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Kinetic versus Thermodynamic Control over Growth Process of Electrodeposited Bi/BiSb Superlattice Nanowires

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ABSTRACT

The growth mechanism of the electrodeposited single crystalline nanowires is generally considered to follow a three-dimensional to two-dimensional (2D) transition mode, and as for the 2D growth, it is ordinarily considered as a plane growth mode (layer-by-layer growth mechanism). We report in this Letter the growth of Bi/BiSb superlattice nanowires by adopting a charge-controlled pulse electrodeposition technique, and to our best knowledge, different growth modes of the nanowires, the 2D plane growth mode, the tilted plane growth mode, and the curved plane growth mode, were first observed. These growth modes were gathered and analyzed from the perspectives of crystal growth as well as kinetics and thermodynamics. It is shown that the superlattice nanowires are good structures for studying the growth mechanism of electrodeposited nanowires. This work will deeply benefit the understanding of the growth process of the electrodeposited nanowires and provide important experiment data to crystal growth theory.

One-dimensional (1D) nanostructures such as nanowires, nanorods, nanobelts, and nanotubes have become the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanoscale devices.[1–3] Superlattice nanowires (SLNWs) are the structure which integrates the advantages of both quantum wires and quantum dots, and the electronic transport along the wire axis is made possible by the tunneling between adjacent quantum dots, while the uniqueness of each quantum dot and its zero-dimensional characteristics is maintained by the energy difference of the conduction or valence bands between different materials.[4] Various fabricating methods of 1D nanostructure have been explored in recent years, and among them the template-based electrochemical method is widely used because this technique is simple, inexpensive, and fast and it operates at near room temperature. A variety of SLNWs, such as Co/Cu,[5,6] Ni/Cu,[7,8] CoNiCu/Cu,[9,10] Ag/Co,[11] Au/Co,[12] Co/Pt,[13] Bi/Sb,[14] and BiTe/BiSbTe,[15] have been fabricated in a single bath using a template-based electrochemical method.

There is much research work concerning the growth mechanism of electrodeposited nanowires.[16–18] It is generally considered that the growth mechanism of an electrodeposited single crystalline nanowire follows a 3D to 2D transition mode, and as for the 2D growth mode it is generally considered as a plane growth mode. Much theoretical and experimental work on thin film growth has been done based on the atomic scale mechanism of epitaxial nucleation and growth and their influence on the resulting surface morphology.[19–27] It has been well recognized that the selection of a specific growth mode in a given system is often the outcome of the interplay between growth kinetics, characterized by a set of atomic rate processes, and thermodynamics, measured by the system's overall tendency toward lower free energy configurations.[21] Compared to the growth mechanisms of thin films, the direct observation of the growth of the electrodeposited single crystalline nanowires still has not been realized because of the difficulty of in situ observations. In this study, we successfully fabricated Bi/BiSb SLNWs with a short bilayer thickness. Through observation of the nanowire images and analysis of SLNW growth data, various growth modes, including the plane growth mode, the tilted plane growth mode, and the curved plane growth mode, have been found and confirmed. Most of the SLNWs in the previous studies[5–15] had a large bilayer thickness which made it hard to observe the interfaces between segments. Although some of them had a smaller bilayer thickness with distinct interfaces, and some even had a concave shape,[7,8,12] no detailed studies about the growth mechanism were per-

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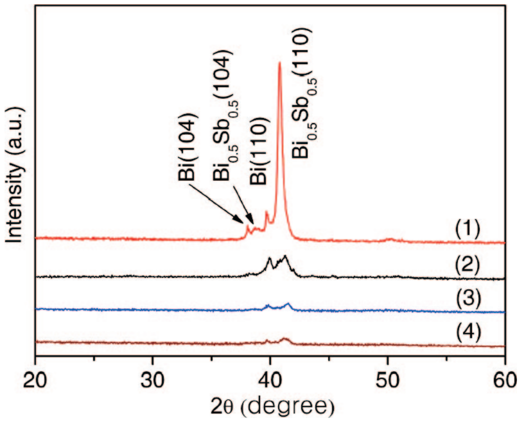

Figure 1. XRD patterns of the pulsed electrodeposited Bi/BiSb SLNWs with modulated time intervals of (1) $T_1 = 0.5$ s and $T_2 = 0.25$ s, (2) $T_1 = 1$ s and $T_2 = 0.25$ s, (3) $T_1 = 1$ s, $T_2 = 0.5$ s, and (4) $T_1 = 3$ s and $T_2 = 0.5$ s.

formed. In our case, the obtained SLNWs have a short bilayer thickness (about several tens of nanometers) and a much clearer interface. Particularly, the SLNWs with a short bilayer thickness can show detailed growth process of the electrodeposited nanowires. On the basis of our experimental data, we also discuss in detail the various growth modes from the crystal growth perspective as well as the kinetics and thermodynamics perspectives.

X-ray diffraction (XRD) patterns of the electrodeposited SLNWs with different modulated time intervals (Figure 1) show that all the diffraction peaks can be indexed to the rhombohedral space group $R\bar{3}m$ (to which Bi and Bi−Sb alloys belong), and the sharp diffraction peaks at 40.78° and 39.69° correspond respectively to BiSb alloy [110] and Bi [110] directions (curve 1 in Figure 1), indicating the highly preferential orientation of the nanowires. One also can see that the diffraction peak intensity decreases with increasing the pulsed time interval (or the bilayer thickness), and there are no satellite peaks besides the main Bragg peaks.

The highly preferential orientation provides a firm proof of epitaxial growth along the nanowire compared to the previous results.[14,15] The decreased intensity of the diffraction peaks with increasing the pulsed time interval was considered mainly due to the larger misfit of the lattice induced by the increased bilayer thickness. When there is a small difference of the lattice parameter between the two segments, such as pure Bi and $Bi_{0.5}Sb_{0.5}$ (2.6% variation of the lattice constant between them), the following layer would grow with the same lattice parameter. In such a situation the misfit is accommodated by an elastic strain in the deposit, and as the segment thickness increases, it is energetically more favorable to accommodate the misfit by generating dislocations at the interface, leading to the heterogeneous nucleation of the new deposit,[28,29] which will thus reduce the peak intensity of the main Bragg diffractions. This XRD result indicates that the epitaxial growth will be realized if the SLNWs have a small bilayer thickness.

It is a common method to determine the bilayer thickness of a superlattice thin film by the satellite peaks surrounding both sides of the main Bragg peak if the bilayer periodicity is retained throughout the multilayer structure.[30–33] However, in our XRD patterns of the nanowires, no satellite peaks were found. We attribute it to the misalignment of the nanowires array induced by different growth environment of each SLNW. Because even for the SLNWs grow with the same growth direction, there would exist a misalignment in the SLNWs if the initial nucleation of each nanowire grows with a slight time difference, not to mention the diameter difference, the solution, and current fluctuations. Valizadeh also found that there is only pure Ag and Co or pure Au and Co diffraction peaks in the XRD patterns of the electrodeposited Ag/Co[11] or Au/Co[12] multilayered nanowires.

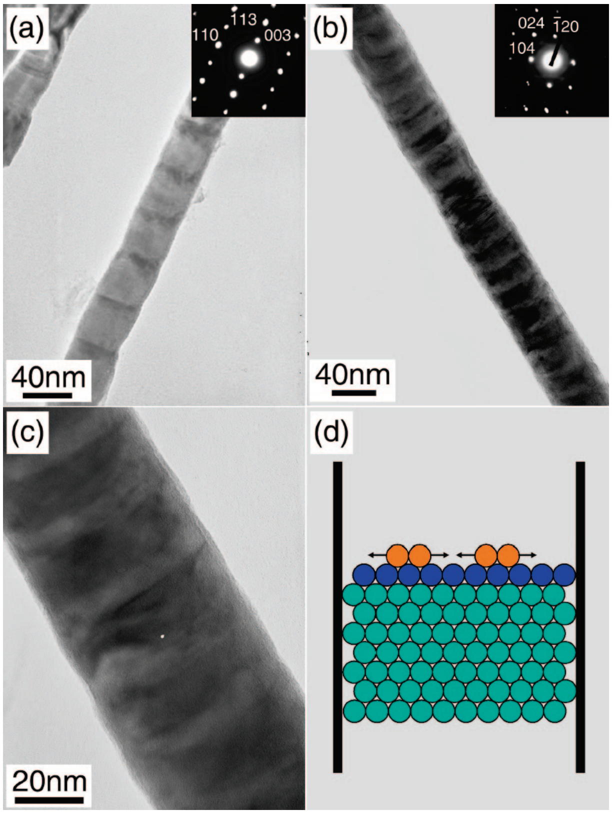

Figure 2. Typical TEM images of epitaxial Bi/BiSb superlattice nanowires with a plane growth mode. (a, b) TEM images of low magnification, the insets are the corresponding SAED patterns. (c) Higher magnification TEM image of (b). (d) Schematic representation of a 2D plane growth mode, the atoms in blue represent the growth front and the growth plane of a SLNW, the atoms in orange represent the nucleus center of the 2D plane growth. The arrows represent the extending of the nucleus in the plane.

Figure 2 shows typical transmission electron microscopy (TEM) images of epitaxial Bi/BiSb SLNWs with a plane growth mode, in which the darker sections correspond to pure Bi segments and the brighter sections correspond to BiSb segments. Nevertheless, the contrast of these two segments is not so strong as in the previous study on Bi/Sb SLNWs,[14] which is due to the fact that the atomic ratio of Bi and Sb in BiSb segments is about 1:1 according to the energy dispersive spectrometry, and the difference in the atomic weight between Bi and BiSb is relatively lower than that between Bi and Sb. The modulated structure of Bi/BiSb SLNWs can be clearly seen in panels a and b of Figure 2. The sharp and obvious interfaces were clearly manifested in Figure 2c, in which the bilayer thickness is consistent along the whole nanowire. The corresponding selected area electron diffraction (SAED) patterns shown in the upper insets of panels a and b of Figure 2 indicate that the SLNW is single crystalline and some of the diffraction points have a tail or are even brighter due to the overlap of the diffraction points of the two segments, similar points of Fourier transforms calculated from high-resolution images have been reported along the different lattice directions in the junction region of GaAs/GaP SLNW[34] and InAs/InP heterostructure.[35] Furthermore, high-resolution transmission electron microscopy (HRTEM) observations show no dislocations along the interface verifying a strictly epitaxial growth of the SLNWs (see the Supporting Information Figure S2). According to the traditional 3D to 2D growth mode, the direction of the initial 2D growth plane which is a result of nucleation and competition between different planes should be parallel to the wire axis. In Figure 2, the interfaces of Bi and BiSb layers are strictly normal to the nanowire axis, we believe this kind of growth mode is consistent with the traditional 2D plane growth mode of the electrodeposited nanowires. This growth process is a thermodynamic equilibrium state under the specific growth conditions and is controlled by thermodynamics. Otherwise the 3D island morphology should be observed, and it is consistent with the layer-by-layer growth mechanism in molecular beam epitaxy.

It is interesting that some of the SLNWs with a tilted interface have also been observed, as shown in Figure 3. We should affirm that the tilted structure was observed in this electrodeposited SLNW structure with a modulated composition for the first time and had not been observed in electrodeposited nanowires with pure element or alloy nanowires. Since the axis of the nanowires should be parallel to the axis of the AAM pores, at a particular time in the deposition process the segment with the same composition should grow simultaneously. Nevertheless, the direction of the growth plane shown in Figure 3 is not parallel to the axis of AAM pores but with a tilted angle, indicating that the SAED pattern could not determine the traditionally considered growth direction of a nanowire. To account for this, we propose a step growth mode, in which all the steps have the same growth direction and are parallel to the wire axis, as schematically illustrated in Figure 3d. In this case, it should be a nonequilibrium growth process controlled by kinetics, because the reduced ions do not have enough kinetic energy to jump from one step to another due to the existence of the Ehrlich−Schwoebel barrier[36,37] which hinders the descent of atoms to lower levels, and this is the so-called step-flow growth mechanism in thin film growth.[38] However, this step-flow growth mechanism could not be applied to the growth of the SLNWs with the tilted interface shown in Figure 3, because it is controlled by thermodynamics; instead, we call it a step growth mechanism. The difference is that in step-flow growth mode the adatoms (reduced ions) have enough energy to diffuse to the step edge and thus the growth is controlled by thermodynamics, while in step growth mode the diffusing energy needed for the reduced ions is much smaller, and therefore the growth is governed by kinetics.

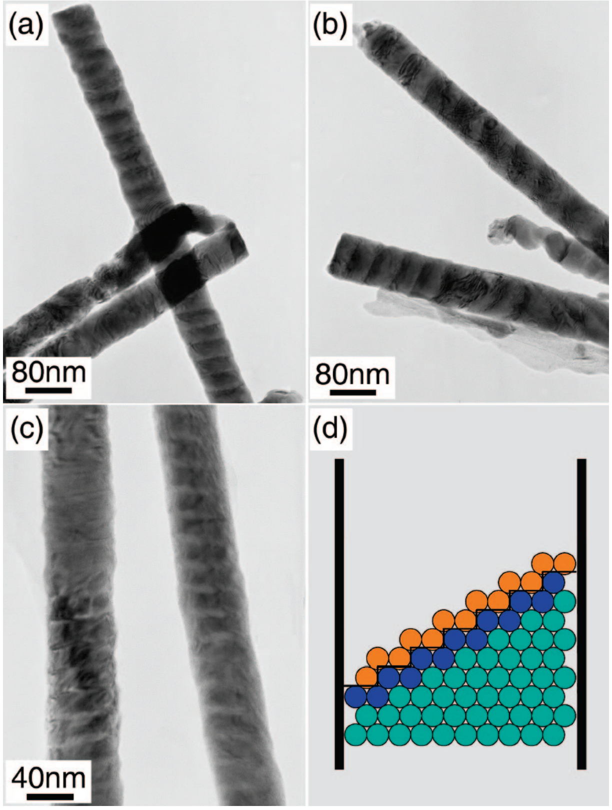

Figure 3. Typical TEM images of epitaxial Bi/BiSb superlattice nanowires with a tilted interface. (a−c) TEM images of the tilted growth. (d) Schematic representation of the tilted plane growth mode, the atoms in blue represent the growth front and the growth plane of a SLNW, the atoms in orange represent a new layer growth controlled by kinetics.

Actually, the seemingly tilted interface is composed by the vicinal surfaces of all the steps, and the role of surface steps has been well-known for decades in the context of thin films growth on vicinal surfaces.[39] Johnson et al.[40] pointed out that a miscut above a certain critical slope (which depends on growth conditions) leads to stable growth in a step-flow mechanism in GaAs thin films epitaxy, and the same reason can be applied to the stable tilted growth. Nevertheless, the vicinal surface in the tilted growth is different from that in thin film growth, it is a 2D limited system and the terrace is much smaller. The tilted plane growth mode also showed that the deposition rate is relatively high and the diffusion rate of the reduced ions is relatively low in all AAM pores in our experiment.

The tilted growth mode is a stable growth process controlled by kinetics but not a thermodynamic equilibrium state. Under certain growth conditions, such as when there is a thermal fluctuation or ion concentration variation, the diffusing ability of the reduced ions will enhance, leading to the transition of the growth mode. Indeed, this transition has been observed as shown in Figure 4a, in which the tilted growth mode transits to a common plane growth mode after a several bilayer adjustment. Figure 4b schematically illustrates the transition from a tilted growth mode to a plane growth mode. It is believed that there is a thermal fluctuation at this moment, the reduced ions those in red in the figure

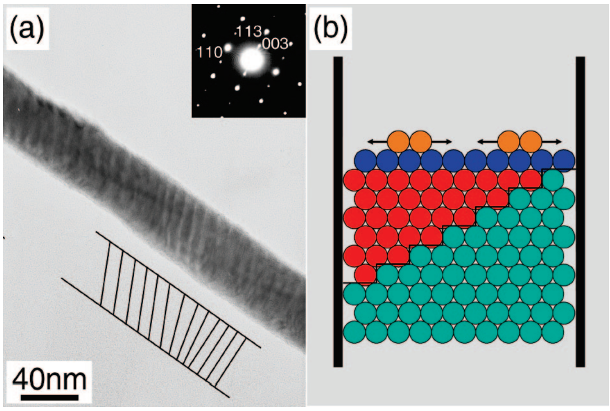

Figure 4. Transition from a tilted plane growth to a plane growth. (a) A TEM image: the upper inset is the corresponding SAED pattern; the lower drawing is the schematic diagram. (b) Schematic representation of the transition: the atoms in Cambridge blue represent the tilted growth mode, the atoms in red represent those that jumped over the Ehrlich−Schwoebel barrier, and the atoms in blue represent the new plane growth front and growth direction.

have the necessary energy to jump over the Ehrlich−Schwoebel barrier or the ion concentration has a variation, which allowed the reduced ions enough time to relax to an even stable state in the time interval prior to the deposition of another ion.[41] In this situation the transition process is controlled by thermodynamics. It is speculated that the transition from the plane growth to the tilted plane growth is also possible when there is a thermal fluctuation or ion concentration variation.

A curved interface in the SLNWs is also observed as shown in Figure 5. Wang et al.[7] and Valizadeh et al.[12] reported a concave texture in the growth of electrodeposited Ni/Cu and Au/Co SLNWs. They attributed it to the gold electrode, in which the gold partially entered into the pores and adhered preferentially to their walls before sealing the pores, leading to the formation of a small basin at each hole extremity. From panels a−c of Figure 5, one can see that the curved interface is just like a bowl, and the initial bowl-like growth plane is a product of the competition of different planes, as schematically illustrated in Figure 5d. After the formation of the initial bowl-like plane, the growth is a stable growth process controlled by kinetics and is a thermodynamic nonequilibrium state. Apparently, the bowl-like interface is also composed of many parallel steps, and the vicinal surfaces of these steps composed the curved interface. As in the tilted growth mode, the reduced ions grow on all the steps simultaneously. It was found that the bowl-like growth can maintain at least 10 μm along the SLNWs, indicating that this kind of growth mode is a stable growth process. Figure 5e shows the growth model of the bowl-like growth of SLNWs; it matches very well with the TEM images shown in Figure 5c. The bowl-like growth will result in a composition difference in the cross section normal to the nanowire axis and leads to the gradual contrast change between segments along the nanowires, which further proves that this growth mode is a step growth mechanism.

From the above discussions, we can conclude that the SLNW with a modulated composition is a suitable structure to study the growth mechanism of the electrodeposited nanowires. We systematically studied the growth mechanism of Bi/BiSb SLNWs under a relatively higher deposition rate and a relatively lower diffusion rate of the reduced ions in all AAM pores and found that different growth modes are all permitted, but the exact growth mode of the nanowire is exclusively determined by the initial plane shape induced by the 3D to 2D transition. The 2D plane growth mode is a layer-by-layer growth mechanism and is controlled predominantly by thermodynamics, while the tilted plane growth and the curved plane growth modes are a stable step growth mechanism controlled mainly by kinetics and are not a thermodynamic equilibrium state due to the Ehrlich−Schwoebel barrier. These nonplanar growth modes will transit to a 2D plane growth mode under certain growth conditions shown above.

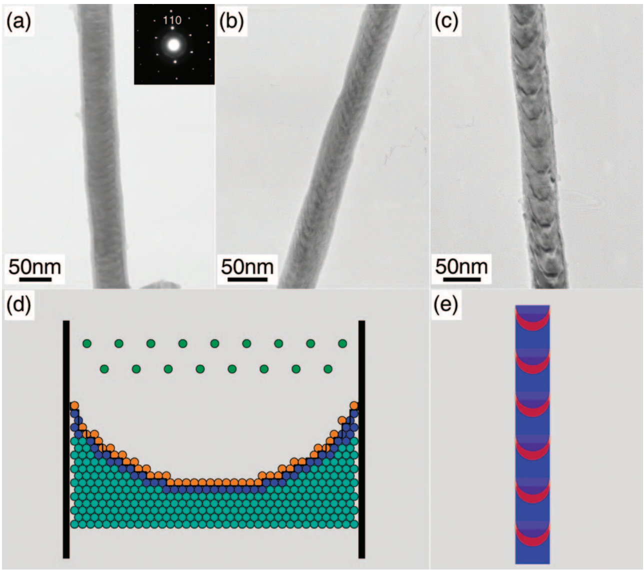

Figure 5. Typical TEM images and models of epitaxial Bi/BiSb superlattice nanowires with a bowl-like surface growth. (a) TEM image of a bowl-like SLNW with a small curvature, the upper inset is the corresponding SAED pattern. (b, c) TEM images of a bowl-like SLNW with a larger curvature. (d) Schematic representation of a bowl-like growth mode, the atoms in blue represent the growth front and growth plane of a SLNW, the atoms in orange represent a new layer growth controlled by kinetics, and the atoms in green represent the ions in the electrolyte arriving to the growth front. (e) Schematic scenograph of a bowl-like growth SLNW, the red area and the blue area correspond to Bi and BiSb segments of the Bi/BiSb SLNW respectively, the transition color between the two main colors corresponds to the composition superposition due to the bowl-like surface growth.

The growth of the electrodeposited nanowires is a process governed by a competition between kinetics and thermodynamics. Precise controlling of the growth process and the properties of the electrodeposited nanowires will be possible only after a deep understanding of this competition. The different growth modes and the transition of the growth mode from the nonplanar modes to planar mode are universal, depending strongly on the controlling factors. We expect the amorphous nanowires will be obtained if the growth process is controlled completely by kinetics. On the other hand, the SLNWs grown in a complete plane growth mode will be achieved if the growth process is mainly controlled by thermodynamics. The two conditions might be realized by adding appropriate surfactants in the electrolyte to promote either kinetics or thermodynamics factors.

This work demonstrates a new method to observe the growth process of electrodeposited nanowires through a superlattice structure and presents a new growth model for this kind of nanowire. It will favor a deep understanding of the growth process of electrodeposited nanowires and provide important experiment data to crystal growth theory.

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Supporting Information Available: Detailed description of the experimental setup strategy, synthesis and structural analysis methods, and HRTEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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