Observation of defect state in highly ordered titanium dioxide nanotube arrays

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2014 Nanotechnology 25 275603
(http://iopscience.iop.org/0957-4484/25/27/275603)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 141.24.47.169
This content was downloaded on 13/07/2014 at 12:01

Please note that terms and conditions apply.
Observation of defect state in highly ordered titanium dioxide nanotube arrays

Hongchao Zhang\textsuperscript{1,3}, Min Zhou\textsuperscript{2,3}, Qun Fu\textsuperscript{1}, Bo Lei\textsuperscript{1}, Wei Lin\textsuperscript{1}, Heshuai Guo\textsuperscript{1}, Minghong Wu\textsuperscript{1} and Yong Lei\textsuperscript{1,2,3}

\textsuperscript{1} School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, People’s Republic of China
\textsuperscript{2} Institute for Physics and IMN MacroNano\textsuperscript{®}, Technical University of Ilmenau, Ilmenau 98693, Germany

E-mail: yong.lei@tu-ilmenau.de

Received 9 March 2014, revised 17 April 2014
Accepted for publication 12 May 2014
Published 24 June 2014

Abstract

For the first time, a conductive-substrate induced electro-deposition approach is employed to achieve highly ordered TiO\textsubscript{2} nanotube arrays based on an anodic aluminum oxide template. Different from other methods, the morphology and parameters of arrays can be adjusted easily through changing the exposure area of a conductive layer. All these arrays are used as matrices to explore the defect state emission by photoluminescence (PL) spectra. Interestingly, we find that the emission from blue edge to red edge (\(~450\text{ nm} – 600\text{ nm}\)) are apparently quenched in the ordered nanotube arrays, especially when compared to the PL spectra of nanowire arrays, single nanotube and nanoparticles. This distinct result originates from passivation of oxygen vacancies residing along the tube walls when the tubes are interconnected, which is further evidenced by the observation of PL spectra with crystalline phase and sintering. The passivation of defects suggests valuable charge transport perpendicular to the long axis of the tubes in the ordered arrays. This point is particularly significant to the design of highly efficient devices and the applications in various energy-related fields.

Keywords: nanotube array, defect state, photoluminescence

(Some figures may appear in colour only in the online journal)

1. Introduction

Titanium dioxide (TiO\textsubscript{2}), also known as titanium (IV) oxide or titania, is the naturally existing oxide of titanium. With its commercial production appearing in the early 20th century, this material has drawn extensive attention due to its wide applications ranging from energy to environmental fields [1–4]. Recently, enormous efforts have been devoted to the studies of TiO\textsubscript{2} nanomaterials, which has led to many promising applications in areas of photovoltaics, photo-/photoelectro-catalysis, photo-/electro-chronics, sensors, electronic data storage medium, battery, etc. Aiming at pursuing high conversion efficiency in all these areas, a deep understanding of defect states in both bulk and surface is primarily important [5–8], because the characteristic electronic and geometrical structure associated with defect states endow TiO\textsubscript{2} with unique macroscopic properties [9, 10]. For example, oxygen vacancies are able to induce room temperature ferromagnetism of TiO\textsubscript{2} [11]. Intra-band-gap states originating from defects lead to charge recombination and the transport properties related to phonons in TiO\textsubscript{2}-based dye-sensitized solar cells and photo-/photoelectrochemical-catalytic cells [12–14]. Excess electrons located on the oxygen vacancy states would affect surface absorption and reactivity of key adsorbates, such as O\textsubscript{2} or H\textsubscript{2}O on TiO\textsubscript{2} [15, 16]. Therefore, there is a great significance in deeply understanding defect states and exploiting the dependence of the properties of TiO\textsubscript{2} on the defect states.

Among the unique properties of TiO\textsubscript{2}, the movement of charge carries is primarily important for many applications.
Theoretical and experimental results indicate a strong relationship between the defect states and charge transport of TiO₂ [13, 18, 19]. With regard to conventional TiO₂ nanoparticles, inefficient interparticle electron transfer has been known as an obstacle for charge collection [6, 20]. It is expected that one-dimensional (1D) ordered structure, especially nanotube arrays with high surface-to-volume ratio, would result in fast charge transport [21]. However, previous studies show that charge transport in nanotube-array-based devices is not obviously faster than common nanoparticle-based devices [22]. In general, different distributions of trap states can accelerate the charge transport in TiO₂ nanotubes than in TiO₂ nanoparticles, while excitonic states decelerate the charge transport in TiO₂ nanotubes [21–23]. It has been implied that charge transport in nano-TiO₂ occurs by diffusion mediated by shallow traps, but meanwhile, deep traps lead to unfavorable recombination [24–26]. Trapping and detrapping states may be attributed to lower mobility in nano-TiO₂ than the bulk material, and thus it is of great interest to understand how defect states of conventional TiO₂ nanotubes may differ from those of TiO₂ nanoparticles and bulk materials.

In previous work, our group has employed photoluminescence (PL) spectroscopy to illuminate the defect states of TiO₂ nanowires and anodic aluminum oxide (AAO) templates [27, 28]. We presented a growth model of TiO₂ nanowires in an AAO template by sol-gel approach to clearly explain why the nanowires grew from center to the walls of pores. This approach was not suitable for uniform nanotube arrays in a large scale. Inspired by these studies, a novel conductive-substrate induced electro-deposition approach is rationally designed to obtain controllable TiO₂ nanotube arrays. Considering that materials can only be deposited on conductive substrate within an electric-field-assisted hydrolysis approach, which is quite different from the electrolyte electrolysis in conventional electro-deposition, there are two growth directions within the AAO template as shown in scheme 1. One is along the conductive substrate, the other one is vertical to the conductive substrate. If the spurring time of substrate metal (e.g. Cu) can be adjusted randomly, the exposed area of conductive substrate would be changed correspondingly, along with the horizontal growth rate. Suitable thickness of Cu contributes to proper horizontal growth, leading to nanotube array. Exposure of too little conductive substrate results in few growth trends, so we cannot get any 1D nanostructures. Meanwhile, long spurring time of Cu results in continuous conductive layer, and thus nanowire arrays can be finally obtained rather than nanotube arrays. This approach is obviously different from other widely used methods for 1D nanostructures, such as sol-gel, hydrothermal, and atomic layer deposition, where the materials fully cover and depend more on the template. It is expected that a facile preparation of pore-through nanotube arrays can be realized without any complex processes and expensive equipment, serving as a matrix with clean surface for the full studies of basic physical/chemical theory and practical application.

Herein, a conductive-substrate induced electro-deposition approach is first employed to achieve highly ordered nanotube arrays based on AAO template. Different from other methods, we can easily achieve 1D nanotube arrays through adjusting the exposure area of the conductive layer. All these arrays serve as matrixes to explore the dependence of defect states.

**Scheme 1.** The schematic diagram of growth mechanism demonstration of TiO₂ nanotube arrays. (a) deposition of Cu on the back side of the template through physical vapor deposition; (b) electro-deposition; (c) removing the template.
state emission on crystalline phase and sintering by PL spectra, which can provide significant information for intrinsic carrier transport and further expanding the applications of TiO$_2$ nanotube arrays in energy and environmental fields.

2. Experimental details

2.1. Fabrication of AAO template

The template is prepared by a two-step electro-chemical anodization process of aluminum foil [29–31]. Before oxidation, the aluminum foils are rinsed in acetone and water to remove the adsorbed contamination and electro-polished in perchloric acid (in ethanol with volume ratio of 1:9) under 18 V. Then the alumina foil is oxidized twice under 55 V in 0.3 mol L$^{-1}$ oxalic acid solution for 12 h and 6 h, respectively. The alumina originating from the first oxidation is removed to form patterned reliefs to induce the second oxidation. After oxidation, a template with 90–100 nm pore diameter and 135 nm interpore distance can be obtained. The pore-widening process is conducted in 5 wt% phosphoric acid at 32 °C to remove the back barrier layer and enlarge the diameters of nanopores.

2.2. Deposition of metal electrode

Before the electrodeposition, we sputter 40 nm Cu film on the back of the AAO template as an electrode by vacuum thermal evaporation using physical vapor deposition. During the thermal evaporation, the vacuum degree in the vacuum chamber is 8 × 10$^{-4}$ Pa, and the evaporation rate of 0.3 ~ 0.5 nm s$^{-1}$. The thickness of Cu can be changed by the deposition time.

2.3. Electrochemical deposition

The electro-deposition is conducted in the constant voltage mode with a three-electrode system of potentiostatic system (PGSTAT302N), containing an AAO working electrode, Ag/AgCl reference electrode and a platinum foil counter electrode. The electrolyte consists 0.05 g L$^{-1}$ TiF$_4$ and 0.05 g L$^{-1}$ NiCl$_2$·6H$_2$O, where the pH value is adjusted to 1.8 with NaHCO$_3$.

2.4. Removing the template

The template is removed by NaOH (1 mol L$^{-1}$) after electrodeposition for further characterization.

2.5. Characterization

The scanning electron microscope (SEM) images are taken by JSM-6700F, JEOL (Japan Electron Optics Laboratory Co. Ltd). The transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns are achieved on JEM-2010F (JEOL). The x-ray diffraction (XRD) measurements are recorded on a 3KW D/MAX2200V PC (RIGAKU Corporation) x-ray diffractometer (Cu-Kα radiation) equipment. The photoluminescence (PL) measurements are carried out on a Hitachi, F-70 000. The excitation wavelength is 330 nm.

3. Results and discussion

The free-standing ordered TiO$_2$ nanotube arrays were fabricated by the conductive-substrate induced electro-deposition approach according to the following steps (scheme 2), and the details can be found in the experimental sections.

Inspired by the consideration that the horizontal growth rate of materials is directly related to the conductive substrate, we found the sputtering time of Cu, which is related to the thickness of the Cu layer, indeed plays an essential role in the final morphology of arrays during the electro-deposition processes. Under the same deposition time (TiO$_2$ for 10 min), the dependence of the final morphology on the thickness of the Cu layer can be observed clearly, as shown in figure 1(a).

When the thickness of Cu is less than 30 nm, it is hard to get any 1D nanostructure through electrochemical deposition (figure 1(b)) no matter how long the deposition time is. This is because the exposure area of conductive Cu is too small to support electric-field-assisted hydrolysis processes. If the thickness increases to 30–50 nm, the growth of TiO$_2$ along the template can be seen in figure 1(c) due to having enough exposure of Cu as conductive sites for electro-deposition, which is evidenced by the shortened diameter of pores from the back view of the template after Cu deposition as shown in the inset image of figure 1(c), and thus the formation of nanotube arrays is achievable within expectation. Moreover, nanowires appear when the thickness of Cu is more than
50 nm (figure 1(d)) owing to a too-rapid hydrolysis rate induced by the continuous conductive layer. Totally different from other electro-deposition processes, the types of nanostructure are determined by the thickness of the conductive layer rather than only the deposition time, which has previously been long neglected.

Following these steps, the nanotube arrays can be achievable. Each nanotube is uniform and nearly parallel, but connects with one another. The hollow structure is clearly observed from the top view in figure 1(c). The out-diameter of each nanotube is about 90–100 nm, which is in good agreement with the pore diameter of the AAO template. The thickness of each nanotube is ∼36 nm and can be adjusted easily by changing the deposition time of TiO<sub>2</sub> (figure S1), indicating the high controllability of this conductive-substrate induced electro-deposition approach.

With the help of this fabrication approach, various TiO<sub>2</sub> nanotube arrays can be obtained so as to fully understand the defect state emission. The as-obtained TiO<sub>2</sub> nanotube arrays with 10 min deposition time were post-treated for 5 h at high temperatures of 350 °C, 450 °C, 550 °C, 650 °C and 750 °C, respectively. The x-ray powder diffraction (XRD) in figure 2(a) shows the pure rutile phase TiO<sub>2</sub> when the temperature is higher than 550 °C. If the annealing temperature is below 550 °C, the nanotube arrays consist of both the rutile phase and the anatase phase. Shown in figures 2(b)–(f) are corresponding SEM images. The overall nanotube morphology is maintained, implying the obtained TiO<sub>2</sub> arrays have a highly stable structure. However, when the annealing temperature is higher than 550 °C, a close observation reveals that the slight collapse of the nanotube array can be largely attributed to deintercalation of H<sub>2</sub>O and phase transition. For convenience, hereafter, we designate various TiO<sub>2</sub> nanotube arrays as ‘NT-Temperature’, where NT refers to nanotube and the temperature is the annealing temperature.

In order to confirm the nature of defect states, photoluminescence (PL) spectroscopy was performed on nanotube arrays with different annealing temperatures (figure 3(a)). The observed line shapes of the five samples are clearly similar, except for the intensity. From the projection on PL intensity-temperature section, we find the intensity of peak increased rapidly from 350 °C to 450 °C until reaching the maximum value at 550 °C, and then decreased at higher temperatures. Since TiO<sub>2</sub> is an indirect bandgap semiconductor, the free
exciton recombination can be excluded [11]. The observed broad visible luminescence is primarily determined by the defect states. Detailed analysis of the PL spectrum provides more insight into the nature of defect states in different samples, and thus the deconvolution of the peak is necessary. Taking NT-350 for example, the broad emission analyzed with multi-peak Gaussian fitting method in figure 3(b) can be fitted with three Gaussian sub-bands centered at 415 nm (peak 1), 471 nm (peak 2) and 531 nm (peak 3).

In general, PL spectra of anatase TiO$_2$ are attributed to three kinds of physical origins: (I) self-trapped excitons located at TiO$_6$ octahedra (STE); (II) oxygen vacancies; and (III) surface state [27, 28]. As for the 415 nm sub-band, it has been reported from PL spectra of TiO$_2$ anatase single crystals, nanowire arrays and nanoparticles that this peak should be assigned to self-trapped excitons localized on TiO$_6$ octahedra [11, 32]. Meanwhile, the PL bands at 471 nm and 531 nm should originate from the oxygen vanacities associated with

Figure 2. (a) XRD patterns and (b)–(f) SEM images of TiO$_2$ nanotube arrays annealing for 5 h at different temperatures: (b) 350 °C; (c) 450 °C; (d) 550 °C; (e) 650 °C; (f) 750 °C.
Ti$^{3+}$/F and F$^+$, respectively [33]. Simply, due to the loss of an O atom in TiO$_2$ lattice, the electron pair trapped in the vacancy cavity (V$_O$) will generate an F center [34]. One of the electrons in F centre may occupy the adjacent Ti$^{4+}$ ion, yielding a Ti$^{3+}$ center and a F$^+$ (a single electron associated with oxygen vacancies) center, which will form shallow and deep trap states, respectively, as shown in the following equations.

$$V_O + 2e^- \rightarrow F$$
$$F + Ti^{4+} \rightarrow F^+ + Ti^{3+}$$
$$V_O + e^- \rightarrow F^+$$
$$Ti^{3+} + e^- \rightarrow Ti^{3+}$$

Hence, Ti$^{3+}$ center and F$^+$ center are formed due to the loss of an oxygen atom. Shallow and deep-trap states are established at 0.51 [35] and 0.8 eV [36] below the conduction band. The sub-band centered at 471 nm, which is coincident with shallow trap, can be assigned to Ti$^{3+}$ states, while PL emission centered at 531 nm results from the deep-trap state associated with the F$^+$ center [27]. The literature has suggested that the 415 nm sub-band probably originates from the intrinsic states in bulk rather than from surface states [27], while the 471 nm and 531 nm sub-bands of anatase TiO$_2$ powders can be assigned to surface defect states [37]. Some studies also report an intraband surface state of a nanocrystalline anatase TiO$_2$ film and identify the trap with Ti atoms adjacent to oxygen vacancies at the surface. Hence, it is reasonable to assign these two bands to the oxygen vacancies on the surface area of the nanotube arrays. Overall, all the locations of these trap centers responsible for the strong visible PL from TiO$_2$ nanotube arrays can be understood from the schematic band diagram shown in figure 3(d). The photogenerated electrons are initially excited to the conduction band of TiO$_2$ on irradiating UV-light (330 nm) and then relaxed to the defect states.

Quite similar with NT-350, observation of defect states can also be seen from the broad peak in the PL spectrum of NT-550 in figure 3(c), which is fitted with only two Gaussian bands centered at 422 nm (peak 1) and 468 nm (peak 2). It is of interest to pay attention to the following two parts: (I) The overall intensity of the broad peak and the separated intensity of the two Gauss fit peaks are stronger than those of NT-350,
implying the existing of more intrinsic STE and oxygen vacancies at the surface. Considering the constant morphology of nanotube arrays, this increase results from the gradually increased crystallization of TiO₂, which contributes more to the PL signals; (II) The area ratio of 422 nm sub-band to 468 nm sub-band is obviously increased. Note that the peak centered at 422 nm is more related to intrinsic STE, while the peak around 468 nm results from oxygen vacancies at the surface. It is concluded that the concentration of surface oxygen vacancies increases more rapidly than STE with rising temperature. (III) The sub-peak centered at ~531 nm is hard to be seen in the detailed spectrum. Even more remarkable, looking through all the PL spectra of TiO₂ nanotube arrays, we find an extremely distinct point that the emissions from blue edge to red edge (~450 nm–600 nm) are apparently quenched in the ordered nanotube arrays, especially when comparing them to the PL spectra of TiO₂ nanowire arrays [27], nanoribbons [11], a single nanotube [6] and nanoparticles [32]. The PL bands induced by other kinds of defects, such as hydroxyl (OH) species, are also missing in the spectra. It is regarded that photoluminescence is mainly a surface phenomenon, and thus a change in the surface environment would lead to significant influences on the PL process. Although the nanotube arrays possess a large surface area, the defect-related PL emission is found to be weaker.

Many factors have been regarded to influence the PL intensity, such as morphology [6], incident electric-field vector [6, 38], coordination number [39] and so on. MaHale et al. has checked the possible effects of PL spectra under vertically and horizontally polarized incidental light, respectively [6]. There is no difference in the PL spectra for these two experiments; thus, the difference in the spectra of nanotube arrays and other morphologies is not a consequence of the different alignments of the tubes relative to the incidental electric field vector. Additionally, PL quenching by oxygen may require a sufficient number of O₂ binding sites, where hole traps associated with oxygen vacancies are located on (101) facets, while electron traps associated with under-coordinated Ti atoms prevail on the (001) surfaces [39]. Considering the polycrystalline nature of nanotubes, which is evidenced by polycrystalline rings in SAED patterns of figure S2, the influences of different distribution of emissive traps due to coordination number on independent facets can also be excluded when compared to conventional TiO₂ morphology. Alternatively, the interparticle connections in the nanotube arrays could passivate a subset of more blue-to-red emitting traps, or permit interparticle transport that competes with the radiative recombination from these traps. The diminished red-edge PL in the ordered arrays may result from passivation of traps residing along the tube walls when the tubes are interconnected.

To evidence this hypothesis, we should pay more attention on at least two results. One is the PL spectrum of samples under annealing temperatures higher than 550 °C. When the annealing temperature keeps rising, the resulting intensity of blue-to-red edge PL is weaker and weaker (figure 3(a)). These changes are attributed to more exposure of samples in air at high temperatures, which allow increased Ti⁴⁺ and corresponding phase transition from anatase to rutile as shown in the XRD patterns in figure 2(a). More importantly, this transformation leads to the change of the morphology of the nanotube array. Except for the effects of phase transition, more and more interconnection between nanotubes further decreases the surface area. As indicated by the comparison between NT-650 and NT-750, the emissions at the blue-to-red edge decrease because all these detectable emissions result from defect states at the surface. The second evidence comes from the dependence of PL spectra on thermal treatment time. The nanotube arrays were annealed at 550 °C for different periods of time as shown in figure 4, figure 5 shows the similar trend of the change on the morphology and phase. The blue-shift and weaker peaks evidence the decrease of blue-to-red edge PL and as-mentioned conclusion.

Well-known research has indicated that deep traps lead to unfavorable recombination [24–26]. The dominating charge carrier recombination is the Shockley–Read–Hall recombination, which occurs when a charge is trapped by the defect [40, 41]. From this viewpoint, decreasing deep-trap defect states are essential to reduce the recombination. The highly ordered TiO₂ nanotube arrays obtained in our approach are beneficial to suppress this PL radiative recombination and hence to increase the lifetime of the charge carriers for transport, especially for the one between interconnected nanotubes within the arrays. As a result, our data showed that there is significant charge transport perpendicular to the long axis of the tubes in highly ordered arrays [6], which is significant to the design of highly efficient devices.

Although a deep understanding of the role of defect states is in its infancy and there are some contradictory statements on the role of oxygen vacancies related to the performance of semiconductors, it has been demonstrated that the defect states of TiO₂ play an important role on controllable adjustment of macroscopic properties, such as visible light response, charge separation, charge transport and absorption selectivity. We are looking forward to further efforts in this area to rationally engineer the defects in TiO₂, aiming to tune its properties in a desired manner for advancing environmental and energy-related applications.

4. Conclusions

In conclusion, we first employed a conductive-substrate induced electro-deposition approach to achieve highly ordered TiO₂ nanotube arrays based on an anodic aluminum oxide template. This approach is totally different from other methods, such as sol-gel, hydrothermal and atomic layer deposition, where the materials fully cover and depend more on the template. It is expected that a facile preparation of pore-through nanotube arrays can be realized without any complex processes and expensive equipment, while the parameters of nanotube arrays can be adjusted easily by changing the exposure area of the conductive layer. All these arrays can serve as a matrix with clean surfaces for the full studies of basic physical and chemical theory and practical
The photoluminescence (PL) spectroscopy is an efficient tool to explore the dependence of defect-state emissions on the various TiO₂ nanotube arrays. The PL emission of TiO₂ nanotube arrays are attributed to two kinds of physical origins: (I) self-trapped excitons located at TiO₆ octahedra (STE) and (II) oxygen vacancies, including Ti³⁺, F and F⁺. Interestingly, we find the emission from blue edge to red edge (∼450 nm–600 nm) is apparently quenched in the ordered nanotube arrays, especially when compared to the PL spectra of nanowire array, single nanotubes and nanoparticles. This distinct result originates from passivation of oxygen vacancies residing along the tube walls when the tubes are interconnected, which is further evidenced by the observation of PL spectra with crystalline phase and sintering. The passivation of defects suggest significant charge transport perpendicular to the long axis of the tubes in the ordered arrays, which is significant to the design of highly efficient devices and the applications in various energy-related fields.

Figure 4. (a) XRD patterns and (b)–(f) SEM images of TiO₂ nanotube arrays annealing at 550 °C for different times: (b) 3 h; (c) 8 h; (d) 10 h; (e) 12 h; (f) 16 h.
PL spectra of different samples annealing at 550 °C for different times.

Acknowledgments

This work is supported by Shanghai Thousand Talent Plan and Program, Innovative Research Team in University (No. IRT13078), European Research Council (ThreeDsurface: 291685), BMBF (ZIK-3DNanoDevice: 03Z1MN11), and Volkswagen-Stiftung (Herstellung funktionaler Oberflächen: I/83 984).

References


[38] Hendry E, Koeberg M, O’Regan B and Bonn M 2006 Local field effects on electron transport in nanostructured TiO2 revealed by terahertz spectroscopy Nano Lett. 6 755

