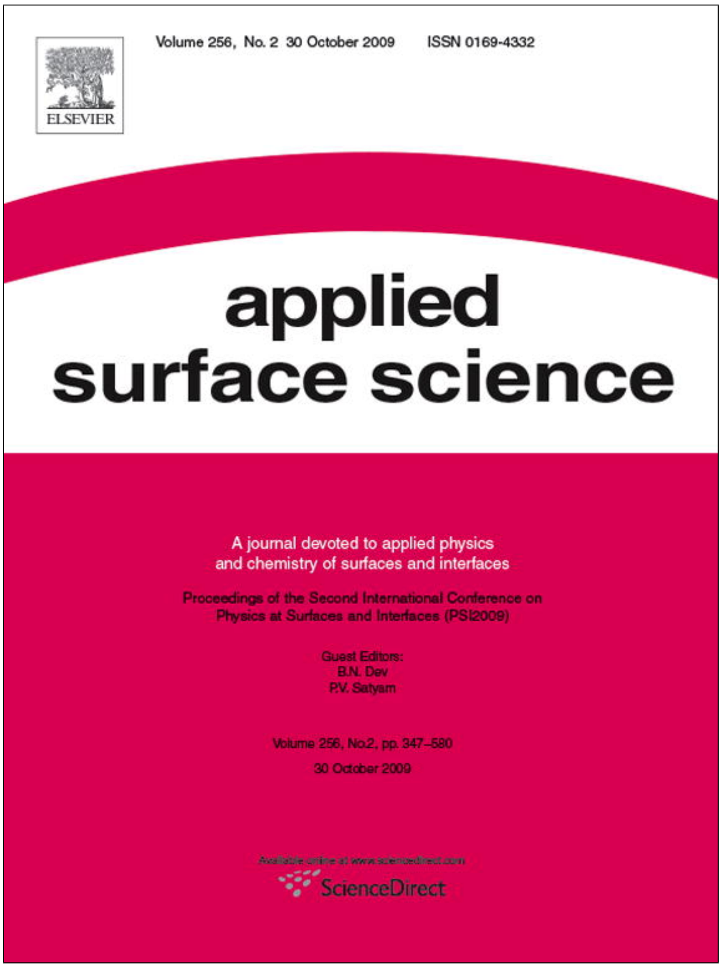

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Growth of well-aligned Bi nanowire on Ag(1 1 1)

Hong Liang Zhang [a], Wei Chen [a,b,*], Xue Sen Wang [a], Junji Yuhara [c], Andrew Thye Shen Wee [a,**]

[a] *Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore*
[b] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore*
[c] *Department of Physics Science and Engineering, School of Engineering, Nagoya University, Furo-Cho, Chikusa-ku, Nagoya 484-8603, Japan*

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ABSTRACT

We report the fabrication of one-dimensional (1D) Bi nanowires grown on Ag(1 1 1) with average lateral width from 9 to 20 nm by physical vapor deposition in ultra high vacuum conditions. *In situ* low-temperature scanning tunneling microscopy analyses reveal that the preferred growth of 1D Bi nanostructures is driven by the highly anisotropic bonding in the crystallographic structure of the Bi(1 1 0) plane. The Bi nanowires grow along Bi$[1\,\bar{1}\,0]$ direction and align with the $[1\,\bar{1}\,0]$ directions on Ag(1 1 1). The growth of the Bi nanowires proceeds in a bilayer growth mode resulting from the layer pairing in Bi(1 1 0) which saturates the dangling bonds and lowers the total energy.

1. Introduction

Since the discovery of the carbon nanotube [1], one-dimensional nanostructures (nanowires, nanotubes, nanoribbons and nanorods) have attracted much attention because of their superior electrical, optical and thermal properties [2–4]. It is well known that bismuth (Bi), a typical group-V semimetal, possesses unique physical properties due to its highly anisotropic Fermi surface, small effective electron mass and long Fermi wavelength (~40 nm at room temperature), and a small energy overlap between the conduction and valence bands [5–8]. Bi nanostructures are expected to exhibit more interesting physical properties resulting from quantum confinement and the finite size effect [9], such as surface superconductivity [10] and extremely large magnetoresistance [11]. It has been shown that Bi nanowires with diameters larger than 70 nm are metallic, while a semimetal to semiconductor transition occurs when the diameter decreases to below 50 nm [12]. In addition, Bi nanowires are potentially high-efficiency thermoelectric materials due to the enhanced thermoelectric coefficient originating from the quantum confinement effect [13,14]. In recent years, much work has been done to fabricate 1D Bi nanostructures with controlled dimensions and crystalline structures using electrodeposition aided with anodic alumina membranes (AAM) [15–17] and vapor phase deposition [18–20].

In this article, we demonstrate the growth of well-aligned Bi nanowires with uniform width by a physical vapor deposition method. *In situ* low-temperature scanning tunneling microscopy (STM) analyses reveal that the preferred growth of 1D Bi nanostructure is driven by the highly anisotropic bonding in the Bi crystallographic structure.

2. Experimental details

The experiments were carried out in a home-built multi-chamber ultra-high vacuum (UHV) system housing a low-temperature STM with a base pressure better than 6×10^{-11} mbar [21,22]. The STM was operated with a Nanonis controller (Nanonis, Switzerland). Ag(1 1 1) substrate was cleaned by repeated Ar$^+$ sputtering and annealing cycles to 800 K. Then the cleanness of the sample was checked by STM images showing sharp step edges and smooth terraces. Bi was thermally evaporated from a Knudsen cell onto the clean Ag(1 1 1) substrate kept at room temperature (RT) in the growth chamber with base pressure better than 3×10^{-10} mbar. Bi deposition rate was constant at 0.05 ML/min [1 ML is defined as 1 atomic layer of Bi(1 1 0), i.e., 9.3×10^{14} cm^{-2}], and was calibrated using a quartz microbalance (QCM) and STM. STM images were obtained in constant-current mode with a chemically etched tungsten tip at 77 K.

3. Results and discussion

The most stable Bi crystals in ambient condition have a rhombohedral (RHL) lattice structure (R-3m space group, a = 4.75 Å) with two atoms per unit cell, and can also be described by hexagonal lattice basis set [5], as shown in the left panel of

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[*] Corresponding author at: Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore.
[**] Corresponding author.
E-mail addresses: phycw@nus.edu.sg (W. Chen), phyweets@nus.edu.sg (A.T.S. Wee).

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Fig. 1(a). Each atom has three nearest neighbors linked through strong covalent bonds and three next-nearest neighbors sustained by weaker van der Waals bonds. The 2D lattice structure of Bi(1 1 0) is illustrated in Fig. 1(b). We have investigated the coverage-dependent growth processes and structures of Bi on Ag(1 1 1) using low-temperature STM. It reveals the typical alloying and de-alloying processes observed for metal on metal systems which are nonsoluble in bulk phases. These processes involve two sequential stages, including: (i) at low coverage, Bi atoms are incorporated into the topmost layer of the Ag(1 1 1), resulting in the formation of $BiAg_2$ alloy with a $\sqrt{3} \times \sqrt{3}$ R30° superstructure (data not shown here) embedded into the Ag(1 1 1) top layer or on top of the Ag(1 1 1), referred to as alloying process; and (ii) since Ag and Bi are nonsoluble in bulk phases, the $BiAg_2$ alloy gradually convert into an ordered Bi(1 1 0) monolayer supported on Ag(1 1 1) when Bi coverage above a critical value of about 2/3 ML, referred to as de-alloying process [23].

The observed STM image in Fig. 1(c) confirms that the Bi monolayer has a zigzag-chain structure with a rectangular unit cell of $a = 4.7 \pm 0.1$ Å and $b = 4.5 \pm 0.1$ Å, consistent with the Bi(1 1 0) lattice shown in Fig. 1(b). From this image, we can derive that Bi$[\mathbf{1\,\bar{1}\,0}]$| and Bi[0 0 1] directions are parallel to Ag$[\mathbf{1\,\bar{1}\,0}]$ and Ag$[1\,1\,\bar{2}]$, respectively. Therefore, considering the lattice constant of Ag is 2.89 Å, the adsorption relationship between Bi(1 1 0) and Ag(1 1 1) is determined to be Bi$[\mathbf{1\,\bar{1}\,0}]$||Ag$[\mathbf{1\,\bar{1}\,0}]$ and Bi[0 0 1]||Ag$[1\,1\,\bar{2}]$ with $7|\mathbf{a}_{\mathrm{Bi}[1\,\bar{1}0]}| = 11|\mathbf{a}_{\mathrm{Ag}[1\,\bar{1}\,0]}|$ and $20|\mathbf{a}_{\mathrm{Bi}[0\,0\,1]}| = 19|\mathbf{a}_{\mathrm{Ag}[1\,1\,\bar{2}]}|$. A proposed model illustrating this relationship is presented in Fig. 1(d). Recently, Jeffrey et al. [24] have investigated the structure of Bi(1 1 0) thin film electrodeposited on Au(1 1 1). A relationship with Bi$[\mathbf{1\,\bar{1}\,0}]$||Au$[\mathbf{1\,\bar{1}\,0}]$ $(7|\mathbf{a}_{\mathrm{Bi}[1\,\bar{1}0]}| = 11|\mathbf{a}_{\mathrm{Au}[1\,\bar{1}\,0]}|)$ and Bi[001]||Au$[11\bar{2}]$ $(20|\mathbf{a}_{\mathrm{Bi}[0\,0\,1]}| = 19|\mathbf{a}_{\mathrm{Au}[1\,1\,\bar{2}]}|)$ was also determined based on X-ray data and STM observation. It is worth noting that the lattice structure of Ag(1 1 1) (a_{Ag} = 2.89 Å) is similar to that of Au(1 1 1) (a_{Au} = 2.88 Å). As such, the Bi(1 1 0) films adopt same structure on both Ag(1 1 1) and Au(1 1 1).

Increasing the Bi coverage to more than 1 ML gives rise to the preferred growth of Bi nanowires with well-defined shapes, as shown in Fig. 2(a) and (b) for 1.3 ML and 1.5 ML deposition, respectively. Bi nanowires with typical lengths of 100 nm are formed after 1.3 ML Bi deposition. Statistical width histogram (bottom of Fig. 2(a)) reveals that the average wire width is 9 nm. The line profile in Fig. 2(d) and height histogram in Fig. 2(e) indicate that the nanowire height retains the value of 6.6 ± 0.3 Å. It is also worth noting that the nanowires are aligned in the same direction and their long axes are found to be parallel to the Ag$[1\,\bar{1}\,0]$ direction. Three different nanowire directions rotated by 120° with respect to each other can be typically observed, reflecting the threefold symmetry of the underlying Ag(1 1 1) substrate. Increasing the Bi coverage to 1.5 ML enlarges the nanowires with the typical lengths raised to 150 nm and average widths to 12 nm [Fig. 2(b)]. Fig. 2(f) shows a representative atomic resolution image of the surface of the nanowire. It exhibits a rectangular unit cell of $a = 4.7 \pm 0.1$ Å and $b = 4.5 \pm 0.1$ Å highlighted by the green rectangle, similar to the unit cell of Bi(1 1 0). The long axis of the nanowire is aligned along the Bi$[1\,\bar{1}\,0]$ direction. Therefore, the orientation relationship of nanowires with Ag(1 1 1) is Bi$[1\,\bar{1}\,0]$||Ag$[1\,\bar{1}\,0]$ and Bi[0 0 1]||Ag$[1\,1\,\bar{2}]$. It is also worth to note that the corner atoms in the unit cell protrude and appear brighter than the centre one in STM image, which is attributed to the pairing relaxation of (1 1 0) layers [25].

It is known that for some solid materials with highly anisotropic bonding structure, they are able to naturally grow into 1D nanostructures via anisotropic diffusion and attachment [4,26]. The preferential growth of compact Bi nanowires elongated along the $[1\,\bar{1}\,0]$ direction implies an enhanced surface

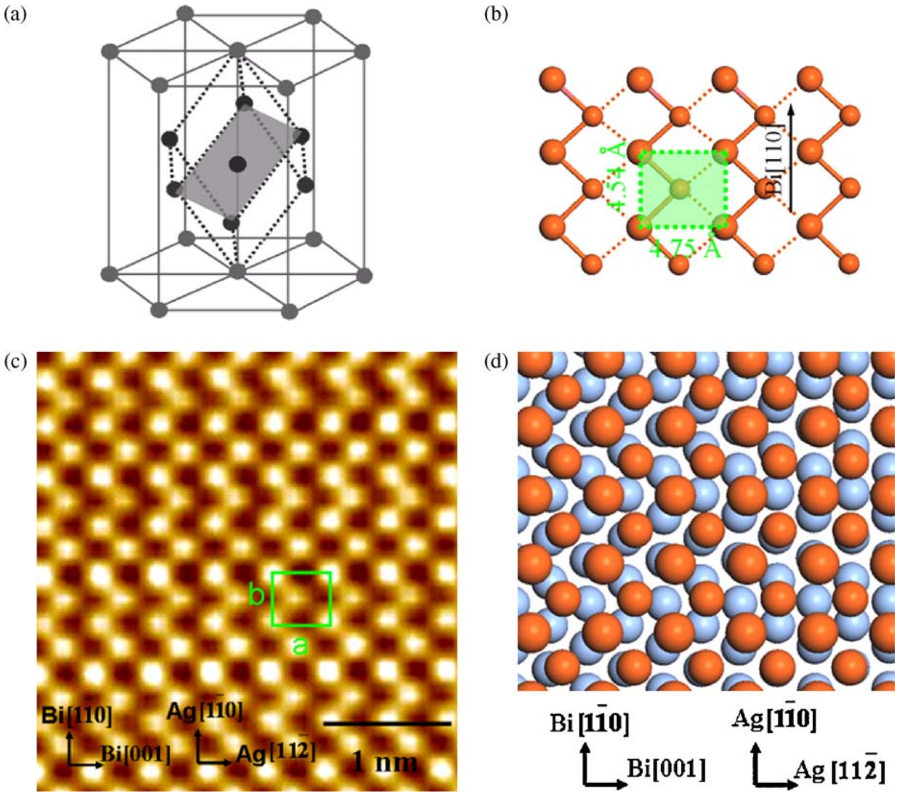

Fig. 1. (a) Schematics of Rhombohedral structure of bulk α-Bi, with a (1 1 0) plane shaded by grey; (b) top view of atomic configuration of Bi(1 1 0) plane. (c) Atomic resolution STM image (taken at $V_s = -0.5$ V, $I_t = 400$ pA) of 1 ML Bi deposited on Ag(1 1 1) at RT, showing the formation of Bi monolayer with Bi(1 1 0) plane. (d) Proposed model for the adsorption relationship between Bi(1 1 0) and the Ag(1 1 1).

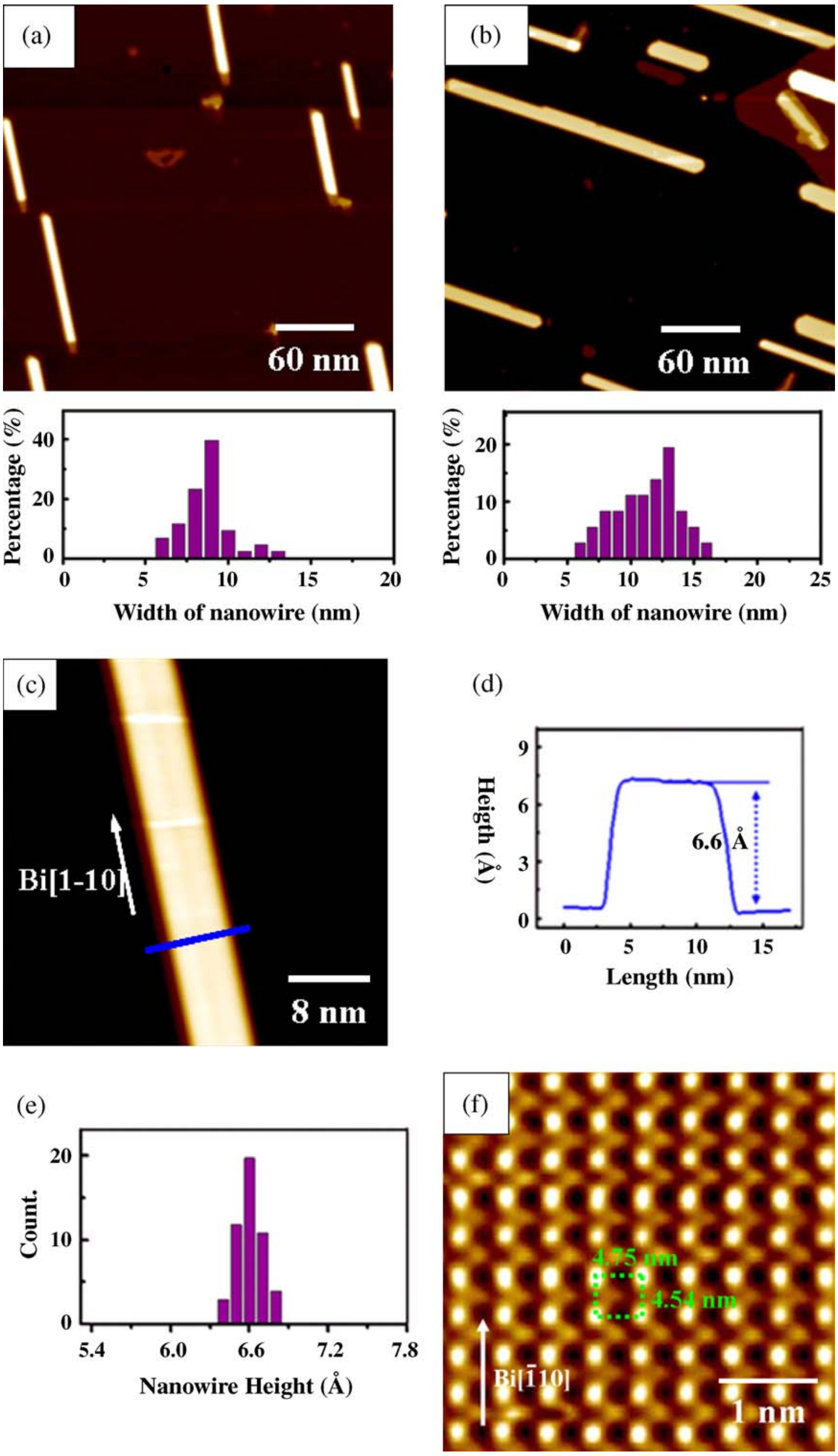

Fig. 2. Topographic STM images (top) and corresponding histograms of the Bi nanowire width (bottom) on Ag(1 1 1) after (a) 1.3 ML and (b) 1.5 ML Bi deposition, respectively. (c) Close-view STM image of a Bi nanowire and (d) A line profile (bottom) along the blue line in the panel (c); (e) Height histogram of Bi nanowires, showing the height is kept at 6.6 Å with a narrow distribution. (f) Atomic resolution STM image on top a Bi wire, showing the favorable growth direction (arrow) of Bi nanowires is along the $[1\,\bar{1}\,0]$.

and edge diffusion along this direction and preferential attachment of Bi atoms at the ends. Bulk Bi crystal has highly anisotropic bonding. As shown in Fig. 1(b), the surface structure of Bi(1 1 0) is characterized by zigzag covalently bonded atomic chains along the $[1\,\bar{1}\,0]$ direction (solid lines) and weaker bonds in the perpendicular direction (dashed lines). Therefore, Bi adatoms on the surface are more likely to diffuse towards the ends to form stronger covalent bonds and be incorporated there, resulting in preferential growth along Bi$[1\,\bar{1}\,0]$ direction. This is consistent with the recent reports by Scott et al. on the growth of Bi on graphite, where Bi nanowires elongated along the Bi$[1\,\bar{1}\,0]$ direction grown at the step edges of graphite [18,19]. The authors attributed the driving force for the preferential growth of Bi to efficient Bi diffusion along the $[1\,\bar{1}\,0]$ direction favoring Bi incorporation at the end of the Bi zigzag chains. Similarly, the growth of Bi needle structures on Au was largely driven by the faster diffusion and preferential incorporation of Bi in the $[1\,\bar{1}\,0]$ direction [26].

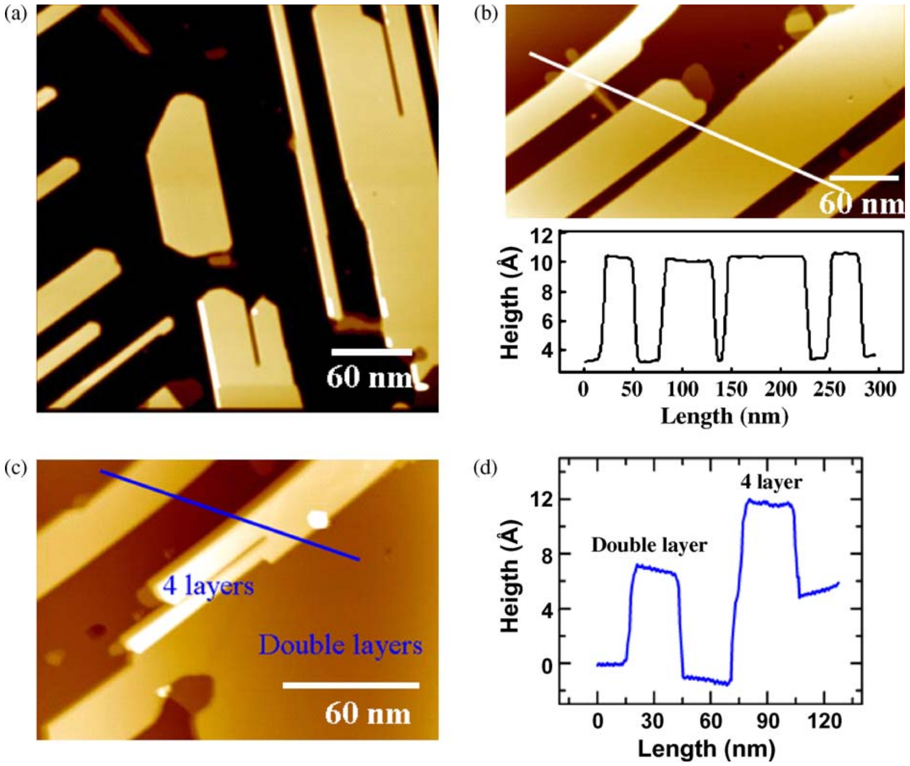

Fig. 3. STM images of Bi nanowires with increasing coverage: (a) after 1.75 ML deposition, Bi nanowires aggregate to form wide flat stripes. (b) After 2 ML deposition, with the height profile along the black line indicating that the stripes are bilayer Bi(1 1 0); (c) an STM image shows Bi wire with a thickness of 13.2 Å and (d) cross-sectional profile along the line marked in STM image.

Fig. 3 shows the morphological evolution of Bi nanowires with more Bi deposition. The width of the nanowires increases and some coalesce with neighboring nanowires to form 2D islands. The height profiles taken across the Bi nanowires show that the nanowires maintain a uniform thickness of 6.6 ± 0.3 Å, which is twice the interlayer spacing of Bi(1 1 0) (3.28 Å) [5,27]. Therefore the Bi nanowires observed here correspond to the stacking of two atomic layers of Bi(1 1 0). With further Bi deposition, Bi nanowires 13.2 ± 0.3 Å thick (4 atomic layers of Bi(1 1 0)) were also observed at some areas, as shown in Fig. 3(c) and (d). These observations suggest that the layer thickness of Bi nanowires are quantized into double (1 1 0) layers units (i.e., 6.6 Å) and the growth exhibits even-number layer stability. This is consistent with recent observation of the magic thickness of Bi ultra thin films on Si(1 1 1) surface where Bi(1 1 0) 2D islands with even-number layers (i.e., 2 ML_{110}) are dominant [27,28]. This stability is attributed to the energetically preferred pairing of two neighboring layers. On a bulk-terminated Bi(1 1 0) surface, due to the bond breaking, 50% of the Bi atoms on the surface have dangling bonds which come from unpaired electrons in Bi p_z-orbitals, making the film energetically unstable [5,29]. In the even-number layer films, these dangling bonds are completely saturated by layer pairing of the neighboring (1 1 0) plane. As such all the atoms are threefold coordinated, leading to the stabilization of (1 1 0) surface. In contrast, odd-number layer films are not stable since the dangling bonds of the top layer are unable to be saturated by layer pairing.

4. Conclusion

In summary, the growth of well-aligned Bi nanowires with uniform height has been achieved on Ag(1 1 1) by physical vapor deposition in ultrahigh vacuum. It is found that the preferred wire growth in Bi$[1\bar{1}0]$ direction is driven by the stronger covalent bonding along the wire axis over relative weak van der Waals forces perpendicular to the axis. We also demonstrate that growth of Bi nanowires adopts a double layer growth mode resulting from the layer pairing of atomic layers to saturate the dangling bonds.

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