Synthesis of Single-Crystal TiO\(_2\) Nanowire Using Titanium Monoxide Powder by Thermal Evaporation

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TiO\(_2\) nanowires were synthesized successfully in a large quantity by thermal evaporation using titanium monoxide powder as precursor. X-ray diffraction results showed that all the products were pure rutile phase of TiO\(_2\). According to microstructural observations, the nanowires have two typical morphologies, a long straight type and a short tortuous type. The straight nanowires were obtained at a wide temperature range of 900–1050 °C, while the tortuous ones were formed below 900 °C. Transmission electron microscopy characterization revealed that both the straight and the tortuous nanowires are single-crystal rutile TiO\(_2\). The preferential growth direction of the nanowires was determined as [110] orientation according to electron diffraction and high-resolution image analyses. The morphological change of TiO\(_2\) nanowires was discussed by considering the different atomic diffusion rates of Ti atoms caused by the phase transformation in Ti substrate at around 900 °C.

KEY WORDS: Rutile-TiO\(_2\); Alloy nanowires; Transmission electron microscopy (TEM) characterization; Crystal structure identification; Growth mechanism; Thermal evaporation

1. Introduction

With the development of global economy, environment pollution and energy shortage have become two challenging issues confronted by humans at present and in future. Since the discovery of water splitting at TiO\(_2\) anodes\(^\text{[1]}\) in 1972, TiO\(_2\) nanomaterials have been extensively studied in order to obtain hydrogen energy at low cost. Until now, various forms of TiO\(_2\) materials, including particles, nanowires/rods and films, have been successfully synthesized by chemical or physical methods. Correspondingly, applications of these TiO\(_2\) nanomaterials have been extended widely ranging from photo-catalysis\(^\text{[1]–10]}\) and photo-voltaic\(^\text{[11,12]}\) to microelectronics\(^\text{[13,14]}\) and sensors\(^\text{[15,16]}\). Among the above mentioned various forms of TiO\(_2\) materials, single crystal nanowires have gained great attention for their large aspect ratio and surface areas. In order to obtain nanowires, it is necessary to confine the growth in one direction which can be realized by physical confinement (such as template) or chemical adsorption confinement. Up to now, TiO\(_2\) nanowires have been successfully produced by template-directed method\(^\text{[17]}\), anodization\(^\text{[18,19]}\), as well as hydrothermal techniques\(^\text{[20,21]}\). However, most of these wet chemical methods may introduce contamination during the synthesis process and are difficult to integrate with modern silicon based semiconductor industry. Although a few literature\(^\text{[22,23]}\) has reported the synthesis of TiO\(_2\) nanowires by catalyst-assisted vapor phase fabrication based on vapor-liquid-solid (VLS)\(^\text{[24]}\) or vapor-solid-solid (VSS)\(^\text{[25]}\) mechanisms, in which a Ni or Au thin layer was used as catalyst, it is still a challenging work to find reliable conditions under which single-crystal nanowires are synthesized efficiently.

In this work, a large quantity of TiO\(_2\) nanowires were synthesized by thermal evaporation using titanium monoxide powder as precursor. Two kinds
of morphology were observed by varying the growth temperatures in a range of 850–1050 °C, which was characterized in detail and discussed according to the phase transformation in the Ti substrate.

2. Experimental

Single-crystalline TiO$_2$ nanowires were grown by atmospheric-pressure thermal evaporation in an alumina tube furnace at different growth temperatures. Commercially pure Ti (TA1: Ti 99.5%; Fe 0.2%; O 0.15%; H 0.12%; C 0.05%; N 0.03% in weight percent) plate was used as the substrates. Samples were firstly cut from Ti plate using electric sparkle, and then mechanically polished using SiC sand paper (2000#). After that the samples were ultrasonicated for 10 min in acetone, methanol and deionized water in sequence. Then residual water droplets on sample surface were blown away and then dried out in drying oven at 70 °C for 8 h. Next the samples were coated with a thin Au layer (about 20 nm thick) deposited with a Cressington 208HR. Fine meshed TiO powder (0.2 g, 99.99% purity, maintop.com.cn, Beijing) was loaded at the center of a 5 cm long quartz boat. The Au/Ti substrate sample was placed in the quartz boat about 2 mm away downstream from TiO powder. The quartz boat was placed in an alumina tube furnace, heated at a rising rate of 6 °C/min to the synthesis temperature, then kept at that temperature for 1 h, and finally air-cooled to room temperature. High purity Ar carrier gas (99.999%) was introduced into the alumina tube with a flow rate of about 100 SCCM (SCCM denotes cubic centimeter per minute at standard temperature and pressure conditions (STP)) for 1 h before the heating program was initiated, and lasted the whole heating process until the furnace temperature cooled down to room temperature.

X-ray diffraction (XRD) was carried out using a D/Max 2400 diffractometer working at 0.15418 nm to determine the phase of the products. The microstructures and morphologies of the obtained nanowires were investigated by scanning electron microscopy (SEM, Zeiss Supra 35) and transmission electron microscopy (TEM, JEOL 2100) equipped with an Oxford Link ISIS energy dispersive X-ray spectroscopy (EDS) system.

3. Results

The XRD spectrum of the initial Ti substrate coated with Au layer is shown in Fig. 1(a), which corresponds to α-Ti (PDF card 65-3362) with a space group of P6$_3$/mmc. As the coated Au layer was very thin (about 20 nm), no peaks of Au was found in the XRD spectrum. Fig. 1(b) and (c) are the XRD results of the synthesized products grown at 850 and 1050 °C, respectively. The main products grown at 850 and 1050 °C are both rutile TiO$_2$, as indexed on the peaks with rutile crystal structure. Besides those peaks from rutile TiO$_2$, additional weak peaks (denoted by "↗") in Fig. 1(b) come from the TiO intermediate layer between Ti substrate and rutile TiO$_2$ nanowires, which is the normal oxide phase formed on the surface of the metal Ti substrate. For comparison, the standard XRD data of rutile phase TiO$_2$ (PDF card 65-0692) is also shown in Fig. 1(d).

Morphologies of the products were firstly investigated by SEM. Fig. 2(a)–(c) are low magnification SEM images of the samples grown at 1050, 900 and 850 °C, respectively. It was observed that nanowires were successfully fabricated in the whole experimental temperature range from 850 to 1050 °C. In Fig. 2(b) and (c), most nanowires are ended with an Au particle at the top, which implies a typical Au-catalyzed VLS$^{[24]}$ or VSS$^{[25]}$ growth mechanism of the nanowire. However, in Fig. 2(a) less Au particles are observed, it is believed that most of them are exhausted during nanowire growth at a temperature as high as 1050 °C. The growth temperature has an important effect on the morphology of the obtained nanowires. Firstly, the length of nanowires decreases evidently with decreasing growth temperature. As shown in Fig. 2(a)–(c), the length of nanowires at different growth temperature is approximately 20 µm at 1050 °C, 1 µm at 900 °C, and several hundred of nanometers at 850 °C. On the contrary, diameters of the nanowires grown at different temperatures have not changed much. Most nanowires have diameters in the range of 50–200 nm, which are mainly determined by the size of Au particles$^{[24]}$. Secondly, the shape of nanowires changes evidently in the lower growth temperature range of 850–900 °C. At 900 °C or higher temperatures most nanowires are straight, while they become curving at 850 °C. The corresponding high magnification SEM images are shown in Fig. 2(a’)(e’), respectively. Obviously, both of straight and tortuous nanowires are grown from the corner of rutile TiO$_2$ pyramidal grains.

The detailed microstructure of TiO$_2$ nanowires was further investigated by TEM. Fig. 3(a) is a bright
field (BF) image of a typical nanowire obtained at 1050 °C, the inset is the corresponding selected-area electron diffraction (SAED) pattern. This SAED pattern is a single-crystal pattern of rutile TiO$_2$ in [001] zone axis, which is consistent with the XRD results in Fig. 1(c). The black particle at the top of the TiO$_2$ nanowire is identified as Au catalyst according to EDS analysis, which was survived after 1 h growth at 1050 °C. Combining the BF image and SAED pattern, the growth direction of the nanowires obtained at 1050 °C is determined to be [110] direction, which is also verified by the corresponding high-resolution TEM image (HRTEM) as shown in Fig. 3(b). Fig. 3(c) is a BF image of two curving nanowires obtained at 850 °C, which have a tortuous morphology. One corresponding HRTEM image is shown in Fig. 3(d), in which the interplanar spacing of 0.32 nm corresponds to the (110) plane of rutile TiO$_2$. Again, the tortuous nanowire is also single-crystal rutile TiO$_2$ and grows along [110] direction.

4. Discussion

It was observed that the growth temperature has a significant effect on the morphology of TiO$_2$ nanowires. Long and straight nanowires were synthesized at a temperature above 900 °C, while short tortuous ones were obtained below 900 °C. This morphological difference could be understood by considering the following two factors which affect the growth of nanowires. The first factor is the origin of Ti for the nanowire growth. The principal gaseous species over TiO(s) precursor powders are Ti(g) and TiO(g), although small amount of TiO$_2$, O and O$_2$ also exist$^{[26]}$. However, the vapor pressure of TiO powder is extremely low. At 1806 K (1533 °C), the calculated values are $P$(Ti)=$(7.68\pm1.08)\times10^{-3}$ Pa and $P$(TiO)=$(2.21\pm1.25)\times10^{-3}$ Pa$^{[26]}$. It implies that the supply of Ti atoms from vapor TiO and Ti is not sufficient enough for the growth of TiO$_2$ nanowire. In pure metal Ti, at 1000 °C $D_{Ti}\approx10^{-13}$ m$^2$/s, $D_o\approx10^{-10.3}$ m$^2$/s; while at 900 °C $D_{Ti}\approx10^{-13.3}$ m$^2$/s, $D_o\approx10^{-11}$ m$^2$/s; and at 850 °C $D_{Ti}\approx10^{-17}$ m$^2$/s, $D_o\approx10^{-13.2}$ m$^2$/s, where $D_{Ti}$ and $D_o$ represent atomic diffusion coefficient of Ti and O in Ti substrate$^{[27]}$. In this study, nanowires were synthesized within pure Ar atmosphere. The oxygen species in Ti substrate and residual oxygen in tube furnace may contribute to the growth of TiO$_2$.
nanowires, while Ti atoms come from TiO vapor or Ti substrate. Therefore, despite of the vapor TiO and Ti, the supply of solid Ti atoms from the metal Ti substrate is critical for the growth of TiO$_2$ nanowires.

The second factor is related to the atomic diffusion from Ti substrate, which contributes to the growth of nanowire directly. Ti can easily react with oxygen to form a TiO$_2$ film due to its good affinity to oxygen. Titanium oxidation in pure oxygen and air has been widely studied and atomic diffusion processes involved in oxidation of Ti have been discussed in detail. Badescu and Momirlan$^{[28]}$ reported that there is a predominant diffusion of oxygen through the grain boundaries of the oxide layer, and the oxidation site is the metal-oxide interface at a temperature range of 800 to 1000 °C; while at the temperatures above 1000 °C, a considerable increase of the Ti cations diffusion through the oxide layer is observed. On the other hand, Czerwinski and Szpunar$^{[29]}$ studied the surface tomography with XRD and showed that TiO$_2$ growth at 900 °C was controlled by the surface diffusion of Ti cations to the ledges located on the sidewalls of pyramidal grains. For the growth of TiO$_2$ nanowires in this study, the dominate reaction happens at the interface between the Au particle and TiO$_2$ layer below it. This is common in a typical metal-catalyzed growth process based on VLS$^{[24]}$ or VSS$^{[25]}$ mechanism. As the diffusion of Ti atom from the substrate to the nanowire growth, its diffusion rate will definitely influence the growth rate of nanowire.

As well known, the pure Ti metal has a $\alpha \rightarrow \beta$ phase transformation point at 882 °C$^{[27]}$. This transformation point becomes a little higher when oxygen concentration in Ti is high (0.18 wt%)$^{[27]}$. At 900 °C or higher temperatures, the Ti substrate contains $\beta$ phase which has a bcc structure with $a$=0.332 nm, while at 850 °C the Ti substrate remains $\alpha$ phase with an hcp structure ($a$=0.295 nm, $c$=0.468 nm). Because atoms stack more closely in $\alpha$ phase than in $\beta$ phase, atoms in $\beta$ phase diffuse much more easily than those in $\alpha$ phase$^{[27]}$. The self-diffusion of Ti in the $\beta$ phase is about three orders of magnitude faster than that in $\alpha$ phase. Thus at 900 °C or higher temperatures, O and Ti atoms in Ti substrate can diffuse quickly in $\beta$-Ti to the surface and supply adequate atoms for nanowire growth, which leads to the formation of long and straight nanowires. However, at 850 °C atoms diffuse much more slowly in $\alpha$ phase which cannot supply adequate O and Ti atoms for the nanowire growth, thus short and tortuous nanowires formed.

In order to affirm this assumption, further detailed experiments were carried out at 870, 880, 890 and 900 °C using TiO source powders, and the corresponding SEM images are shown in Fig. 4(a)–(d). At 870 °C a large amount of nanowires are obtained, but the shape of these nanowires are tortuous. At 880 °C the shape of nanowires remains curving, but at 890 °C nanowires are rarely formed. However, at 900 °C a large amount of nanowires appear again, and their shape becomes straight. The great change in the shape of nanowires should be due to the different diffusion rate of Ti atoms caused by $\alpha \rightarrow \beta$ phase

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**Fig. 3** Bright field (left) and high-resolution (right) TEM images of the straight nanowire obtained at 1050 °C (a) and (b), and the tortuous nanowire obtained at 850 °C (c) and (d). They are both single-crystal rutile TiO$_2$ grown along [110] direction.
transformation in Ti substrate, as the change of Ti or TiO vapor pressure can be neglected for only 10 °C intervals in growth temperature.

It is necessary to point out that at the temperature above 900 °C, a small percent of nanowires were observed having a curving top end on a straight trunk, which is different from those entirely tortuous nanowires grown below 900 °C. The formation of the curving end on the top of straight nanowires should also be related to the insufficient diffuse of Ti atoms at the late growth stage. After a fast growth of the straight trunk, Ti atoms from the metal Ti substrate are difficult to diffuse such a long way (the straight trunk of grown nanowire) to arrive at interface between Au particle and TiO₂ nanowire at the top end. In such a case, the catalytic effects of Au particles were weakened and straight growth of TiO₂ nanowires was slowed down. Hence a tortuous top part was formed due to the insufficient supply of Ti atoms from the substrate. Further investigations on these top curving nanowires will be carried out in future works.

5. Conclusion

A large quantity of rutile TiO₂ nanowires were fabricated in a wide temperature range from 850 to 1050 °C by thermal evaporation, using bulk Ti coated with a thin Au layer as substrate and TiO powders as precursors. The obtained TiO₂ nanowires are single crystals grown along [110] direction with diameters in a range of 50–200 nm. The growth temperature had an effect on the morphology of TiO₂ nanowire products. At 900 °C or higher temperatures long and straight nanowires were fabricated, while below 900 °C short and tortuous nanowires were obtained. The morphological difference was considered being related to the different atomic diffusion rates caused by α → β phase transformation in Ti substrate at around 900 °C. It was believed that the β-Ti substrate at high temperature enabled fast atomic diffusion for the growth of long and straight nanowires.

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