The surface lattice structure and the morphology are studied with spot profile analyzing low-energy electron diffraction (SPA-LEED) and scanning tunneling microscopy (STM). The crystalline structure of the Bi film and the roughness of the interfaces are studied by synchrotron based x-ray scattering techniques as grazing incidence x-ray diffraction (GIXRD) and x-ray reflectivity (XRR), respectively.

II. EXPERIMENTAL

The experiments were performed in two separate ultrahigh vacuum (UHV) chambers equipped with a SPA-LEED [17, 18] system and a STM system, respectively, both with a base pressure less than 2 × 10−10 mbar. Precisely oriented Si(001) samples (Boron doped, resistivity = 8–12Ωcm) were degassed at 870 K for 6 hours prior to flash annealing at 1470 K for a few seconds by direct current to remove the native oxide. The resulting sharp (2×1) LEED pattern at room temperature indicates a clean and defect free surface. The sample was cooled down to 80 K by using a liquid nitrogen cryostat attached to the sample holder. Intermediate temperatures were achieved by heating the sample by radiation from a tungsten filament attached to the temperature con-

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†Corresponding author: gr_juwadi@uni-due.de

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The deposition of Bi (purity = 99.9999%) was carried out by thermal evaporation from a directly heated ceramic crucible mounted in a water-cooled copper shroud. A flux of $R = 0.6$ bilayer (BL)/min (1 BL = $1.14 \times 10^{15}$ cm$^{-2}$, i.e., density in a (111) Bi bilayer bulk plane) was maintained during each deposition process in the SPA-LEED system. The deposition rate was monitored by a quartz microbalance mounted on the evaporator. The temperature was calibrated by the observation of bilayer intensity oscillations of the (00)-spot during Bi deposition at 150 K [15], and further confirmed by the bilayer intensity oscillations of the (00)-spot during homoepitaxial growth of Bi(111) at low temperatures [23].

The morphology of the film prepared in the SPA-LEED chamber was additionally studied with x-ray scattering methods, i.e., grazing incidence x-ray diffraction (GIXRD) and x-ray reflectivity (XRR), of synchrotron radiation (10 keV x-ray radiation with a wavelength of 0.124 nm) at HASYLAB (DESY, beamlines BW2 and W1) after transferring the samples to ambient conditions.

III. RESULTS AND DISCUSSION

A. Growth and morphology

The recipe of fabricating Bi(111) films is a three step approach [15]: (1) deposition of 17 BL Bi on Si(001) at 150 K ($T_D = 150$ K). Quasi 12-fold symmetry spots surrounding the central (00)-spot appear due to the superposition of two 90° rotated hexagonal domains as indicated by dotted parallelograms. Additionally, a ring of diffuse intensity (radius = $k_{ring}$) surrounding the first order hexagonal spots is also visible. At the same time, the two domain spots from underlying Si(001) surface, i.e., (2×1) and (1×2) spots are also visible, indicating the discontinuous nature of the film.

The diffraction conditions were chosen by varying the electron energy and therefore, the scattering phase $S = k_\perp d/2\pi$, where $k_\perp$ is the component of the electron momentum transfer perpendicular to the surface and $d$ is the interlayer spacing of Bi(111) film, i.e., the bilayer step height (bulk value: $d_{bulk} = 0.394$ nm). For integral scattering phase $S = n a$ a Bragg- or in-phase condition is observed, for $S = n + 1/2 a$ an anti-Bragg- or out-of-phase condition. Since electrons interfere constructively at the in-phase condition, they are not sensitive to surface roughness. In contrast, electrons interfere destructively at an out-of-phase condition and are most sensitive to steps at the surface [18]. The parallel scattering vector $k_{\parallel}$ will be expressed in percent units of the first Brillouin zone (%BZ) of Si(001) along [110] direction, where 100 %BZ corresponds to the reciprocal lattice vector of the Si(001) surface, i.e., $2\pi/a_{Si(001)}$ with $a_{Si(001)} = 0.384$ nm. In the STM chamber, the sample was cooled down to 135 K to record the topography. To index the crystal face of bulk Bi, we adopt the conventional rhombohedral indexing (111) and (110) orientations, which correspond to (001) and (012) orientations in hexagonal coordinates [11].
1. Deposition at 150 K

Figure 1 shows the variation of the (00)-spot intensity during Bi deposition at 150 K. The electron energy was chosen at out-of-phase scattering condition for Bi(111) bilayer surface (i.e., a step height of 0.394 nm), i.e., $S = 3.5$, since it is most sensitive to the steps at the surface [18]. The intensity plot clearly indicates two distinct regions symbolized by (I) and (II): (I) discontinuous region of irregular intensity variation, which extends up to the 5.6 BL, (II) continuous region with regular intensity oscillation, which extends beyond that.

In the region (I), the intensity undergoes drastic changes as obvious from Fig. 1. Initially, after the formation of a wetting layer (cf. first intensity maximum after deposition of 0.2 nm Bi), the intensity drops sharply. We attribute this behavior to the formation of highly disordered Bi crystallites. From the existence of Si-(2×1) spots, we conclude that the film on top of the wetting layer is not continuous (Fig. 2). As the coverage is increased, the intensity recovers, indicating a sharp transition into an ordered crystalline structure. As the coverage is further increased, the crystallites remain ordered. Figure 2 shows the LEED pattern recorded at 4.7 BL coverage, which clearly shows sharp 12-fold symmetry first order spots surrounding the (00)-spot. The 12-fold symmetry of the first order spots arise from the incoherent superposition of two hexagonal (1×1) domain spots rotated by 90° with respect to each other (Fig. 2). Due to the two-fold symmetry of the underlying substrate, i.e., Si(001)-(2×1) and -(1×2) reconstructions, obviously the Bi grows in registry with the substrate lattice. Additionally, a pronounced ring of diffuse intensity surrounding the first order spots is also visible. Interestingly, the real-space distance $a_{\text{ring}} = 0.322 \text{ nm}$, which can be directly estimated by $a_{\text{ring}} = 2\pi/k_{\text{ring}}$, almost matches with the distance of the {011} lattice planes of the Bi(110) surface [9], i.e., $a_{\text{Bi(110)}} = 0.328 \text{ nm}$ with the remaining compressive strain of $\sim 1.8\%$. The rectangular symmetry of Bi(110) crystallites shows a rotational disorder around the (110) axis, giving rise to the diffuse ring of the diffracted intensity. This indicates that Bi grows with two different orientations, i.e., Bi(111) and Bi(110) at low coverages. However, the (111) crystallites are dominant and grow epitaxially as compared to the (110) crystallites. Moreover, the intensity of the ring weakens as the temperature increases during annealing and vanishes completely above 230 K. This behavior suggests that the Bi(110) crystallites may have nucleated at defect sites like grain boundaries and vacancies. Such kind of thermally metastable structure was also reported in a previous publication [24]. Moreover, an analogous allotropic form was also observed previously in a Bi/Si(111) system at room temperature [8, 9, 25], where the Bi(110) orientation undergoes a complete transformation into the Bi(111) orientation after 4.5 ML coverage showing an coverage dependent structural transformation. We have, however, not observed such a complete structural transformation in this system.

In the second region (II), beyond 5.6 BL coverage, the (00)-spot intensity starts to oscillate in a bilayer mode with coverage. Figure 3(a) shows the LEED pattern recorded at 5.6 BL coverage. An absence of Si-(2×1) spots right after deposition clearly indicates a continuous Bi(111) film. Additionally, we observed a ring of diffuse intensity along with sharp hexagonal spots as in the case of the 4.7 BL coverage. This suggests that still two crystallites, i.e., (110) and (111) exist at this coverage simul-
FIG. 4: LEED patterns of 17 BL (6.6 nm) Bi film on Si(001): (a) recorded right after deposition at 150 K ($T_D = 150$ K) and (b) recorded after annealing from 150 K to 450 K ($T_A = 450$ K). The quasi-12-fold first order spots surrounding the (00)-spot reflects solely the (111) orientation of the crystal. The ring observed in the low coverage regime is vanished. The LEED spots show a slightly diffuse background and are all elongated perpendicular to the dimer orientation of the Si(001) surface after annealing to 450 K. The elongation becomes more apparent showing series of satellite spots when individual spots are zoomed in.

taneously. However, as the coverage increases at 150 K, the ring intensity drops slowly, and only the first order (111) spots remain.

At 17 BL coverage, the ring vanishes completely showing only the Bi(111) spots with broadened profile as shown in the Fig. 4(a). Broaded profile of the spot arises due to kinetic roughening in the growth front. This argument can be understood more easily from Fig. 1, where the oscillation amplitude of the (00)-spot intensity slowly decreases with increasing coverage due to slow buildup of surface roughness. From the row distance $a_{\text{Bi(111)}} = 0.388$ nm of the film, which is calculated from the distance $k_{01}$ between the (00)-spot and the first order spots by $a_{\text{Bi(111)}} = 2\pi/k_{01}$, it is concluded that the film is strained by 1.3%, as compared to the bulk Bi(111) row distance $a_{\text{bulk}}$.

2. Annealing at 450 K

After annealing of the 17 BL (6.6 nm) template film to 450 K, each of the higher order LEED spots is elongated in the [110] or [101] direction of the Si(001) substrate (Fig. 4(b)). The (00)-spot exhibits the elongation along both directions indicating a plus sign due to the overlapping of both domains. A careful analysis displays a clearly resolved spot splitting of all spots into a linear series of satellite spots as shown in the inset of Fig. 4(b). Such kind of spot splitting is observed when the surface shows a wave-like weak periodic height undulation, due to strain fields caused by an ordered array of misfit dislocations.

The dislocations are generated at the interface to accommodate both Bi(111) and Si(001) lattices [15, 16]. Both Bi(111) and Si(001) lattices match perfectly in a ratio of 11:13 along the direction perpendicular to the Si dimer rows. This is quite similar to the system of Bi(111)/Si(111)-7×7, where a “magic mismatch” of 6:7 ratio has been observed [8]. However, along the Si dimer rows, the Bi row distance almost matches the Si dimer distance. The remaining compressive strain of 2.3 % is accommodated by the periodic array of interfacial misfit dislocations.

The periodic height undulation acts as a phase grating for electrons and, therefore, all LEED spots show a splitting [18]. From the separation of the satellite spots, i.e., $1.9 \% \text{BZ}_{\text{Si(001)}}$, an average distance between the interfacial misfit dislocations of $\langle a_{\text{dis}} \rangle = 20$ nm was derived. A detail study of the geometry of the dislocation network and the surface height undulation as derived from the LEED intensity of the satellite spots as well as surface corrugation from the STM topography can be found elsewhere [16, 26]. A detail STM analysis of the surface height undulation will be published in a forthcoming publication [27].

Thus, with this recipe, it is possible to fabricate ultrathin Bi(111) films. A minimum thickness of a continuous film was achieved at the coverage of 5.6 BL (2.2 nm), which still can withstand annealing at 450 K (Fig. 3(b)). Unlike the LEED pattern of 17 BL film as shown in Fig. 4(b), sharp spots were observed for 5.6 BL film (Fig. 3(b)). This suggests that the dislocation density in thinner films is much lower and disordered due to insufficient interaction of the strain fields [27].

3. Additional deposition at 450 K

Additional deposition of Bi was carried out on the 17 BL (6.6 nm) template film at 450 K. It was observed that the intensity of the satellite spots slowly diminished
FIG. 5: LEED pattern of nominal 25 nm (64 BL) Bi film on Si(001) and corresponding STM topography ($U_{\text{bias}} = 1.8$ V, $I_{\text{tunnel}} = 17$ pA). The film was prepared according to the recipe described in this paper. The sharp LEED spots verify the atomically smooth surface of the film as shown by large terraces in the STM topography. Some screw dislocations were also encountered during the measurement. The long running steps in the topography shows the average height of $d_{\text{step}} \sim 0.4$ nm, confirming the bilayer step height.

and turned into a sharp single spot with higher intensity [16]. This behavior indicates the smoothing of surface by reducing the amplitude of the height undulation. A complete capping of the surface corrugation was observed after deposition of additional 19 nm Bi on the template film. This was confirmed by the LEED pattern and the STM topography as shown in Fig. 5. From the FWHM of the (00)-spot at out-of-phase condition and the STM surface topography, respectively, an average terrace size of $\langle \Gamma \rangle > 100$ nm was derived. The lattice parameter of the film matches with the bulk value of Bi(111) $a_{\text{bulk}}$, indicating a complete lateral relaxation of the film.

B. Bulk crystallinity, surface and interface roughness

The bulk morphology of the film was investigated by performing x-ray measurements at the beamlines BW2 and W1 at HASYLAB. A Bi(111) template film, prepared in the SPA-LEED chamber using the recipe described earlier [15], was examined by grazing incidence x-ray diffraction (GIXRD) and x-ray reflectivity (XRR) measurements.

Figure 6 shows the intensity along the crystal truncation rod, i.e., CTR (10L) - rod of the Bi(111) film and the...
schematically represented in-plane location of the CTRs of the corresponding system. The Si(001)-(2×1) spots of the underlying substrate are sketched with gray spheres and the hexagonal Bi(111) spots are denoted with elongated colored spheres. The two 90° rotated domains, caused by the two different substrate domains, are shown with different colors and can be clearly distinguished by the direction of the spot elongation. In each of these two rotational domains exist two different twin domains, which are named “A” and “B” (rotated by 180° around the surface normal). The existence of these two twin domains can be verified by their Bragg conditions in the CTR measurements. On the (10L) CTR the Bragg conditions of both species, A-type and B-type, are present. The CTR intensity shows well the hexagonal Bi(111) spots are denoted with elongated colored spheres. The two 90° rotated domains, caused by the two different substrate domains, are shown with different colors and can be clearly distinguished by the direction of the spot elongation. In each of these two rotational domains exist two different twin domains, which are named “A” and “B” (rotated by 180° around the surface normal). The existence of these two twin domains can be verified by their Bragg conditions in the CTR measurements. On the (10L) CTR the Bragg conditions of both species, A-type and B-type, are present. The CTR intensity shows well

IV. CONCLUSION

Despite the large lattice misfit (Δa = 18%) and the difference in crystal symmetry, Bi(111) grows commensurately on Si(001). At low coverage regime (≤ 17BL), rotationally disordered Bi(110) crystallites are also observed, which are low in density and thermally unstable. This experimental behavior suggests that the rectangular (110) crystallites may have nucleated at the defect sites like grain boundaries and vacancies. After a continuous layer forms at 5.6BL, the growth proceeds in a 2D-layer mode. Because of the inherent 2.3% lattice mismatch, the film relaxes towards the bulk values during annealing via the formation of a periodic array of misfit dislocations at the interface. Highly ordered surface height undulation was observed via spot splitting in LEED spots. The height undulation results due to the strain fields caused by an array of dislocation network. The sub-A height corrugation can be capped completely with additional Bi deposition resulting in extremely smooth terraces (terrace size > 100 nm). Such films are relaxed both vertically and laterally to the bulk value. Additionally, the high crystalline quality of the films with an abrupt interface ensures a large potential for future applications and research.

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