

A Protocol for Fabrication of Barium-doped Tantalum Nitride Nanorod Arrays

Yanbo Li (✉ yblee.cn@gmail.com)

Domen's Lab, The University of Tokyo

Kazunari Domen (✉ domen@chemsys.t.u-tokyo.ac.jp)

Domen's Lab, The University of Tokyo

Jun Kubota

Domen's Lab, The University of Tokyo

Method Article

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Abstract

In this protocol, we describe the detailed procedure for fabrication of barium-doped tantalum nitride nanorod array for application in photoelectrochemical water splitting. Tantalum oxide nanorods are first grown in-situ on a tantalum substrate by a through-mask anodization method using porous anodic alumina as a mask. The tantalum oxide nanorods are then converted into tantalum nitride nanorods by nitridation in ammonia atmosphere. The results reported in the associated publication demonstrate that the barium-doped tantalum nitride nanorods show high solar energy conversion efficiency for water splitting after modifying with a cobalt-phosphate oxygen evolution co-catalyst.

Introduction

Vertically aligned nanowire/nanorod arrays are promising building blocks for devices such as photodetectors, light emitting devices, and solar cells.¹⁻⁴ Deposition of functional materials into nanoporous templates is a facile “bottom-up” technique for the fabrication of vertically aligned nanowire/nanorod arrays.⁵ Due to its simple fabrication process and controllable structures, porous anodic alumina (PAA) membrane is widely used as the template material.^{6,7} In a conventional process, PAA templates are first formed on top of substrates and then precursor materials are deposited into the templates to form nanowires/nanorods by liquid-phase deposition such as electrodeposition or vapor-phase deposition such as chemical vapor deposition (CVD) and atomic layer deposition (ALD).⁸⁻¹⁰ The materials that form the nanowires/nanorods are either from the electrolyte for electrodeposition or from the vapor for CVD and ALD. Alternatively, the metal substrates beneath the PAA templates could be used as the sources to grow metal oxide nanorods in a process called “through-mask anodization”.^{11,12} This novel anodization method results in nanorods grown directly from the metal substrate having more intimate contact and better mechanical stability, which is more favorable from the practical point of view. In this protocol, we report the fabrication of barium-doped tantalum nitride (Ba-Ta₃N₅) following the procedure depicted in the flow diagram in figure 1. Starting with a clean tantalum (Ta) substrate, a thin layer of aluminum (Al) is deposited on the Ta substrate. The Al layer is first anodized thoroughly to form a PAA mask on top of the Ta substrate. Then, through-mask anodization of the Ta substrate is performed after adjusting the pore size of the PAA mask. During the through-mask anodization process, tantalum oxide (Ta₂O₅) formed by anodization is partially filled into the nanochannels of the PAA mask. Vertically aligned Ta₂O₅ nanorod array is obtained after selectively etching the PAA mask. After that, barium Ta₂O₅ precursor is loaded on the surface of the Ta₂O₅ nanorods. Finally, vertically aligned Ba-Ta₃N₅ nanorod array is achieved by nitriding the Ba-loaded Ta₂O₅ nanorod array in ammonia atmosphere. Using the above-described method, vertically aligned Ba-Ta₃N₅ nanorod array with uniform diameter and length was fabricated on a large scale. As shown in the associated publication, the Ba-Ta₃N₅ nanorod array modified with a cobalt-phosphate co-catalyst showed high solar energy conversion efficiency when used as a photoanode for photoelectrochemical water splitting. This method can also be applied to other materials (e.g., Nb, Zr, Ti) to fabricate vertically aligned nanorod arrays of metal oxides/nitrides for different applications. 

Reagents

- Tantalum sheet, 0.1 mm in thickness, 99.95% purity (Nilaco, cat. no. TA-413325) - Acetone ($(\text{CH}_3)_2\text{CO}$), 99.5% purity (Kanto) - Isopropyl alcohol ($(\text{CH}_3)_2\text{CHOH}$), 99.9% purity (Wako) - Aluminum evaporation slug, diam. \times L 6.3 mm \times 6.3 mm, 99.999% trace metals basis (Sigma-Aldrich, cat. no. 433705-25G) - Oxalic acid (HOOCCOOH), 98.0% purity (Wako) - Phosphoric acid (H_3PO_4), 85.0% purity (Wako) - Boric acid (H_3BO_3), 99.5% purity (Kanto) - Barium nitrate ($\text{Ba}(\text{NO}_3)_2$), 99.0% purity (Kanto) - Nitrogen (N_2), 99.99995% purity (Taiyo Nippon Sanso) - Ammonia (NH_3), 100 v/v% (Sumimoto) - Hydrochloride acid (HCl), 35.0~37.0% purity (Wako)

Equipment

- Thermal evaporator (ULVAC VFR-200M/ERH) - DC power supply, maximum output: 650 V, 1.2 A (Matusada Precision RK650-1.2) - Magnetic stirrer - Two-electrode electrochemical cell, cell volume: 300-500 ml, counter electrode: Pt or graphite - Water bath, temperature: 0-80 °C - Natural convection oven (AS ONE DOV-450) - Tube furnace, maximum heating temperature: 1100 °C, tube inner diameter: 24 mm, tube length: 70 cm - Mass flow controller (KOFLOC 8500) - Hume hood (Dalton)

Procedure

Ba-doped Ta_3N_5 nanorods are fabricated following the steps depicted in the flow diagram in Fig. 1. The detailed procedure is as follows: 1. Preparation of Ta substrate. Ta sheet is cut into desired size (e.g., $1 \times 5 \text{ cm}^2$). The Ta substrate is then cleaned in acetone and isopropyl alcohol by sonication, each for 10 min. Finally, it is dried thoroughly with a N_2 gun before loading into the evaporation chamber. 2. Deposition of aluminum layer. Aluminum slug with a weight of 0.5 g is loaded on a tungsten evaporation boat. Ta substrate is put 30 cm above the aluminum source. The evaporation chamber is pumped to a base pressure of $3 \times 10^{-3} \text{ Pa}$ with a diffusion pump. Aluminum layer is evaporated on the Ta substrate at a rate of 10-30 nm/s. The deposition rate and thickness are measured with a quartz crystal thickness monitor. The thickness of the Al layer deposited on the Ta substrate is about 2-3 μm . 3. Growth of PAA mask. The Al-coated Ta is anodized in 0.3 M oxalic acid solution at 40 V to form a PAA mask. The electrolyte is cooled with a water bath to a temperature of $\sim 5 \text{ }^\circ\text{C}$ and under stirring with a magnetic stirrer. The Al layer is anodized thoroughly until the pores reach the Ta substrate. This can be judged from the anodizing current, which decreases to nearly 0 when the anodization of Al is completed. The variation of the diameter of the nanorods can be achieved in this step. PAA masks with different pore sizes can be fabricated by varying the anodizing voltage. Correspondingly, the composition and concentration of the electrolyte should be changed to achieve a stable anodization. 4. Widening the pores of the PAA mask. The pore size of the PAA mask is about 30 nm. To widen the pore size of the PAA mask, the sample is dipped into a 5% H_3PO_4 solution for 90 s. The temperature of the solution is heated to 60 °C with a water bath. After etching, the sample is rinsed with pure water. The diameter of the nanorods can also be varied in a certain range by changing the etching time. 5. Through-mask anodization. The Ta substrate coated with PAA mask is

then anodized in 0.5 M H_3BO_3 solution at room temperature under stirring. The anodizing voltage is ramped from 0-650 V at a rate of 0.1 V/s and kept at 650 V for 1 h. Caution should be taken with the high voltage used here. The length of the nanorods can be varied by either the anodizing voltage or anodizing time.

6. **Selective etching of the PAA mask.** After the growth tantalum oxide nanorods by through-mask anodization, the PAA mask is selectively etching with a 5% H_3PO_4 solution. The sample immersed in the H_3PO_4 solution is put into a natural convection oven held at 60 °C for about 4 h. After that, the sample is thoroughly rinsed with pure water and dried with a N_2 gun.

7. **Loading of Ba precursor.** Ba precursor is loaded on the surface of the tantalum oxide nanorods by dipping the sample into a 0.1 M $\text{Ba}(\text{NO}_3)_2$ aqueous solution for about 10 s and then dried with a N_2 gun.

8. **Nitridation.** The tantalum oxide nanorods loaded with Ba precursor are then nitrided in a horizontal tube furnace. The sample is loaded into an alumina boat and placed in the center of the heating zone. The tube is sealed with air-tight flanges. Before heating, the tube is purged with N_2 to get rid of air. The furnace is then heated at a rate of 20 °C/min to 1000 °C under NH_3 flow (5 sccm). The temperature is kept at 1000 °C for 2 h and then cooled naturally to room temperature. After that, the tube is purged with N_2 again to get rid of NH_3 before taking out the sample. Caution should be taken with the hazardous NH_3 . The furnace is put into a fume hood in case that there is any leak of NH_3 . The gas outlet of the tube furnace is connected to a NH_3 trap consisting HCl solution.

Timing

The approximate time required for each step is given below: 1. Preparation of Ta substrate: 30 min 2. Deposition of aluminum layer: 1 h 3. Growth of PAA mask: 2 h 4. Widening the pore size of the PAA mask: 5 min 5. Through-mask anodization: 3 h 6. Selective etching of the PAA mask: 4 h 7. Loading of Ba precursor: 5 min 8. Nitridation: 5 h

Troubleshooting

Following procedure described above, sample with good uniformity should be achieved. In case of a problem, please check below for possible reasons and solutions:

1. **Problem:** PAA mask damaged in step 3. **Possible reasons:** the surface of the Ta substrate is not clean; the Al layer is contaminated during thermal evaporation; heat generated during anodization is not well dissipated. **Solutions:** use extra clean process (such as RCA clean process for removing organic contaminants) for Ta substrate; clean the deposition chamber and improve the vacuum condition of the evaporation system; increase the stirring speed.

2. **Problem:** sample damaged in step 5. **Possible reason:** the thickness of the PAA mask is not enough. **Solution:** increase the thickness of the Al layer.

3. **Problem:** sample damaged in step 8. **Possible reason:** there is residual air in the tube or the tube is leaking. **Solution:** make sure the tube is purged thoroughly with N_2 and check leak before heating.

Anticipated Results

Figure 2a shows the photograph of the Ta_2O_5 nanorods obtained after step 6. The sample exhibits a uniform green color which originates from light interference in the nanostructured film. After nitridation in step 8, the color of the sample is transformed from green to red, as shown in figure 2a. Figure 2b shows a typical scanning electron microscopy (SEM) image of the cross section of $\text{Ba-Ta}_3\text{N}_5$ nanorod array. The nanorods have a uniform diameter and length of about 60 nm and 600 nm, respectively. There is an inter-layer (mainly consisted of Ta_2N) between the nanorods and the Ta substrate. Due to the outstanding mechanical stability of the sample, the nanorod structure is not damaged although a high nitridation temperature is used. 

References

1. Yan, R. X. et al. Nanowire photonics. *Nat. Photonics* 3, 569-576 (2009). 2. Zhai, T. et al. One-dimensional inorganic nanostructures: synthesis, field-emission and photodetection. *Chem. Soc. Rev.* 40, 2986-3004 (2011). 3. Long, Y. Z. et al. Yu M, Recent advances in large-scale assembly of semiconducting inorganic nanowires and nanofibers for electronics, sensors and photovoltaics. *Chem. Soc. Rev.* 41, 4560-4580 (2012). 4. Osterloh, F. E. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.* 42, 2294-2320 (2013). 5. Shingubara, S. Fabrication of nanomaterials using porous alumina templates. *J. Nanopart. Res.* 5, 17-30 (2003). 6. Li, Y. et al. Fabrication of highly ordered nanoporous alumina films by stable high-field anodization. *Nanotechnology* 17, 5101-5105 (2006). 7. Li, Y. B. et al. High-speed growth and photoluminescence of porous anodic alumina films with controllable interpore distances over a large range. *Appl. Phys. Lett.* 91, 073109 (2007). 8. Nielsch, K. et al. Uniform nickel deposition into ordered alumina pores by pulsed electrodeposition. *Adv. Mater.* 12, 582-586 (2000). 9. Fan, Z. et al. Electrical and photoconductive properties of vertical ZnO nanowires in high density arrays. *Appl. Phys. Lett.* 89, 213110 (2006). 10. Sander, M. S. et al. Template-assisted fabrication of dense, aligned arrays of titania nanotubes with well-controlled dimensions on substrates. *Adv. Mater.* 16, 2052-2057 (2004). 11. Mozalev, A. et al. Nucleation and growth of the nanostructured anodic oxides on tantalum and niobium under the porous alumina film. *Electrochim. Acta* 48, 3155-3170 (2003). 12. Li, Y. et al. Vertically aligned Ta_3N_5 nanorod arrays for solar-driven photoelectrochemical water splitting. *Adv. Mater.* 25, 125-131 (2013).

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Figures

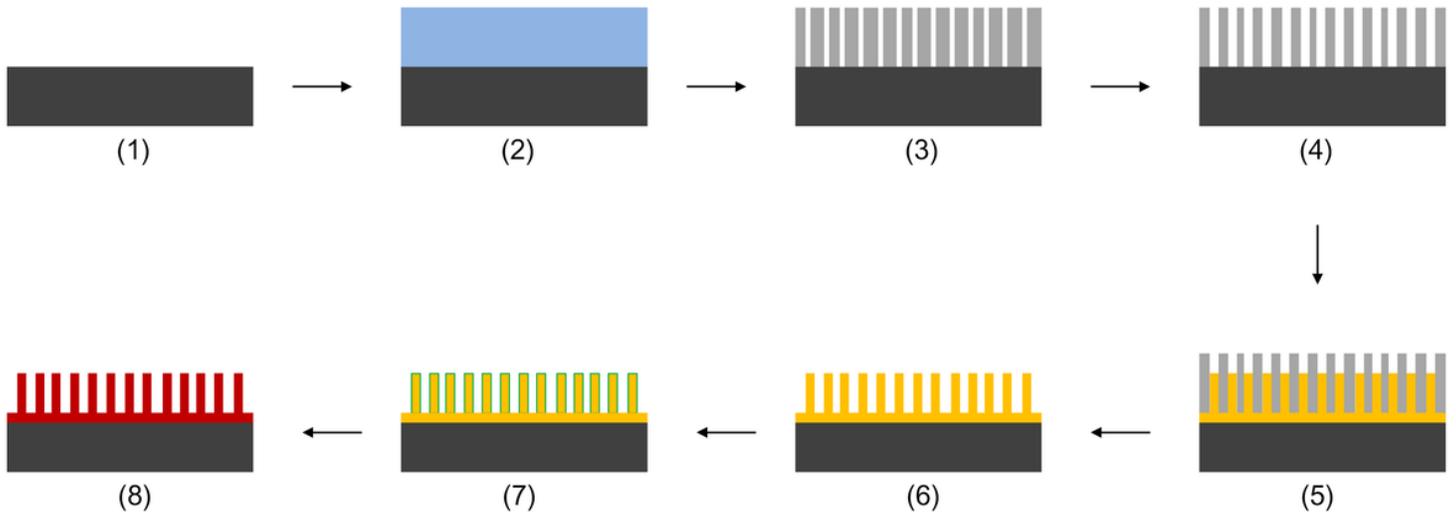


Figure 1

Flow diagram for the fabrication of Ba-Ta₃N₅ nanorod arrays.

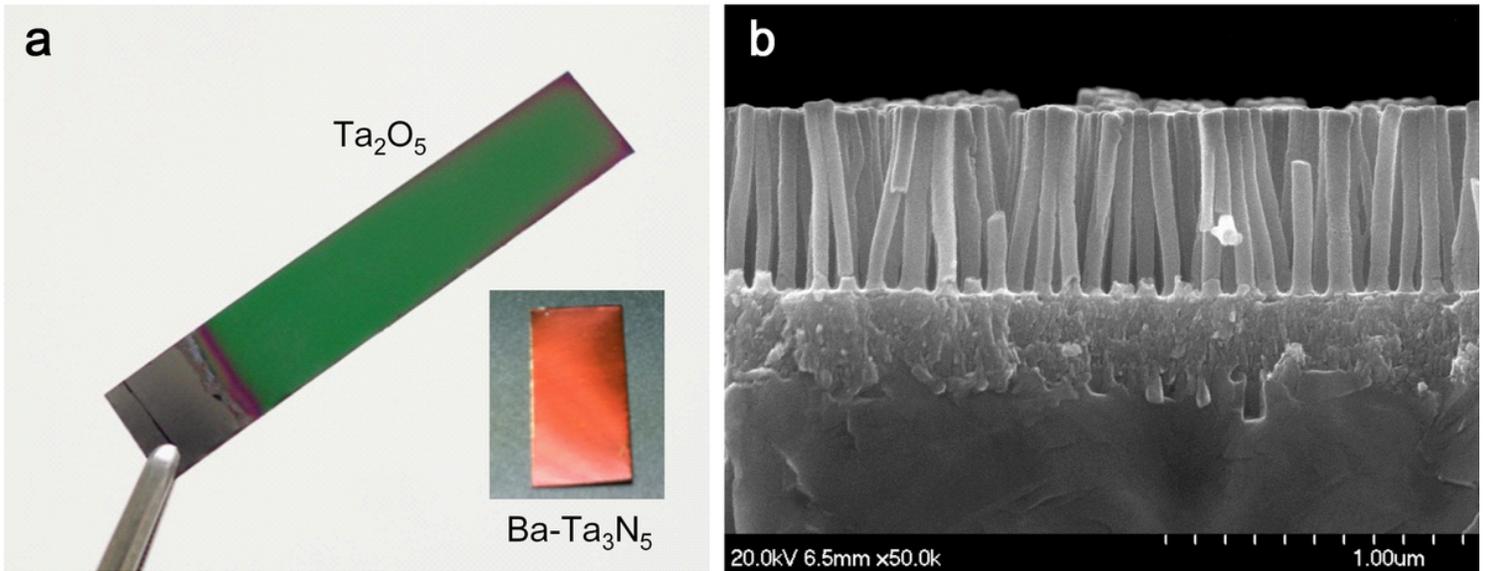


Figure 2

Morphology of the fabricated samples. (a) Photographs of the Ta₂O₅ nanorod and Ba-Ta₃N₅ nanorod arrays. (b) Typical SEM image of the cross section of Ba-Ta₃N₅ nanorods grown on Ta substrate.