Polymorph-Tuned Synthesis of $\alpha$- and $\beta$-Bi$_2$O$_3$ Nanowires and Determination of Their Growth Direction from Polarized Raman Single Nanowire Microscopy


Abstract: We report polymorph-tuned synthesis of $\alpha$- and $\beta$-Bi$_2$O$_3$ nanowires and their single nanowire micro-Raman study. The single crystalline Bi$_2$O$_3$ nanowires in different phases ($\alpha$ and $\beta$) were selectively synthesized by adjusting the heating temperature of Bi precursor in a vapor transport process. No catalyst was employed. Furthermore, at an identical precursor evaporation temperature, $\alpha$- and $\beta$- phase Bi$_2$O$_3$ nanowires were simultaneously synthesized along the temperature gradient at a substrate. The growth direction of $\alpha$-Bi$_2$O$_3$ nanowires was revealed by polarized Raman single nanowire spectra. For thin $\beta$-Bi$_2$O$_3$ nanowires with a very small diameter, the polarized Raman single nanowire spectrum was strongly influenced by the shape effect.

Keywords: bismuth oxide · nanowires · photoluminescence · polarized Raman microscopy · polymorphism

Introduction

Bismuth oxide (Bi$_2$O$_3$) polymorphs are semiconductors with a band-gap energy of 2 to 3.96 eV, a high refractive index of 2.3 at 633 nm, ion conductivity, and dielectric permittivity as well as remarkable photoconductivity and third-order optical non-linear property.[1–5] These versatile physical properties make Bi$_2$O$_3$ an attractive candidate material for gas sensing, optical coating, electrochromic devices, and photovoltaic cells. Bi$_2$O$_3$ has four different polymorphs, known as $\alpha$, $\beta$, $\gamma$, and $\delta$ phases, each with unique physical properties.[6–8] Thermal phase transitions of Bi$_2$O$_3$ polymorphs, however, have not yet been revealed clearly. $\alpha$-phase is thermodynamically stable at room temperature and is transformed into $\delta$ phase at 729°C.[6–8] On cooling, the $\delta$ phase is changed into $\beta$-phase near 650°C and then to $\alpha$ phase or converted into $\gamma$ phase at 640°C.

Synthesis of one-dimensional Bi$_2$O$_3$ nanostructures has been recently investigated by various synthetic methods.[9–15] Kim et al. and Qiu et al. synthesized $\alpha$- and $\beta$-phase single crystalline Bi$_2$O$_3$ nanowires (NWs), respectively, using a gold film or a Bi catalyst.[13,14] Huang et al. obtained $\delta$-Bi$_2$O$_3$ NWs through oxidation of Bi NWs synthesized by an anodic alumina oxide (AAO) method.[15] Li et al. synthesized Bi-Bi$_2$O$_3$ core-shell NWs and Bi$_2$O$_3$ nanotubes (NTs) using templates.[16]

Raman spectroscopy is useful for detailed investigation of crystalline nanomaterials because it is a simple, in-situ, and non-destructive tool.[17–28] In particular, Raman spectroscopy is suitable for the study of crystallinity and phase transitions of metal oxide NWs which show distinct physical properties depending on the crystal structures.[22–24] Recently, selective imaging of a single GaN NW[20,21] and phase transition of VO$_2$ nanoparticles have been demonstrated via Raman spectroscopy.[25] New phenomena such as nanoscale optical antenna have been also observed in Raman scattering of semiconductor NWs.[26,30]

In this paper, we report synthesis of $\alpha$- and $\beta$- Bi$_2$O$_3$ NWs and their structure analysis by polarized Raman single NW microscopy. First, single crystalline $\alpha$- or $\beta$-Bi$_2$O$_3$ NWs are...
selectively synthesized by changing the heating temperature of Bi powder. Second, at the same Bi heating temperature, both the α- and β-Bi$_2$O$_3$ NWs can be simultaneously synthesized on substrates placed along the temperature gradient. Furthermore, we analyzed the crystal structures of a single α-Bi$_2$O$_3$ NW with polarized Raman spectroscopy. The growth directions of the NWs were clearly identified from the polarization dependence of Raman spectra. We have also observed that shape effect strongly influences the Raman spectra of thin β-Bi$_2$O$_3$ NWs.

**Results and Discussion**

**Morphology-tuned synthesis:** We synthesized α- and β-Bi$_2$O$_3$ NWs simply by mixing oxygen with Bi vapor obtained by heating Bi powder without any catalyst. 1% oxygen mixed with Ar flowed continuously into the high-temperature zone during the reaction. α-Bi$_2$O$_3$ NWs were formed after a reaction time of 5 min when Bi precursor was heated at 800–850°C. β-Bi$_2$O$_3$ NWs were obtained after a reaction time of 30 min when Bi was heated at 550–600°C. When the precursor heating temperature was in the range of 700–750°C, we simultaneously synthesized α- and β-Bi$_2$O$_3$ NWs along temperature gradient. α-Bi$_2$O$_3$ NWs were synthesized on a substrate placed at a 500°C region and β-Bi$_2$O$_3$ NWs were obtained on a region at 350°C, after a reaction time of 10 min. Thus, the Bi evaporation temperature and substrate temperature play important roles in the selective synthesis of α- and β-phase of Bi$_2$O$_3$ NWs.

The morphology and crystal structure of Bi$_2$O$_3$ NWs were investigated by field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), and transmission electron microscope (TEM). Figure 1a,c shows the FESEM images of α- and β-Bi$_2$O$_3$ NWs, respectively, and Figure 1b,d the corresponding XRD patterns. Most of the peaks in Figure 1b are indexed to monoclinic α-Bi$_2$O$_3$ with lattice parameters of $a = 5.848$, $b = 8.166$, $c = 7.510$ Å (JCPDS card no. 27-0053) and a space group $P2_1/c$. Figure 1d indicates tetragonal β-Bi$_2$O$_3$ NWs, with lattice parameters of $a = 7.742$, $c = 5.631$ Å (JCPDS card no. 27-0050) and a space group $P4_2/c$. Diameters of α- and β-Bi$_2$O$_3$ NWs are in the range of 70–150 and 15–40 nm, respectively. The lengths of the NWs are a few micrometers.

The TEM images in Figure 2a,d exhibit α- and β-Bi$_2$O$_3$ NWs, respectively. The selected area electron diffraction (SAED) pattern in Figure 2b reveals single crystallinity of α-Bi$_2$O$_3$ NWs and is assigned to a monoclinic Bi$_2$O$_3$ phase with a growth direction of [010]. The SAED pattern in Figure 2e indicates that β-Bi$_2$O$_3$ NWs have a tetragonal structure and are single crystalline with a growth direction of [010]. Repetitive TEM measurements of other NWs showed identical results. Figure 2c,f are high-resolution TEM (HRTEM) images of α- and β-Bi$_2$O$_3$ NWs, showing clear lattice fringes and confirming again the single crystallinity of Bi$_2$O$_3$ NWs. The lattice spacings of 3.25 and 4.03 Å in Figure 2c match with those of (002) and (020) planes of α-Bi$_2$O$_3$. The HRTEM image of a β-Bi$_2$O$_3$ NW in Figure 2f displays lattice spacings of 4.00 and 5.48 Å that correspond to (200) and (001) planes, respectively. Insets in panels c and f are the two-dimensional fast Fourier transformation (FFT) images from HRTEM and agree with panels b and e. Compositional analysis of Bi$_2$O$_3$ NW ensemble reveals that as-synthesized products contain Bi and O in approximately 2:3 ratio, and that there are no other impurities and/or metal catalysts (Figure 2g). These results suggest that in this experiment Bi$_2$O$_3$ NWs grow by a VS mechanism.\[31]\n
**Photoluminescence (PL):** The band gaps of α- and β-Bi$_2$O$_3$ NW ensemble were investigated by photoluminescence (PL). Figure 3 shows PL spectra of Bi$_2$O$_3$ NW ensemble obtained at room temperature using a He–Cd laser at 325 nm. α-Bi$_2$O$_3$ NW ensemble shows a broad peak at 400 nm corresponding to a band gap of 3.09 eV. β-Phase NW ensemble shows a broad peak near 440 nm matching to a band gap of 2.81 eV. Compared with bulk α- and β-Bi$_2$O$_3$ (α: 433.5 nm, β: 482.4 nm), the NW ensemble shows blue shifts of 34 and 42 nm, respectively. This can be ascribed to the quantum confinement effect, similar to the PL results of Bi$_2$O$_3$ nanoparticles and NTs.\[9,12\]

**Growth direction and Raman band symmetries of α-Bi$_2$O$_3$ NWs revealed by polarized Raman spectra:** Figure 4 shows the Raman spectra of α- and β-Bi$_2$O$_3$ NW ensembles, which are quite distinct from each other.

The Raman band intensity, $I$, for a mode with Raman tensor, $R$, is dependent on the polarization configuration of Bi$_2$O$_3$. The Raman image of a β-Bi$_2$O$_3$ NW in Figure 2f displays lattice spacings of 4.00 and 5.48 Å that correspond to (200) and (001) planes, respectively. Insets in panels c and f are the two-dimensional fast Fourier transformation (FFT) images from HRTEM and agree with panels b and e. Compositional analysis of Bi$_2$O$_3$ NW ensemble reveals that as-synthesized products contain Bi and O in approximately 2:3 ratio, and that there are no other impurities and/or metal catalysts (Figure 2g). These results suggest that in this experiment Bi$_2$O$_3$ NWs grow by a VS mechanism.\[31\]
incident and scattered lights \((I = | \hat{e}_i \cdot R \cdot \hat{e}_s |^2)\), where \(\hat{e}_i\) and \(\hat{e}_s\) are the unit vectors of incident and scattered light polarizations, respectively. Thus, we can identify vibrational mode symmetries of crystals by obtaining Raman spectra using differently polarized light. Most importantly, the growth direction of a single-crystalline NW can be determined from the polarized Raman spectra by comparison with bulk crystals, as discussed below.

Polarized Raman spectra of \(\alpha\)-Bi\(_2\)O\(_3\) NW were recorded at four scattering geometries, \(z(\alpha z)\), \(z(\beta z)\), \(z(\gamma z)\), \(z(\delta z)\), according to Porto notation (see Figure 9 for the laboratory axes; \(x, y, z\)). For example, the \(z(\alpha z)\) notation indicates that incident and scattered lights propagate along \(z\) and \(\alpha\) axes, respectively, and they are polarized along \(\beta\) and \(\gamma\) axes, respectively. The factor group analysis predicts that \(\alpha\)-Bi\(_2\)O\(_3\) crystal with a monoclinic unit-cell structure \((C_{4h}^{(2)} P_{21}/c)\) space group, four molecules in a unit cell) has 57 optical vibrations \((15 A_g, 15 B_g, 14 A_u, 13 B_u)\), among which \(A_g\) and \(B_g\) modes are Raman active. Denisov et al. identified the symmetries and frequencies of these 30 Raman active \(A_g\) and \(B_g\) modes for a bulk single-crystal \(\alpha\)-Bi\(_2\)O\(_3\). We compared our polarized Raman spectra of \(\alpha\)-Bi\(_2\)O\(_3\) NW with the polarized Raman spectra of bulk \(\alpha\)-Bi\(_2\)O\(_3\) to identify the long axis (growth direction) of the NW (see the Supporting Information, Table S1). Our Raman spectra in Figure 5 obtained at the \(z(\beta z)\), \(z(\alpha z)\), \(z(\gamma z)\), \(z(\delta z)\) polarization geometries are similar to the bulk spectra obtained (see Figure 9) for the laboratory axes; \(x, y, z\). Therefore, \(x, y, z\) and \(\beta, \gamma, \delta\) axes of the NW correspond to the bulk crystal axes of \(b, c', a\), respectively. Since the NW axis is along \(x\) direction in the lab coordinate (see Figure 9), we assign the growth direction of the \(\alpha\)-Bi\(_2\)O\(_3\) NW to be along the crystal axis \(b\) \([010]\) direction). This assignment coincides with those from SAED and HRTEM (Figure 2 a–c).

![Figure 2. TEM images of a) an \(\alpha\)-Bi\(_2\)O\(_3\) NW and b) \(\beta\)-Bi\(_2\)O\(_3\) NW. SAED patterns and HRTEM images corresponding to a) and d) are shown in the second and third column, respectively. The zone axes of NWs for b) and e) are [010] and [001], respectively. Insets in panel c and f are the two-dimensional FFT from the HRTEM. g) EDS spectrum of Bi\(_2\)O\(_3\) NW ensembles.](image)

![Figure 3. PL spectra of \(\alpha\) - and \(\beta\)-Bi\(_2\)O\(_3\) NW ensemble obtained at room temperature using a Cd–He laser at 325 nm.](image)

![Figure 4. Raman spectra of \(\alpha\)- and \(\beta\)-Bi\(_2\)O\(_3\) NW ensembles recorded at room temperature.](image)

![Figure 5. Polarized Raman spectra of a single \(\alpha\)-Bi\(_2\)O\(_3\) NW. The scattering geometry is noted for each spectrum.](image)
From the polarized Raman spectra, we can assign the vibration mode symmetries as follows. The Raman experiment was done in two polarization configurations with incident light polarization parallel and perpendicular to the NW axis (x direction). For both polarization configurations, the scattered light was detected as a function of $q$, the angle between the scattered light polarization and the NW axis, using a polarizer in front of a spectrometer. When both incident and scattered light polarizations are in the x direction, only $A_g$ vibrational modes are excited ($\Gamma(x) = A_g$ and thus $\Gamma(\varepsilon_x) \times \Gamma(R) \times \Gamma(\varepsilon_x) = A_g \times A_u \times A_g \supseteq A_g$, see references [21] and [32] for details). For the $z(\varepsilon_y)z, z(\varepsilon_x)z,$ and $z(\varepsilon_z)z$ polarization geometries, only $A_u, B_g,$ and $B_u$ modes are excited, respectively, since y and z axes have a $B_u$ symmetry.

The polarization angle dependence becomes clearer in Figure 7a,b showing the band intensities in the Raman spectra in Figure 6a,b by the polar plots, respectively. In Figure 7a, three bands at 68, 102, and 152 cm$^{-1}$, which are maximum at $\theta = 90^\circ$, have a $B_g$ symmetry (indicated by the dashed lines to the left in Figure 6a) and other bands that are maximum at 0 and 180$^\circ$ have an $A_g$ symmetry. In Figure 7b, six bands showing maxima at 180$^\circ$ are assigned to $B_u$ bands. Thus, $A_u$ and $B_u$ bands are clearly distinguished in these polar plots. From this polarization dependence of Raman band intensities in Figure 7a,b, 12 $A_u$ and 6 $B_u$ bands are directly assigned.

**Shape effect on polarized Raman spectra of $\beta$-Bi$_2$O$_3$ NWs:**

While the crystal structure and polarized Raman spectra of bulk $\alpha$-Bi$_2$O$_3$, the most stable polymorph, have been investigated in detail,[13] polarization dependence of the Raman spectra of $\beta$-Bi$_2$O$_3$ has not been reported to date. In the present experiment, we have observed the polarized Raman spectra of a single $\beta$-Bi$_2$O$_3$ NW (Figure S1). We suggest that the polarized Raman spectra of $\beta$-Bi$_2$O$_3$ NWs are strongly influenced by the shape effect.

Polarization dependence of Raman spectra of a NW, which has a large aspect ratio, can be influenced by its shape, orientation, crystal symmetry.[24,27–29] For a semiconductor NW, the Raman intensity is proportional to the
The square of the local electric field inside the NW and is dependent on the optical resonance inside the NW. For a very thin NW, the light polarization perpendicular to the NW axis could not be confined inside the NW. Only the component of the light polarization parallel to the NW axis could be confined inside the NW and provide an effective internal electric field that significantly contributes to Raman scattering \( (I(\phi) \propto \cos^2 \phi \text{ where } \phi \text{ is the angle between the NW axis and the incident light polarization}) \).[24-27,28] When the incident light polarization is perpendicular to the NW axis, only a small part of the electric field can interact with materials inside a NW and the Raman band intensity decreases, which is called a shape effect. If the diameter of the NW is very thin, this shape effect can overwhelm the effect of the crystal symmetry.

Figure 8 shows the polarized Raman spectra of a single \( \beta\)-Bi\(_2\)O\(_3\) NW recorded at four polarization geometries \( z(zz), z(yy)z, z(xy)z, \) and \( z(xy/z) \). The intensity of the Raman spectrum recorded at \( z(zz)z \) with both the incident and scattered light polarization parallel to the NW axis, is particularly strong compared to those at other polarization geometries. This feature is quite distinct from the polarized Raman spectra of single \( \alpha\)-Bi\(_2\)O\(_3\) NWs, of which the four polarized Raman spectra show comparable intensities (Figure 5). Such shape effect has been reported recently by Fan et al. in the Raman spectra of single wurtzite CdS NWs having a 60 nm diameter.[28] In the present experiment, \( \beta\)-Bi\(_2\)O\(_3\) NWs have much smaller diameters (\( \approx 25 \) nm) than \( \alpha\)-Bi\(_2\)O\(_3\) NWs (\( \approx 100 \) nm). Such small diameters of \( \beta\)-Bi\(_2\)O\(_3\) NWs make shape effect quite dominant for \( \beta\)-Bi\(_2\)O\(_3\) NWs as compared to \( \alpha\)-Bi\(_2\)O\(_3\) NWs.

![Figure 8. Polarized Raman spectra of a single \( \beta\)-Bi\(_2\)O\(_3\) NW. The diameters of \( \beta\)-Bi\(_2\)O\(_3\) NWs are estimated to be \( \approx 25 \) nm from the TEM images (Figure 2d).](www.chemeurj.org)

**Conclusion**

Single crystalline \( \alpha\)- and \( \beta\)-Bi\(_2\)O\(_3\) NWs have been successfully synthesized by a vapor transport method without using any metal catalyst. Polymorph tuning of Bi\(_2\)O\(_3\) NWs has been established by controlling the Bi precursor heating temperature and/or substrate temperature. The polarization dependence of the Raman spectra revealed the growth direction and band symmetries of \( \alpha\)-Bi\(_2\)O\(_3\) NW, \( \beta\)-Bi\(_2\)O\(_3\) NWs show strong shape effect on the polarized Raman spectra. The convenient and simple synthetic method for \( \alpha\)- and \( \beta\)-Bi\(_2\)O\(_3\) NWs may be extended for the synthesis of other metal oxide NWs. The micro-Raman probe of their crystallographic properties may become useful for the structure analysis of other polymorphic metal oxide nanostructures.

**Experimental Section**

**Synthesis:** Single-crystalline Bi\(_2\)O\(_3\) NWs were synthesized in a 1-inch diameter quartz tube placed in a horizontal one-zone furnace. Bi powder (0.05 g, 99.99%, Sigma–Aldrich) in a small alumina boat was used as a bismuth source. A Si (100) substrate was cleaned by acetone and placed 8 cm from the Bi precursor. No catalyst was employed. Argon gas mixed with 1% oxygen gas was supplied to provide an oxidative atmosphere. The evaporation zones were maintained at 550–850°C for the reaction time of 5–30 min.

**Characterization:** The as-synthesized products were analyzed with FESEM (Philips XL30S). XRD patterns of the as-grown NWs were obtained by a diffractometer (RIGAKU D/MAX-RC) with a CuK\(_{\alpha}\) radiation source. TEM images and SAED patterns were taken by a TEM (JEOL JEM-2100F). Elemental composition of Bi\(_2\)O\(_3\) NWs was investigated by energy-dispersive X-ray spectrometry (EDS) attached to the TEM.

**Micro-Raman spectroscopy:** Figure 9 shows the schematic of our micro-Raman experiment. Raman spectra of Bi\(_2\)O\(_3\) NWs were recorded by a home-built Raman microscope. The incident light of a He/Ne laser (632.8 nm, 3 mW) was focused on NW ensembles or a single NW through an objective lens (×100, NA=0.7). The Raman scattered light was collected by the same objective lens and sent to a spectrometer. Polarization-dependent Raman spectra were recorded by rotating the polarization of the incident light using a \( \lambda/2 \) waveplate and detecting the scattered light with a specific polarization. A polarizer coupled with a \( \lambda/4 \) waveplate was placed in front of the entrance slit of the spectrometer and rotated to select the scattered light in a specific polarization direction.

![Figure 9. Schematic of a micro-Raman experiment.](www.chemeurj.org)

**Acknowledgements**

This research was supported by the NRL (20090083138), Nano R&D program (20090083221), and Center for Nanostructured Materials Technology (2009K000468) from MEST, Korea. FESEM and TEM analysis was performed at the KBSI in Daejeon.

Received: June 14, 2010
Published online: November 30, 2010

**FULL PAPER**

**α- and β-Bi2O3 Nanowires**