A Strategy to Prepare Wafer Scale Bismuth Compound Superstructures

Chuan Fei Guo, Jianming Zhang, Meng Wang, Ye Tian, and Qian Liu*

The design and fabrication of well aligned nanostructures or super-nanostructures are of great interest in recent decades because such nanostructures are good units for electronic and photoelectric nanodevices including solar cells, nanogenerators, UV lasers, and field emission devices.[1-6] Directing the growth of nanostructures with a single crystalline (SC) epitaxial substrate has been a quite important strategy toward aligned, high-quality SC nanostructures.[3,7-11] Chemical vapor deposition (CVD) is a commonly used method for growing well aligned nanostructures on epitaxial substrates, for which a metallic thin film (typically gold) is often required, annealing at high temperatures to form metal nanoparticles as catalysts.[3,7-9,12] However, this method suffers from the fact that the metallic nanoparticles are not easy to remove after growth, as well as non-uniformity of products from zone to zone, and is therefore not suitable for large area nanodevices. An alternative method, solution growth directed by a seed layer on epitaxial substrate can grow well aligned 1D nanostructures without metal residues. For instance, Z. L. Wang et al. have successfully obtained vertically aligned ZnO nanorods from a ZnO seed layer on GaN substrate.[10] The success of fabricating arrays of 1D nanostructures has led to extensive investigation of their properties.

In the last decade, 2D nanostructures have attracted increasingly more attention. For example, 2D graphene has been one of the most attractive nanostructures for scientific research.[13,14] However, there are quite few works on the fabrication and properties of vertically aligned arrays of 2D nanostructures, many of which should be promising structures that may lead to practical applications.[11,15] We have previously reported that 2D orthogonal networks (2DONWs) of vertical BiOCl, Bi$_2$O$_2$CO$_3$, and β-Bi$_2$O$_3$ nanowalls, and nested 2DONWs (N2DONWs) of Bi$_2$S$_3$ nanowires are available via topotactic transformations with β-Bi$_2$O$_3$ thin films as the precursors.[16,17] The growth of such complex nanoarchitectures combines both bottom-up and top-down processes, and is directed by lattice match. This is a demonstration that nanostructures can be compatible with thin film technology and modern device fabrication processes. However, the scale of the vertical nanostructures is limited by the size of the precursors, the β-Bi$_2$O$_3$ domains, which are typically 20 µm in diameter. And there are only a small part of domains that can transform to vertical BiOCl networks. It is quite important to have the ability to grow well aligned 2D nanostructures on wafer scale, if we want to take full advantages of their properties and finally to apply them. The key to realize this purpose is to grow wafer scale SC β-Bi$_2$O$_3$ thin films. Herein, we show a route to SC β-Bi$_2$O$_3$ thin films, as well as the synthesis of wafer scale and well aligned BiOCl 2DONWs and Bi$_2$S$_3$ on SrTiO$_3$ (STO) substrate. The supernanostructures present anisotropic electrical property.

We have applied the crystallization of an amorphous BiO$_x$ film on glass substrate to make the β-Bi$_2$O$_3$ thin film. BiO$_x$ is a semiconductor with a bandgap of ~2 eV,[18] it often naturally forms on the surface of metallic bismuth nanostructures, with a thickness of several nanometers.[19] In this work, we use reactive sputtering to deposit flat BiO$_x$ films, which could convert to β-Bi$_2$O$_3$ by thermal annealing at 300–600 °C for hours. Unfortunately, without lattice direction by SC substrate, the β-Bi$_2$O$_3$ thin film is always polycrystalline, with many SC domains in different crystallographic orientations. SC substrates have been proven to be effective for growing wafer scale and well aligned nanostructures owing to lattice direction. Thereupon we tried STO SC substrate, which has a cubic structure with lattice constant $a = 3.905$ Å, very close to the [200] interplanar spacing (3.871 Å) of β-Bi$_2$O$_3$. The lattice misfit between STO [100] and β-Bi$_2$O$_3$ [200] is

$$f = \frac{|d_{200,Bi_2O_3} - d_{100,STO}|}{d_{100,STO}} = 0.88\%$$  (1)

indicating that β-Bi$_2$O$_3$ could match well with STO. It is worth noting that we did the crystallization at 500 °C (actually crystallization begins at ~250 °C) rather than at room temperature, thus thermal expansion should be considered. X-ray diffraction (XRD) data show that from 25 to 300 °C, linear expansion of lattice parameter $a$ for STO and β-Bi$_2$O$_3$ are 0.517% and 0.524% (supplementary information Figure S1), respectively. This tiny difference does not lead to significant change of lattice misfit at crystallization temperature, therefore it can be ignored.

We sputtered a 100–200 nm thick BiO$_x$ thin film on (001)-oriented SrTiO$_3$ (STO) substrate, and then annealed
fig 1. Two routes that lead to the formation of polycrystalline and SC \(\beta\)-Bi\(_2\)O\(_3\) films, respectively. Route 1: (1) deposition of 100 nm BiO\(_x\) film followed by (2) crystallization operated at 500 °C for 3 h. Route 2 introduces a 6 nm thick SC \(\beta\)-Bi\(_2\)O\(_3\) buffer layer: (1) deposition of a 6 nm thick BiO\(_x\) film; (2) annealing at 500 °C for 3 h, leading to the formation of a thin SC \(\beta\)-Bi\(_2\)O\(_3\) buffer layer; (3) deposition of 100 nm BiO\(_x\) film; and (4) crystallization at 500 °C for 3 h. For route 2, from step (1) to step (2) is a heteroepitaxial growth, and from step (3) to step (4) is a homoepitaxial growth.

The film at 500 °C for 3 h (under which amorphous BiO\(_x\) would transform to \(\beta\)-Bi\(_2\)O\(_3\)) (Route 1 in **Figure 1**). Experimental results again indicated that the as-formed film was polycrystalline \(\beta\)-Bi\(_2\)O\(_3\) (Figure S2(a)), similar to the results by using glass or silicon wafer as the substrate. After rinsing in diluted HCl solution, the \(\beta\)-Bi\(_2\)O\(_3\) turned to a BiOCl film with a polycrystalline nature, and corresponding SEM image (Figure S2(b)) shows many BiOCl 2DONW domains in different orientations, confirming that the \(\beta\)-Bi\(_2\)O\(_3\) film is polycrystalline. We also tried pulsed laser deposition followed by annealing, and still no SC \(\beta\)-Bi\(_2\)O\(_3\) thin film was obtained. This is understood because a relatively thick epi-layer will cause quite large stress and elastic energy, so that it finally forms a polycrystalline film, which can relax stress effectively.

When the film is thin enough, however, the result is quite different. We deposited a quite thin (only 6 nm thick) BiO\(_x\) film on STO substrate and annealed it at 500 °C for 3 h. It was then used as the substrate and covered with a 100 nm thick BiO\(_x\) film for crystallization (Route 2). The \(\theta\)-2\(\theta\) scan XRD spectrum in **Figure 2(a)** of the “two-layer” \(\beta\)-Bi\(_2\)O\(_3\) film only shows a strong [002] reflection (except for the (001) peak of the STO substrate) (JCPDS 78-1793), indicating that it is single crystalline with the c-axis normal to the film plane. And this can explain the subsequent highly ordered superstructures of BiOCl shown in **Figure 2(b)**–(d), which will be discussed later on in details. To the best of our knowledge, this is the first report on a SC \(\beta\)-Bi\(_2\)O\(_3\) (a metastable phase at room temperature) film. It is deduced that the 6 nm \(\beta\)-Bi\(_2\)O\(_3\) film is single crystalline and plays the role of a buffer layer (also experimentally proved in Figure S2(a)), which effectively decreases the elastic energy of the system. And the crystallization of subsequent BiO\(_x\) film on the buffer layer is a homoepitaxy process, which is often easier than on a STO substrate. And that is why the 100 nm BiO\(_x\) film converts to a SC \(\beta\)-Bi\(_2\)O\(_3\) film.

**Figure 2.** (a) XRD spectra of a SC \(\beta\)-Bi\(_2\)O\(_3\)/STO sample (red solid line), and corresponding BiOCl film (green solid line), which consists of three sets of mutually perpendicular nanoplate arrays. The left inset depicts the crystallographic orientations of the \(\beta\)-Bi\(_2\)O\(_3\)/STO heterojunction (corresponding to the red solid line of the XRD spectra), while the right inset shows that the BiOCl nanoplates are mutually perpendicular (corresponding to the green solid line). (b) and (c) Low and medium magnification SEM images of the BiOCl film (top view). Inset in panel (b) is a Fourier transformation pattern of the SEM image. (d) Corresponding tilt view.
The epilayer may have three possibilities of strain status. The first possibility is that the 6 nm thick $\beta$-Bi$_2$O$_3$ layer is a stress-free film. For this case, there should be a tetragonal network of misfit dislocations formed at the $\beta$-Bi$_2$O$_3$/STO interface with an interval of ~31.6 nm (this interval can be roughly calculated as $S = d_{||\text{STO}}/f$). The second possibility is that the buffer layer is a fully strained film, and there is no mismatch dislocation. And the third possibility is a mixed case, in which only part of the strain is released by mismatch dislocations. In this case, mismatch dislocations might be found but the interval will be larger than 31.6 nm.

Our transmission electron microscopy (TEM) observation of a focused ion beam (FIB) milled specimen show a dislocation array with a period of ~30 nm (Figure 3(a)) along the [100] direction. However, this does not mean that the film is absolutely free of stress, because the dislocations themselves will also induce a stress field. Especially in our case, we could not accurately locate the dislocation cores (see the high resolution (HR) TEM image in Figure 3(b)), and the stress field may cover a large range to more than ten nanometers. The dark areas in the TEM image could roughly be regarded as the stress fields. Since $\beta$-Bi$_2$O$_3$ has a tetragonal structure, there should be another dislocation array in an equivalent case, along the [110] direction (Figure 3(d)), forming a tetragonal network of dislocations. Therefore, the thin $\beta$-Bi$_2$O$_3$ buffer layer has a high density of dislocations. Selected area electron diffraction (SAED) pattern and corresponding HRTEM image in Figure 3(b) and (c) show that $\beta$-Bi$_2$O$_3$ grows on STO with the c-axis out of plane, and the epitaxial relationship is: (110)$_{\beta}$-Bi$_2$O$_3$//(110)$_{\text{STO}}$ and (001)$_{\beta}$-Bi$_2$O$_3$//(001)$_{\text{STO}}$ (here the subscript ‘$\beta$’ indicates $\beta$-Bi$_2$O$_3$). The TEM analysis agrees well with the XRD results.

The SC $\beta$-Bi$_2$O$_3$ film could transform to 2DONW of BiOX (X = Cl and Br), Bi$_2$O$_3$CO$_3$, $\beta$-Bi$_2$O$_3$, or other bismuth compounds with a lattice parameter of $\sim$2nm$^2 \times 3.9$ Å ($n = 0, 1, 2, 3, 4$). Here we only show BiOCl 2DONW because for other bismuth compounds the morphology is quite similar. Figure 2(b)–(d) are SEM images of a wafer scale (1 cm x 1 cm) BiOCl 2DONW transformed from a SC $\beta$-Bi$_2$O$_3$ film. These images clearly show that there are two sets of vertically aligned BiOCl nanowalls are grown perpendicular to each other on the STO substrate. The area of the 2DONW is limited only by the wafer. We inspected different zones of the sample and all demonstrated quite similar morphology and exactly the same orientations. Corresponding XRD diffraction spectrum (recorded by $\theta$-2$\theta$ scan) in Figure 2(a) (the green solid line) reveals a strong BiOCl [110] peak, together with a set of relatively weak [00l] ($l = 1, 2, 3$) reflections. The structural information indicates that there are two sets of perpendicularly woven nanowalls grown vertically on the substrate (judged from the [110] peak), together with a set of tiled nanoplates (from the [00l] reflections). That is, there are three sets of mutually perpendicular nanowalls, vertical to or parallel to the STO surface. This is confirmed by the SEM images shown as in Figure 2(c) and (d), from which we can see a nanowall network and also some tiled nanoplates.

The morphology of the BiOCl 2DONW could be explained from the unique structure of $\beta$-Bi$_2$O$_3$. For the crystal structure of $\beta$-Bi$_2$O$_3$, it has two equivalent but perpendicular facets, (220) and (2\overline{2}0), with a $d$-spacing of 2.737 Å. The structural information indicates that there are two sets of perpendicularly woven nanowalls grown vertically on the substrate (judged from the [110] peak), together with a set of tiled nanoplates (from the [00l] reflections). That is, there are three sets of mutually perpendicular nanowalls, vertical to or parallel to the STO surface. This is confirmed by the SEM images shown as in Figure 2(c) and (d), from which we can see a nanowall network and also some tiled nanoplates.
However, because NaCl is dissolvable, this process is not well understood. A drop of Bi(NO$_3$)$_3$ solution on a (001)-oriented SC NaCl bulk substrate that topological structure could affect physical properties of materials. For example, Figure 4(b) shows that the current-voltage (I-V) characteristic was measured with a Keithley 2635A source meter. And this can explain the XRD spectrum in Figure 2(a). Based on the above analysis, a β-Bi$_2$O$_3$ film with either the c- or the <110>-axis out of plane can lead to the formation of a 2DONW with three mutually perpendicular nanoplates (in this work, we have the β-Bi$_2$O$_3$ films with the c-axis out of plane).

The SC β-Bi$_2$O$_3$ film could also transform to more complex superstructures such as Bi$_2$S$_3$ self-similar N2DONWs. For the Bi$_2$S$_3$ N2DONW, it is often transformed from BiOCl, BiOBBr, BiOBr$_2$, or β-Bi$_2$O$_3$ 2DONW with lattice directing. It consists of two levels structures. The first level is 2DONW of nanowalls. And for the second level, each nanowall is replaced with a tetragonal network of Bi$_2$S$_3$ nanorods along the [001] direction (Figure 4(a)). It is therefore a nested self-similar hierarchical structure. The Bi$_2$S$_3$ N2DONWs present apparently anisotropic physical properties related to the unique structure. For example, Figure 4(b) shows that the electrical conductivity along the [110] direction is almost twice that along the [100] direction, probably as a result of shorter path and weaker scattering (because of less joints) of electrons. It is apparent that the low resistance path is almost straight, while the high resistance path is zigzag and has more wall-to-wall joints as well. This is a demonstration that topological structure could affect physical properties of materials.

Besides β-Bi$_2$O$_3$ SC films, other SC films or bulks might also be potential for making 2DONWs of bismuth compounds. For example, NaCl has a cubic crystal structure with a = 5.639 Å, which is almost twice that of the $d_{110}$ of BiOCl. A drop of Bi(NO$_3$)$_3$ solution on a (001)-oriented SC NaCl bulk can indeed result in BiOCl 2DONWs shown as in Figure S3. However, because NaCl is dissolvable, this process is not well controllable and BiOCl nanowalls are quite small.

With the β-Bi$_2$O$_3$ films, we are able to make superstructures of many kinds of bismuth compounds including β-Bi$_2$O$_3$ nanowall networks. Interestingly, when the SC β-Bi$_2$O$_3$ wall or plates are big enough, each wall might behave like a β-Bi$_2$O$_3$ film and transform to a 2DONW of BiOCl or N2DONW of Bi$_2$S$_3$, and if these large plates consists of a superstructure itselfs is then possible to make even more levels of ordered hierarchical nanostructures. Figure S4(a) shows two sets of vertically aligned BiOCl nanowall (which could finally transform to Bi$_2$S$_3$ network) formed on a large SC plate of β-Bi$_2$O$_3$, proving that such β-Bi$_2$O$_3$ single crystal can really act as the precursor for more complex hierarchical nanostructures. Figure S4(b)–(d) demonstrate two kinds of three-leveled Bi$_2$S$_3$ hierarchical nanostructures. The first level for panel (b) is stacked nanoplates, and for panels (c) and (d) is 2DONW, respectively; the second level is 2DONW; and the third level is the Bi$_2$S$_3$ network of nanorods. Such nanostructures are made up of organized SC building blocks and possess quite large specific surface, so that they might be used in dye-sensitized solar cells, super capacitors, and lithium-ion batteries.

In conclusion, we have successfully obtained a SC β-Bi$_2$O$_3$ epilayer on STO by RF magnetron sputtering of amorphous Bi$_2$O$_3$ followed by annealing. An ultra-thin β-Bi$_2$O$_3$ film is introduced as a buffer layer that can effectively decrease the elastic energy of the system. The SC β-Bi$_2$O$_3$ epilayer could be transformed into a wafer scale network of β-Bi$_2$O$_3$. BiOX (X = Br, Cl), Bi$_2$O$_2$CO$_3$ nanowalls, and nested self-similar networks of Bi$_2$S$_3$ nanorods. The superstructures present special properties that are related to their unique morphologies, for example, the Bi$_2$S$_3$ nested networks show anisotropic electrical conductivity. This work may provide a platform for novel electronic and photoelectric devices.

**Experimental Section**

**Preparation of Materials**: Bi$_2$O$_3$ films were deposited on clean STO substrate by magnetron sputtering (ULVAC ACS4000-C4), with gas flow rates of 20 and 5 sccm for Ar and O$_2$, respectively. And crystallization was conducted at 500 °C for 3 h in a muffle furnace. SC β-Bi$_2$O$_3$ layer was obtained by a two-step process: we first deposited a 6 nm thick Bi$_2$O$_3$ film on STO, and after crystallization a 100 nm thick Bi$_2$O$_3$ film was again deposited onto it followed by crystallization. BiOCl 2DONW was synthesized by rinsing a SC β-Bi$_2$O$_3$ layer in diluted hydrochloric acid (0.2 M) for 1 min. Bi$_2$O$_2$CO$_3$ 2DONW was formed by incubating a SC β-Bi$_2$O$_3$ layer in blended solution of NaHCO$_3$ (0.04 M) and HNO$_3$ (0.02 M). β-Bi$_2$O$_3$ 2DONW was prepared by annealing the Bi$_2$O$_2$CO$_3$ 2DONW at 320 °C for 1–3 days. And Bi$_2$S$_3$ N2DONW was obtained by incubating the β-Bi$_2$O$_3$ 2DONW in blended solution of thiouacetamide (0.04 M) and HCl (0.02 M) for two days.

**Characterization**: Morphology of the samples was observed by using a scanning electron microscope (Hitachi S4800). TEM images, HRTEM images and SAED patterns were recorded with a field emission transmission electron microscope (FEI Tecnai G2 F20). XRD spectra were recorded with an X-ray diffractometer (Bruker D8 Focus). And I-V characteristic was measured with a Keithley 2635A source meter.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

C. F. Guo and J. Zhang contributed equally to this work. This work was supported by the funds from NSFC (10974037), NBRPC (2010CB934102), International S&T Cooperation Program (2010DFA51970) and Eu-FP7 (No. 247644). The authors thank Dr. K. Peng and Dr. X. Qi for assistance in FIB milling and TEM observations.


Supporting Information

Received: March 12, 2013
Revised: April 19, 2013
Published online: