Synthesized and characterization of open-ended Ta₃N₅ nanotube arrays for the preparation of growth template

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Abstract. In this article, a two-step anodization method was applied to tantalum foils to grow compact open-ended tantalum oxide nanotube arrays, which were subsequently subject to high temperature nitridation. The nitride nanotube arrays were characterized with SEM, XRD, and electrochemical tests including I-V and Mott-Schottky analysis. The phases in the nitrided nanotube arrays may consist of Ta₃N₅, TaN, TaN₀.₅, N-Ta₂O₃, or the amorphous oxide. The duration of the second anodization step was found to play a key role on the microstructure and the carrier density of the nitride nanotube arrays. It is found that the duration of the second anodization has to be more than 20 min to obtain a specimen with a top layer of Ta₃N₅, which can work as a photo electrode or a template for the growth of photo catalyst nanomaterials.

1. Introduction

Nanotube arrays can be employed as capacitors, [1] sensors, photo catalytic electrodes, [2, 3] growth templates, and solar cells due to their small radial size, large axial size, and large surface area [4]. To prepare nanotube arrays, anodic oxidation method was widely employed because of its simplicity and relatively low cost. Highly ordered TiO₂ nanotube array has been grown on Ti substrate using anodic oxidation, [5, 6] and they can be applied as photo electrode to produce hydrogen at a rate of 7.6 mL/h. Al₂O₃ nanotube arrays prepared by anodization, on the other hand, are mainly used as templates for nanomaterial growth. [7, 8].

Ta₂O₅ nanotube arrays can also be prepared by anodization. [9] When the Ta₂O₅ nanotube array was peeled off, the dimpled Ta surface can be used as a template for the fabrication of large area nanoparticle arrays. [10] Ta₂O₅ nanotube array can be transformed by high temperature ammonization into Ta₃N₅ nanotube array. [1, 11] Ta₃N₅ is a semiconductor with a narrow band-gap (2.1 eV), which exhibited a good visible-light photo catalytic performance. After nitridation, the dimpled Ta surface were also used as a substrate for the VLS-CVD growth of InₓGa₁₋ₓN nanowires to fabricate a photo catalyst electrode. [12] The obtained photo anode, however, still exhibited large dark current in the solution, indicating a conductive surface. On the other hand, the thick nanotube array cannot work as a reliable template due to a weak adhesion to the Ta substrate. Also, on the top of the tantalum oxide nanotube array usually exits an amorphous oxide film to block the nozzle of the nanotube and enhance the recombination of
photogenerated electron-hole pairs [11]. To address these problems, it is desired to develop a compact semiconductor nanotube arrays with open ends on the surface of the Ta foil to work as a substrate for the subsequent growth of photo catalyst.

In this article, an open-ended oxide nanotube arrays on the surface of Ta were prepared by a two-step anodic oxidation method, and the nanotube array was subjected to high temperature ammonization to obtain an open-ended, strongly-adhesive, and thin nitride nanotube array. The influence of the anodization duration for the second step on the microstructure, carrier density, and photo-electrochemistry of the nanotube array were studied using SEM, XRD, intermittent photocurrent-voltage scanning test, and Mott-Schottky analysis.

2. Experimental

Ta plates were cut, polished, and ultrasonically cleaned in acetone, ethanol, and deionized water for 5 minutes. The first anodization step was carried out on Ta specimens in sulfuric acid (H2SO4) consisting of 2.5 vol.% of hydrofluoric acid (HF) and 2.5 vol.% deionized water using a voltage of 30 V for 20 min. The obtained film during the first anodization was ultrasonically removed in deionized water. The second anodization of the dimpled Ta specimens was performed in a H2SO4 electrolyte containing 0.95 vol. % of HF and 8.57 vol. % deionized water with 0~10°C water bath at voltages of 15 V for 5, 10, and 20 min, respectively. After cleaning in deionized water and drying in N2, the anodized Ta samples were nitrided at 950°C for 2 h under NH3 with a flow rate of about 100 sccm. The obtained samples are referred to as 5, 10, and 20 min sample, respectively.

The surface morphologies of the obtained samples were examined using a field emission scanning electron microscope (SEM, Zeiss Sigma500, and Netherland). The structures were identified by X-ray diffraction (XRD, Philips, Analytical X’pert, Netherland, Cu Ka radiation, λ=1.5417 Å). The photoelectrochemical experiments were carried out in 1 M KOH aqueous solution illuminated with simulated AM 1.5G (100 mW cm−2) (CEL-S500, Beijing China Education Au-light Co., Ltd). A three-electrode configuration was used in the measurement, with the Ta specimen as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt foil as the counter electrode. Photocurrent versus voltage (I-V) curves were recorded with a potential ranging from -0.5 to 0.5 V (vs. SCE) with a scan rate of 50 mV s-1, and the Mott−Schottky (MS) plots were obtained in the dark at a fixed frequency of 1kHz using an electrochemical workstation (Ivium Technologies).

3. Results and discussion

The surface morphologies of the treated Ta foils were shown by SEM images in Fig. 1. Figs. 1(a, b, c) corresponded to top-view images of the Ta foils anodized for 5, 10, and 20 min during the second step. All the three images showed open-end nanotubes with an inner diameter of approximately 40~50 nm and a density of 125 μm-2. Side-view (45°) images of the three specimens were shown as Figs. 1(d - d’, e - e’, f - f’). Lower magnification images (Figs. 1(d, e, f)) showed that nanotube arrays aligned long certain directions, suggesting the formation of texture from the rolling of the Ta substrate. Higher magnification images (Figs. 1(d’, e’, f’)) revealed a surface morphology of peaks and valleys. The difference in the height of the peaks and valleys, which can be treated as the length of the oxide nanotube, increased with the anodization duration. According to the inset of the Fig. 1f’, the average length of the nanotube array is approximately 150 nm for the sample anodized for 20 min. After nitridation, nanotube arrays remained on the surface and no cracks can be observed (Figs. 1g - i), indicating a strong adherence of the film. Although nanotubes were almost closed for the 5 min sample, both 10 min and 20 min samples had open-ended nanotubes with shrunk inner diameters, which could be ascribed to the volume change from the phase transformation from oxide to nitride on the surface.
Figure 1. SEM images of the nanotube arrays for samples with different anodization time: 5 min (a, d, d', g), 10 min(b, e, e', h), 20 min (c, f, f', i); top-view images of the samples before nitridation (a, b, c); side-view (45°) images of samples before nitridation (d-d', e-e', f-f'); Top-view images of the samples after nitridation (g, h, i)

Figure 2. XRD patterns of the nanotube array electrodes (a) before nitridation, (b) after nitridation
XRD patterns of all the anodization samples only exhibited reflection peaks from the Ta substrate (Fig. 2a), indicating that the oxide nanotube arrays observed from SEM images are all amorphous. After nitridation, the XRD patterns in Fig. 2b revealed that all the nanotube arrays contained TaN, TaN0.5, and Ta2O. Reflection peaks from Ta3N5 phase, on the other hand, can be observed only for the 20 min sample.

Fig. 3a shows the I-V curves of the nitride Ta electrodes illuminated under simulated sunlight (AM 1.5G) in 1 M KOH solution. For 5 min sample, there was no current at all, indicating the presence of an insulate film on the surface. For the 10min sample, there was no photocurrent but an increased dark current which increase with the applied voltage, suggesting a conductive surface. The 20 min sample yielded a photocurrent of 30 μA cm-2 at 1.23 V SCE. Combined with the XRD results (Fig. 2b), it can be inferred that the photocurrent response in 20 min sample should be generated by the Ta3N5 phase, since Ta3N5 is the only semiconductor responding to the sunlight.

Figure 3. Current–potential curves upon intermittent irradiation (a) and Mott-Schottky curves (b) of the tantalum nanotube arrays after nitridation

Fig. 3b showed the MS curve of the nitrided nanotube arrays under the dark at a fixed frequency of 1 kHz. The 20 min sample had a MS curve with a positive slope. For other two samples, MS curves exhibited two segments with a positive slope at lower voltages and a negative slope at higher voltages. Positive and negative slopes in M-S curves usually indicate n-type and p-type semiconductor, respectively. MS curves suggest that the 20 min sample has a relatively thick n-type semiconductor on the surface, while other two samples contained a thin n-type semiconductor on the top and a p-type semiconductor underneath. According to the XRD results, it can be inferred that the n-type semiconductor on the top of the surface should be Ta3N5, and the p-type semiconductor underneath could be the N-doped Ta2O (N-Ta2O) [14]. The 20 min sample could have a thick Ta3N5 layer so that the p-type N-Ta2O at the bottom of the nanotube cannot be detected within the measurement voltage. According to the MS curves, there are ultrathin Ta3N5 layer in the 5 min and 10 min samples even though there were no Ta3N5 peaks can be discerned in their XRD patterns.

The amount of the n-type Ta3N5 can be estimated from the carrier density (ND) of the semiconductor, which can be calculated using the Mott–Schottky analysis as follows: [15, 16]

\[
\frac{1}{C_{sc}^2} = \pm \frac{2}{e \varepsilon_0 \varepsilon_r N_D(N_D - \frac{N_A}{N_D})} \left( E - E_{FB} - \frac{kT}{e} \right)
\]
where $C_{SC}$ is Space charge capacitance; $\varepsilon_0$ is vacuum dielectric constant ($8.854 \times 10^{-12}$ F/m), $\varepsilon_r$ is relative dielectric constant ($\varepsilon_r = 40$ for Ta$_3$N$_5$) [12]. $N_D$ and $N_A$ are the donor and acceptor concentration, respectively, $E$ is applied voltage, $E_{FB}$ is the flat-band voltage, $k$ is Boltzmann constant ($1.38 \times 10^{-23}$ J/K). $T$ is the temperature (K), and $e$ is electron charge ($1.602 \times 10^{-19}$ C).

| Anodizing times | Linearly fitting slopes of M-S curves (n-type) | Carrier density $N_D$ (cm$^{-3}$) |
|----------------|---------------------------------------------|---------------------------------|
| 20 min         | 3.76$\times$10$^7$                        | 8.73$\times$10$^{20}$          |
| 10 min         | 6.43$\times$10$^{10}$                     | 5.10$\times$10$^{17}$          |
| 5 min          | 4.21$\times$10$^{13}$                     | 7.79$\times$10$^{10}$          |

The carrier density $N_D$ of the n-type semiconductor on the top of 5, 10, and 20 min samples can be calculated to be 7.79$\times$10$^{10}$, 5.10$\times$10$^{17}$, and 8.73$\times$10$^{20}$, as shown by the Table 1. The calculated carrier density $N_D$ suggested that the amount of n-type Ta$_3$N$_5$ semiconductor increase as the second anodization duration increases. The fact that the $N_D$ of 8.73$\times$10$^{20}$ is in the normal range of carrier density for a bulk semiconductor indicate that a compact Ta$_3$N$_5$ layer were formed only in the 20 min sample.

![Figure 4](image-url)

Figure 4. Schematic diagrams of the phase distribution for the nanotube arrays on the surface of tantalum.

According to the above analysis, the distributions of the phases in the nanotube arrays was schematically illustrated by Fig. 4. The close-ended nanotubes formed in first step anodization were removed by ultrasonic cleaning. Open-ended nanotubes arrays formed on the previous dimpled surface after the second anodization. The length of the porous nanotubes increased with the increase in the anodization time. For the 5 min sample, the phases from the top to the bottom of the film are TaN, TaN$_{0.5}$, N-Ta$_2$O, and the remnant amorphous oxide (Ta$_x$O$_y$) layer, respectively. The amorphous Ta$_x$O$_y$ layer disappear in the 10 min sample. For the 5 min and 10 min samples, Ta$_3$N$_5$ phase, if present, should be very scarce on the top of the porous nanotube. A continuous and relatively Ta$_3$N$_5$ layer can only appear

on the top of the 20 min sample.

The difficulty for the formation of the compact Ta$_3$N$_5$ phase on the thin nanotube arrays may arise from the higher surface energy. Although thermodynamically favorable with a decrease in Gibbs free energy, the phase transformation would be prohibited owing to an increase in the surface energy due to large lattice mismatch between Ta$_3$N$_5$/TaN and nitride/oxide. With the growth of the nanotube array, however, the strain energy would accumulate. Once the thickness arrives a threshold, the strain energy would surpass the surface energy, and the phase transformation would occur to release the strain and a compact Ta$_3$N$_5$ layer would take place. The proposed scenario can explain the observed experimental results. The insulate amorphous oxide (Ta$_x$O$_y$) layer prevent any current from flowing through the surface of the 5 min sample as shown in the I-V test. This remnant Ta$_x$O$_y$ layer would be transformed into a p-type semiconductor of N-Ta$_2$O in the 10 min sample. At the same time, the metallic TaN layer on the top of the 10 min sample would give rise to a high dark current, inhibiting the sample from being applied in the field of photo catalysis. Due to the formation of the Ta$_3$N$_5$ layer on the surface, the 20 min sample can be qualified as a photo electrode or a template for the subsequent growth of the photo catalyst nanomaterials. Under the current anodization condition, 20 min seems to the minimum time for the second anodization. Longer time, however, would give rise to cracks in the nanotube arrays and lead to the peeling off of the film. Thus, the second step duration during the anodization is crucial for the template preparation of the Ta nanotube arrays.

4. Conclusion

Open-ended and a compact amorphous oxide nanotube arrays were achieved by performing a two-step anodization processes on the pure tantalum foil. The length of tantalum oxide nanotubes was related to the duration of the second anodization. After ammonization, the nanotube arrays may contain Ta$_3$N$_5$, TaN, TaN$_{0.5}$, N-Ta$_2$O, and amorphous oxide phases. The time for the second step anodization also played an important role in the microstructure of the nitrided nanotube arrays. The continuous Ta$_3$N$_5$ top layer only appeared in the sample with anodization time of 20 min, which showed an n-type semiconductor. The two-step anodization processes established in this article enable the treated tantalum foil as a photo electrode or a template for the subsequent growth of photo catalyst nanomaterials.

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