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Study of growth parameters on structural properties of TiO₂ nanowires

Abdollah MortezaAli¹ and Saeideh Ramezani Sani^{2*}

Abstract

In this article, the effect of growth parameters on structural properties of TiO₂ nanowires, synthesized by thermal evaporation process, have been studied. The nanostructures are characterized by scanning electron microscopy and X-ray spectroscopy. Our synthesized TiO₂ nanowires were found, through X-ray diffraction measurements, to be crystalline rutile TiO₂. We studied the effect of growth parameters such as the deposition temperature, the system pressure, and carrier gas flow on the growth and structure of our synthesized nanowires. It was found that their growth was governed by vapor–liquid–solid mechanism because of using Au catalyst. In this mechanism, the Ti layer deposited on the substrate diffused in to the solid Au catalyst; then, a liquid alloy of Au-Ti was formed to serve as preferred sites for the growth of TiO₂ nanowires.

Keywords: TiO₂ nanowires, Growth parameters, Growth mechanism, Thermal evaporation

Background

Semiconductor nanowires are a fundamental importance to the study of size- and dimensionality-dependent chemical and physical phenomena [1]. Semiconducting nanowires have received considerable attention due to their unique physical properties and on dimensional structure. Among these nanostructure materials, TiO₂ nanostructures have emerged as one of the most promising materials because of their potential for gas sensors [2], optical devices [3,4], photocatalysis [5-8], and solar cells [9]. There are some reports to synthesize TiO₂ nanowires by chemical methods [10-13], but to date, there have been a few results on synthesizing of TiO₂ nanowires by thermal evaporation [14-19].

Understanding the growth mechanism is critical in controlling and designing nanostructures. Change of the morphology of nanostructure is a direct consequence of changing synthesis condition which gives them some new optical and electrical properties. Therefore, the technological importance of one-dimensional (1-D) nanostructure and the lack of information on their morphology underline the need for developing growth parameter studying. In the study of Wu et al. [16] in

2005, the influence of reaction on the temperature of synthesis at 850°C elucidated. They also considered the effect of the temperature of synthesis on the reaction time of 1 h on the structure of TiO₂ nanowires [18]. In 2006, Lee et al. [20] studied the controlled growth of TiO₂ nanowires on sapphire and silica by thermal evaporation. Amin et al. [21] in 2007 studied the growth of nanowires under different conditions of substrate, catalytic material, and chemical composition of Ti_xO_y precursor.

In this article, we report structural properties of TiO₂ nanowires, which have been synthesized by thermal evaporation. To explain the effect of growth parameters on the structure of nanowires, we studied the effect of several parameters such as deposition temperature, system pressure, and carrier gas flow on growth and structure of our synthesized nanowires. It was found that nanowires were in the crystalline rutile phase, and their growth was governed by vapor–liquid–solid (VLS) mechanism.

Results and discussion

The effect of deposition temperature

To investigate the effect of deposition temperature, similar substrates were placed at different distances from the source material downstream in a tube furnace, which resulted in different synthesis temperature due to the

* Correspondence: s_ramezanisani@yahoo.com

²Department of Mechanic, Islamic Azad University, Roudehen Branch, Roudehen, Iran

Full list of author information is available at the end of the article

natural temperature gradient along the furnace. The temperature of synthesis was varied among 750°C, 850°C, and 950°C for 1 h. The scanning electron microscopy (SEM) images of TiO₂ nanowires at different deposition temperatures have been represented in Figure 1. Figure 1a shows that no nanowire was obtained when the temperature was controlled at 750°C. Figure 1b (the deposition temperature is 850°C) shows the nanowires with the diameter of

around 60 to 120 nm and length of about 500 to 2,000 nm. As the deposition temperature increases to 950°C, the nanowires become shorter and thicker with length of about 250 to 1,000 nm and diameters of 68 to 150 nm. It can be understood in the light of the fact that in the temperature of more than 850°C, the vapor of a material is very energetic and leads to a short length. It was found that a convenient temperature for controlling the diameter size of nanowires is about 850°C. Synthesis conditions and morphology characteristics of TiO₂ nanowires are listed in Table 1.

The effect of system pressure

To study the influence of system pressure on the crystal structure of nanowire, experiments were performed at different system pressures that were changed from 1,000 to 10 mbar by a rotary pump, while other parameters were maintained unchanged (Table 2). Figure 2 shows SEM images of TiO₂ nanowires at different system pressures. Figure 2a shows the nanowires with a diameter of around 60 to 120 nm. As the system pressure decreases, the nanowires become thinner so that in the system pressure of 60 mbar, the diameter of the nanowires is 60 to 100 nm (Figure 2b), and in the system pressure of 30 mbar, the diameter of nanowires decreases to 40 to 100 nm (Figure 2c). The advantage of using low pressure in the fabrication of 1-D nanostructures can be understood from the fact that lowering the system pressure increases the mean free path, and as a result, the gas phase transfer to deposition surface is facilitated. Also, a low pressure system is beneficial to establish the desired degree of supersaturation for 1-D nanostructure. Figure 2d shows the growth of nanowires at the system pressure of 10 mbar. The image shows that nanowires have irregular morphology. One possibility is that a loss in the absorption of oxygen on the surface causes a decrease in the growth of nanowires. It is noted that the thermal evaporation process is very sensitive to the concentration of oxygen in the growth system [22]. To achieve the high-yield growth of TiO₂ nanowires, a low concentration of O₂ is necessary. In our experiments, the low-concentration of O₂ is likely to come from the system leakage and the adsorption on surface. However, in the system pressure of 10 mbar, there is no enough leakage of air into the reaction system, and as a result, no enough O₂ is absorbed in the surface.

The effect of carrier gas flow

To understand the role of carrier gas flow on structure nanowires, new experiments involving deliberate introduction of Ar into the system were performed.

Figure 1 SEM images of as-synthesized TiO₂ nanowires at different deposition temperatures. (a) Deposition temperature of 750°C where no nanowires was obtained. (b) Deposition temperature of 850°C and (c) 950°C. Scale bar is 1 µm; with the increase of the deposition temperature from 850°C to 950°C, the nanowires become shorter and thicker.

Table 1 Synthesis conditions and morphology characteristics of TiO₂ nanowires at different deposition temperature

Furnace center temperature (°C)	Carrier gas flow (sccm)	System pressure (mbar)	Deposition temperature (°C)	Reaction time (h)	Nanowire diameter (nm)	Nanowires length (nm)
1,050	–	1,000	750	1	–	–
1,050	–	1,000	850	1	60 to 120	500 to 2,000
1,050	–	1,000	950	1	68 to 150	250 to 1,000

Using the unchanged experimental parameters (furnace center temperature, reaction time, system pressure), the gas flow was varied from 50 to 150 sccm. Synthesis conditions of TiO₂ nanowires are listed in Table 3. The SEM images of the TiO₂ nanowires at different carrier gas flows have been represented in Figure 3. It was found that the yield of TiO₂ nanowires increases with the increase of gas flow. Figure 3a (gas flow is 50 sccm) shows the nanowires with a diameter of around 70 to 150 nm and length of about 400 to 1,000 nm. With the increase of the the carrier gas flow to 100 sccm, the nanowires become thinner and longer with a length of about 400 to 1,800 nm and diameter of 40 to 100 nm (Figure 3b). This is understandable from the fact that O₂ plays a key role in the growth of the TiO₂ nanowires. The increase of the concentration of oxygen causes a decrease of the growth of the nanowires. When oxygen concentration is high, in the VLS growth, Ti vapor reacts with oxygen before the formation of droplets of the alloy and prevents the creation of nanowires. Thus, low concentration of oxygen, which causes the increase of the growth of the nanowires, is necessary [19]. The increase of the gas flow from 50 to 100 makes a low-oxygen environment; therefore, more nanowires are produced. Figure 3c shows the growth of nanowires at a gas flow of 150 sccm; in this case, nanowires become shorter, thicker, and denser. The image shows that nanowires are rod-like and have irregular morphology. It was found that a convenient gas flow for controlling the diameter size of the nanowires is about 100 sccm [19].

Crystalline structure of the TiO₂ nanowires

To study the information regarding the crystallinity of the TiO₂ nanowires, X-ray diffraction (XRD) experi-

ments were performed. All of the samples indicated that the TiO₂ nanowires are mainly composed in rutile phase. A typical XRD pattern of the sample is shown in Figure 4. It can be seen that TiO₂ nanowires are in rutile phase (JCPDS: 73–1765) with a dominate reflectance of the (101) plan. The unite cell constants of TiO₂ nanowires are $a = b = 4.58 \text{ \AA}$, and $c = 2.96 \text{ \AA}$, which matched the published value in the JCPDS database (# 73–1765, $a = 4.52 \text{ \AA}$, $c = 2.98 \text{ \AA}$). The Au diffraction peaks (JCPDS: 04–0784) were caused by the diffraction from the catalyst.

Growth mechanism

Understanding the growth mechanism is critical in controlling and designing nanostructures. One possible mechanism is the vapor-solid (VS) growth that TiO₂ nanowires form with no catalytic particles on their tips. In addition to the VS growth, the VLS growth mechanism might also protect the TiO₂ nanowires. According to the VLS growth mechanism, crystal growth was guided by a droplet of liquid alloy. VLS growth is also called catalyst growth. Since Au was used as a catalyst, the growth of the nanowires was mainly dominated by the VLS mechanism. The Ti buffer layer was partially oxidized into a TiO₂ layer by the O₂ gas of atmosphere at an elevated temperature. The Ti layer deposited on the silicon substrate was diffused into the solid Au catalyst; then, a liquid alloy of Au-Ti was formed. The interfacial region between the TiO₂ layer and the liquid Au catalyst formed by the buffer layer-assisted VLS mechanism was in a high-energy state; hence, it provided an active nucleation site for the TiO₂ nanowires. The Ti buffer was introduced onto the surface of the Si substrate to prevent any undesirable diffusion reaction between the Ti vapor source and the Si substrate and also to provide a good nucleation

Table 2 Synthesis conditions and morphology characteristics of TiO₂ nanowires at different system pressures

Furnace center temperature (°C)	Carrier gas flow (sccm)	System pressure (mbar)	Deposition temperature (°C)	Reaction time (h)	Nanowire diameter (nm)	Nanowire length (nm)
1,050	–	1,000	850	1	60 to 120	500 to 2,000
1,050	–	60	850	1	60 to 100	300 to 1,100
1,050	–	30	850	1	40 to 100	300 to 2,500
1,050	–	10	850	1	irregular morphology	irregular morphology

Figure 2 SEM images of as-synthesized TiO₂ nanowires at different system pressures. System pressures of (a) 1,000, (b) 60, (c) 30, and (d) 10 mbar. Scale bar is 1. As the system pressure decreases, the nanowires become thinner.

site for the growth of the nanowires [19]. A typical SEM image and EDX of the TiO₂ nanowires are presented in Figure 5. Results show the nanowires with catalytic material on its tips (the Si signal comes from the substrate).

Conclusions

TiO₂ nanowires were grown by thermal evaporation on a silicon substrate coated with a catalytic Au-coated Ti layer. The effect of several parameters such as deposition temperature, system pressure, and carrier gas flow on growth and structural properties was investigated. It was found that a convenient temperature and gas flow for controlling the diameter size of nanowires are about 850°C and 100 sccm, respectively. The nanowires analyzed with XRD were found to be in rutile phase. The growth of the nanowires was dominantly governed by the VLS mechanism because of using Au as a catalyst.

Methods

TiO₂ nanowires were prepared using a thermal evaporation method similar to that described in our previous studies [19]. In general, the process of synthesis thermal evaporation technique is conducted in a tube furnace, where the source material is at a high-temperature zone and the substrate is in the low-temperature zone. Also, it consists of a rotary pump system and a gas supply. In a typical preparation procedure, a Ti buffer layer with thickness of 50 nm was deposited on the silicon substrate. Then, a gold thin film was deposited as a catalyst on the Ti layer. Then, the TiO₂ nanowires were grown by thermal evaporation in the low-temperature zone of a horizontal quartz furnace. There are several parameters such as deposition temperature, system pressure, carrier gas flow, and reaction temperature that can change the morphology of products. In this study, to explore the growth mechanism of TiO₂ nanowires, a series of experiments were carried out and investigated the effect

Table 3 Synthesis conditions and morphology characteristics of TiO₂ nanowires at different carrier gas flows

Furnace center temperature (°C)	Carrier gas flow (sccm)	System pressure (mbar)	Deposition temperature (°C)	Reaction time (h)	Nanowire diameter (nm)	Nanowire length (nm)
1,050	50	1,000	850	1	70 to 105	400 to 1,000
1,050	100	1,000	850	1	40 to 100	400 to 1,800
1,050	150	1,000	850	1	irregular morphology	irregular morphology

Figure 3 SEM images of as-synthesized TiO₂ nanowires at different carrier gas flows. Gas flow at (a) 50, (b) 100, and (c) 150 sccm. Scale bar is 2 μ m. It was found that the yield of TiO₂ nanowires increase with the increase of gas flow.

of deposition temperature, system pressure, and carrier gas flow on the structural properties of TiO₂ nanowires.

The structure and morphology of the samples were respectively analyzed by XRD (JEOL JDX-8030, Akishima-shi, Japan) and SEM (XL130, Philips, Amsterdam, The Netherlands).

Figure 4 A typical XRD pattern of TiO₂ nanowires. It can be seen that TiO₂ nanowires are in rutile phase with a dominate reflectance of the (101) plan.

Figure 5 A SEM image of TiO₂ nanowires. With an EDX spectrum that displays the existence of Au catalysis on its tip.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

SR carried out the thermal evaporation studies, synthesized TiO₂ nanowires, and wrote the manuscript for publication. AM participated in the idea and the design of the study. Both authors read and approved the final manuscript.

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Author details

¹Laboratory of Surface Physics, Department of Physics, Alzahra University, Tehran 19938, Iran. ²Department of Mechanic, Islamic Azad University, Roudehen Branch, Roudehen, Iran.

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