Morphology Control of Single Crystalline Rutile TiO₂ Nanowires

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Nano-scale metal oxides have been attractive materials for sensors, photocatalysis, and dye-sensitization for solar cells. We report the controlled synthesis and characterization of single crystalline TiO₂ nanowires via a catalyst-assisted vapor-liquid-solid (VLS) and vapor-solid (VS) growth mechanism during TiO powder evaporation. Scanning electron microscope (SEM) and transmission electron microscope (TEM) studies show that as grown TiO₂ materials are one-dimensional (1D) nano-structures with a single crystalline rutile phase. Also, energy-dispersive X-ray (EDX) spectroscopy indicates the presence of both Ti and O with a Ti/O atomic ratio of 1 to 2. Various morphologies of single crystalline TiO₂ nano-structures are realized by controlling the growth temperature and flow rate of carrier gas. Large amount of reactant evaporated at high temperature and high flow rate is crucial to the morphology change of TiO₂ nanowire.

Key Words : TiO₂, Nanowire, Morphology, Vapor-liquid-solid mechanism

Introduction

Titanium dioxide (TiO₂) nano-structures such as nanotubes,1 nanowires,2 nanowhiskers,3 nanorods,4 nanobelts,5 and nanofibers6 have been recently studied by many researchers because of its wide range of applications in gas sensors,7 photocatalysis,8,9 dye-sensitization for solar cells,10,11 and solar water splitting for hydrogen production.12-14 They could be synthesized to single crystalline TiO₂ with different crystal phase, such as anatase, brookite, and rutile. Among the three naturally crystalline TiO₂ phases, rutile TiO₂ usually forms relatively bulky structures with a poorly controlled morphology and low surface area because it is the most thermodynamically stable.

Over the past decade, one-dimensional (1D) nano-structured materials have emerged as promising materials for fundamental studies and possible technological application.15 These structures exhibit physical and chemical properties distinct from their bulk counterparts due to radial confinement, while they retain the advantages of wirelike connectivity. Among them, TiO₂ nanowire as 1D nano-structure particularly attracted much interest because of the unique properties depending on their size.16,17

TiO₂ nanowire is typically achieved using either of the two different synthetic methods developed over the past few years: one is ‘wet-chemistry’ method such as electrochemical,18 sol-gel electrophoresis,19 hydrothermal,20,21 and solvothermal method,22 and the other is ‘dry’ method including thermal evaporation23-25 and metal-organic chemical vapor deposition (MOCVD).26-28 But, the TiO₂ nanowires produced by above ‘wet-chemistry’ method have difficult integrating into device fabrication due to poor crystallinity. Also, they need to handle the additional processes in order to improve their crystallinity which were accompanied the complexity of the processes.

Here, we synthesized the single crystalline TiO₂ nano-structures with rutile phase using chemical vapor deposition (CVD) technique29,30 as ‘dry’ method. We also controlled the morphology of TiO₂ nano-structures, such as nanowire and nanobelt, by changing reaction conditions such as growth temperature and flow rate of carrier gas. It is important to control the morphology of TiO₂ nanowires31,32 because we can adjust their optical and electrical properties by changing the shapes of nano-structures.

Experimental Section

Materials. TiO₂ (~325 mesh, 99.9%) powder was purchased from Aldrich. Isopropyl alcohol was purchased from Duksan. SiO₂/Si wafers were purchased from University Wafer.

Preparation of Metal Covered Substrate as a Catalyst. Silicon (Si) wafers with 200 nm thick thermally grown SiO₂ (University Wafer) were coated with 50 nm thick Ti and then 2 nm thick Ni which are used as catalyst were covered on the Ti layer by thermal evaporation. They were cut into small pieces with the specific size of 5 mm (width) × 5 mm (length). These Ni/Ti/SiO₂/Si substrates were ultrasonically cleaned using isopropyl alcohol using an ultrasound cleaning bath equipped with two 100-W ultrasound generators operated at 28 kHz (Sachan Ultrasonic SH-2100).

Measurements. The scanning electron microscope (SEM) images of the TiO₂ nano-structures were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 to 20 kV, which was performed on the as-synthesized product on substrates. A platinum/palladium alloy (in the ratio of 8 to 2) was deposited with a thickness of about 15 nm on top of the samples. And their single crystalline structure was analyzed with a JEOL 2010 transmission electron microscope (TEM) with energy-dispersive X-ray (EDX) mapping capabilities. Samples for TEM imaging were made by depositing a hexane solution of nanowires (prepared by soni-
cation of as-synthesized substrate in hexane) onto holey carbon 300 mesh copper grids (Structure Probe, Inc.). The X-ray diffraction patterns for the identification of produced nanowires were obtained from a Rigaku diffractometer (D/MAX-1C) with the monochromatic beam of Cu Kα.

**Result and Discussion**

**Synthesis and Characterization of TiO$_2$ Nanowires.** We synthesized the high single crystalline TiO$_2$ nanowires using chemical vapor deposition (CVD) method, as shown in Figure 1(a). Titanium oxide (TiO) powder as a precursor for TiO$_2$ crystal growth was located at the center of the 8 cm quartz boat and then Ni/Ti/SiO$_2$/Si substrate was loaded next to the TiO powder in the quartz boat. Then, quartz boat was placed at the center of the heating zone in a tube furnace (Lindberg/Blue M, 12 in. length) equipped with a 1 in. diameter quartz tube. Before the experiment, the quartz tube was evacuated to below 0.1 torr and flushed several times with high purity Ar gas (99.999%) to minimize oxygen contamination. The furnace was then heated to the reaction temperature in 880 °C at 20 °C/min and was kept for 2 h. During synthetic process, Ar was flowing at 200 sccm and the pressure was maintained at atmospheric pressure (760 torr). The vapor-phase reactants transported by the Ar carrier gas condensed onto the substrate. After the reaction was finished, the quartz tube was cooled to the room temperature at 20 °C/min and then substrate was taken out. The substrate looks purple stains, indicating TiO$_2$ nanowires were synthesized on substrate.

The growth of TiO$_2$ nanowires is governed by two processes including i) Ti (g) + O$_2$ (g) $\rightarrow$ TiO$_2$ (s) and ii) TiO (g) + 0.5 O$_2$ (g) $\rightarrow$ TiO$_2$ (s). As a titanium source, Ti(g) and TiO(g) are generated from the Ti layer deposited on substrate and the loaded TiO powder, respectively. Although we made the quartz tube was evacuated and flushed several times to minimize oxygen contamination before the experiment, a small amount of oxygen still remains in quartz tube, which may come from the leakage of the reaction chamber and residual products in Ar carrier gas. This oxygen gas played an important role in the growth of TiO$_2$ nanowires.

As shown in Figure 1(b), various morphologies of single crystalline TiO$_2$ nano-structures are realized by controlling the growth temperature and flow rate of carrier gas. Reaching to growth temperature, Ni layer deposited on Ti/SiO$_2$/Si substrate turns into the nano-sized liquid droplets as a metal catalyst. We characterized the morphology of TiO$_2$ nanowires using a scanning electron microscope (SEM) and confirmed their crystallinity by a transmission electron microscope (TEM) study. Figure 2(a) shows the representative SEM image of TiO$_2$ nanowires grown on a Ni/Ti/SiO$_2$/Si substrate which were synthesized at 880 °C with 200 sccm Ar for 2 h. The diameter of produced TiO$_2$ nanowires usually range from 25 to 50 nm and their length is up to tens of micrometers.

The XRD peaks of TiO$_2$ nanowire exhibit the tetragonal structure of rutile TiO$_2$ [space group: P42/mnm (No. 136) with lattice constants a = 4.5933 Å and 2.9592 Å (PDF#00-021-1276)] (Figure 2(b)). In Figure 2(c), TEM image and selective area electron diffraction (SAED) pattern obtained from TiO$_2$ nanowire confirm that TiO$_2$ nanowire is single-crystalline. The high-resolution TEM (HRTEM) image taken from the area designated on TiO$_2$ nanowire also shows clear lattice fringes. Figure 2(d) shows the energy-dispersive X-ray (EDX) spectroscopy that confirms the 1:2 ratios of Ti and O atoms in the TiO$_2$ nanowire.

**Thickness Control by Changing Gas Flow Rate.** We
different Ar gas flow rate, as grown on a Ni/Ti/SiO$_2$/Si substrate. According to previous research, the growth of nanowires with long length (Figure 3(a)). At the 150 sccm of Ar gas flow rate, the density of produced TiO$_2$ nanowires depends on the size of the alloy tip, it is reasonable that thicker TiO$_2$ nanowires are obtained with high density as increasing the gas flow rate. With these results, we believe that high gas flow rate can accelerate the growth kinetics of TiO$_2$ nanowires.

Morphology Control by Changing Growth Temperature. We synthesized the TiO$_2$ nanowires at different growth temperature in order to investigate the change of morphology caused by increasing growth temperature. Figure 4 shows the SEM images of TiO$_2$ nanowires produced at different growth temperature with 200 sccm of Ar gas flow rate for 2 h; (a) 860 °C, (b) 880 °C, (c) 900 °C, and (d) 940 °C. At the low growth temperature, the density of produced TiO$_2$ nanowires looks low and their length and diameter are relatively short and thin (15-30 nm), respectively (Figure 4(a)). Upon shifting the growth temperature from 860 °C to 900 °C, the density of produced TiO$_2$ nanowires gradually increased from 15-30 to 35-50 nm, as shown in Figure 4(b). At the higher temperature, the density of produced TiO$_2$ nanowires was high and their length and diameter are relatively short and thin (15-30 nm), respectively (Figure 4(b)). Upon further increasing the temperature to 940 °C, the density of produced TiO$_2$ nanowires was even higher and their length and diameter were relatively short and thin (15-30 nm), respectively (Figure 4(c)).

By increasing Ar gas flow rate, TiO$_2$ thick nanowires were mainly obtained with high density. To investigate the change in the thickness of TiO$_2$ nanowires caused by different flow rate of Ar gas, it is essential to study their growth mechanism. According to previous research, the growth of TiO$_2$ nanowires was processed by vapor-liquid-solid (VLS) mechanism, including that the vapor-phase reactant carried by carrier gas dissolves in the liquid Ni catalysts and then TiO$_2$ nanowires are formed by crystal precipitation through the supersaturation of TiO$_2$ components in liquid Ni catalysts. The nanowire produced by VLS mechanism has an alloy tip which is formed while the precursor dissolves into the catalyst. Compared with low gas flow rate at constant pressure (Atmospheric pressure, 760 torr), high gas flow rate causes large amount of vapor-phase reactant to dissolve in Ni catalysts due to a relatively fast carrying speed even though the equal reaction time. As shown in left insets of Figure 3, the TiO$_2$ nanowires grown at the high gas flow rate have a bigger alloy tip than the TiO$_2$ nanowires grown at low gas flow. Based on the fact that the diameter of TiO$_2$ nanowires depends on the size of the alloy tip, it is reasonable that thicker TiO$_2$ nanowires are obtained with high density as increasing the gas flow rate. With these results, we believe that high gas flow rate can accelerate the growth kinetics of TiO$_2$ nanowires. 

The SEM images of TiO$_2$ nanostructures synthesized at different growth temperature, as grown on a Ni/Ti/SiO$_2$/Si substrate. Figure 4 shows the SEM images of TiO$_2$ nanostructures synthesized at (a) 860 °C, (b) 880 °C, (c) 900 °C, and (d) 940 °C. At the low growth temperature, the density of produced TiO$_2$ nanowires was low and their length and diameter are relatively short and thin (15-30 nm), respectively (Figure 4(a)). Upon shifting the growth temperature from 860 °C to 900 °C, the density of produced TiO$_2$ nanowires gradually increased from 15-30 to 35-50 nm, as shown in Figure 4(b). At the higher temperature, the nanowire density of TiO$_2$ nanowires was high and their length and diameter are relatively short and thin (15-30 nm), respectively (Figure 4(b)). 

By increasing growth temperature, we can synthesize not only the TiO$_2$ thick nanowires but also the TiO$_2$ nanobelts. In order to understand the morphology change influenced by growth temperature, we should consider the synthetic mechanism of TiO$_2$ nanowires. As above mentioned, it is known that the TiO$_2$ nanowires were synthesized by VLS mechanism.
mechanism. However, during the reaction, the high growth temperature at constant pressure (Atmospheric pressure; 760 torr) makes more vapor-phase reactant than low reaction temperature. Because of high temperature and large amounts of vapor-phase reactant around the substrate whose site take places the synthetic process for formation of TiO$_2$ nanowires, there occur not only VLS mechanism but also VS mechanism including that vapor-phase reactant directly grows at high gas flow rate are highly dense and thick, accelerating the high temperature and large amounts of vapor-phase reactant directly dissolves in formed solid nanostructure (i.e. TiO$_2$ nanowire) which was made by VLS mechanism. With this reason, VS mechanism can accelerate lateral growth of TiO$_2$ nanowires. As a result, TiO$_2$ nanobelts were synthesized at high growth temperature.

**Conclusion**

By changing reaction conditions such as gas flow rate and growth temperature, the various morphologies of high single crystalline rutile TiO$_2$ nanostructures such as thin-nanowires, thick-nanowires and nanobelts were synthesized. We also confirm the high single crystalline TiO$_2$ nanowires using SEM, XRD, TEM and EDX. The TiO$_2$ nanowires grown at high gas flow rate are highly dense and thick, because large amount of reactants can dissolve in the Ni catalysts with high carrying speed. With this result, the growth kinetics of TiO$_2$ nanowires is obtained. At high growth temperature, the TiO$_2$ nanobelts were usually obtained. Considering the high temperature and large amounts of vapor-phase reactant around the substrate, crystal growth was governed by VS mechanism as well as VLS mechanism, accelerating lateral growth TiO$_2$ nanowires. We believe that various morphologies of TiO$_2$ nano-structures should be useful for adjusting the properties of TiO$_2$ nanowires such as optical and electrical properties.

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**References**


