Anodic metal oxide nanostructures, fabricated by an electrochemical anodization process with an aid of anodic aluminum oxide (AAO) templates, have attracted much attention for several decades.1-14 Many metals, such as Ta, Nb, Ti, and W, have been studied to synthesize metal oxide nanodots and nanorods with an AAO-assistant anodization process3,4,33-35 since anodic tantalum oxide was investigated in the 90s.3,4,33 Due to the unique nanostructures, physical characteristics, and chemical properties, the anodic metal oxides can be developed as field emitters,7,8,13,19,20 nanocapacitors,14,20,21 optoelectronic devices,10,13,26 catalysts1,2,4,12,29 and biomaterials.29,30

The growth mechanism, such as surface morphology, ions transport and growth point, for anodic nanostructures fabricated using an AAO-assistant anodization process, has been mainly investigated3,4,13,18,19,34. For the growth of Ta2O5, Nb2O5, TiO2 and WO3 nanorods, a transport mechanism of ions in outer AAO template via the first anodization voltage.31,34 The diameter and density of metal oxides are governed by controlling the morphology of anodizing voltage,31,34,35 the wall of nanotubes was ~30% inside the pores and the other ~70% penetrated into the AAO template. Furthermore, no tubular nanostructures were found except the percentage of W element in TiW alloys is larger than 50%, attributing to the formation of void by oxygen bubbles arising from the oxidation reaction of tungsten metal. Besides, the height of the nanotubes is limited by an electric field of 0.82 GV/m due to the dielectric breakdown effect. Finally, a bottom-up growth mechanism at the oxide/metal interface is proposed, based on the observation of the cap structure on the top of the tubular architecture.

In this study, we used an Al-coated TiW alloy layer on Si substrates to fabricate TiW2O5 nanotube arrays via a two-step anodization process. After that, the second anodization process was performed in the same electrolyte containing fluorides,38-44 without AAO template. Neverthless, the conditions for the growth of TiW2O5 nanotubes were both decisive as the second anodization process.34,37 In brief, a two-step anodization process was used on the Al-coated TiW alloy films to fabricate anodized TiW2O5 nanotubes, as shown in Figure 1a.34,31 In order to control the morphology of anodized TiW2O5 nanotubes, the first anodization was carried out in a 0.3 M oxalic acid (H2C2O4) electrolyte, applied by a bias voltage of 10 V to 80 V, and terminated at 1 mA current. Then the second anodization process was performed in the same condition with the bias changed from 40 V to 117 V, expecting that various heights of TiW2O5 nanotube arrays can be prepared. After that, in order to observe the tubular structure, a post-process of sonication was conducted to remove the cap on the top of TiW2O5 nanotubes. In order to remove AAO templates selectively, a wet chemical etching process was carried out for 20-40 min at 60°C in a solution of H2O2 phosphoric acid (H3PO4) and 1.8 wt% chromic acid (H2Cr2O7). Therefore, TiW2O5 nanotube arrays can be exhibited on the Si substrate after selective removal of AAO. This approach can produce self-aligned and height-controlled TiW2O5 nanotubes on a Si substrate.

The AAO current characteristics of all samples were recorded using a Keithley 2400 source-meter. Surface morphology of the TiW2O5 nanotube arrays fabricated by TiW alloy anodization with an aid of Al-coated TiW alloy layers on silicon substrates was characterized using a scanning electron microscope (SEM). Furthermore, the AAO-assistant anodization technology with an aid of anodic aluminum oxide (AAO) for several decades. However, tubular nanostructures have not been reported by using an AAO-assistant anodization technology until now. In this study, we successfully synthesized self-organized TiW2O5 nanotubes with cap structures for the first time by using a two-step anodization process from Al-coated TiW alloy layers. The TiW2O5 nanotubes were observed only in the pores of AAO with large enough pore size, and otherwise the nanotube structures would become solid rods due to the agglomeration of TiW2O5. The wall of nanotubes was ~30% inside the pores and the other ~70% penetrated into the AAO template. Furthermore, no tubular nanostructures were found unless the percentage of W element in TiW alloys is larger than 50%, attributing to the formation of void by oxygen bubbles arising from the oxidation reaction of tungsten metal. Besides, the height of the nanotubes is limited by an electric field of 0.82 GV/m due to the dielectric breakdown effect. Finally, a bottom-up growth mechanism at the oxide/metal interface is proposed, based on the observation of the cap structure on the top of the tubular architecture.

Growth Mechanism of Self-Assembled TiW2O5 Nanotubes Fabricated by TiW Alloy Anodization

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Nanostructures, such as nanodots and nanorods, have been fabricated by the anodization process with an aid of anodic aluminum oxide (AAO) for several decades. However, tubular nanostructures have not been reported by using an AAO-assistant anodization technology until now. In this study, we successfully synthesized self-organized TiW2O5 nanotubes with cap structures for the first time by using a two-step anodization process from Al-coated TiW alloy layers. The TiW2O5 nanotubes were observed only in the pores of AAO with large enough pore size, and otherwise the nanotube structures would become solid rods due to the agglomeration of TiW2O5. The wall of nanotubes was ~30% inside the pores and the other ~70% penetrated into the AAO template. Furthermore, no tubular nanostructures were found unless the percentage of W element in TiW alloys is larger than 50%, attributing to the formation of void by oxygen bubbles arising from the oxidation reaction of tungsten metal. Besides, the height of the nanotubes is limited by an electric field of 0.82 GV/m due to the dielectric breakdown effect. Finally, a bottom-up growth mechanism at the oxide/metal interface is proposed, based on the observation of the cap structure on the top of the tubular architecture.

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nanostructure arrays was examined by a field-emission scanning electron microscope (FESEM, JSM-6500F) and a transmission electron microscope (TEM, JEM-2100F). Auger depth profile was performed by an ESCA PHI 1600 system with a monochromatic Al Ka source and a charge neutralizer.

Results and Discussion

The fabrication of Ti\textsubscript{x}W\textsubscript{y}O nanotubes.—The current as a function of time for Ti\textsubscript{x}W\textsubscript{y}O nanotubes in a two-step anodization process was recorded in Figure 1a, where the ratio of the TiW alloy is Ti:W = 1:1. Applying a voltage of 40 V in the first anodization process, the current plateau period shows the forming of porous AAO, and it ends up at a cliff point labeled as A in Figure 1a. At this moment of the first anodization, the anodic Ti\textsubscript{x}W\textsubscript{y}O nanostructure also starts forming by oxidizing TiW alloy, and its initial morphology are shown in Figures 1b and 1c for top-view and cross-section, respectively. Due to reaching the point A in Figure 1a imperceptibly and discrepantly with different thicknesses of Al layers, after the removal of AAO template, various morphologies such as nanodots, root-like nanostructures, residual Al metal, and unanodized TiW alloy are observed, as shown in Figure 1b. And without the removal of AAO template, the nanodot-like structures are forming inside the AAO pores, as Figure 1c shows. Continuously at the moment of the current downwards and terminated at 1 mA, labeled B in Figure 1a, a tubular nanostructure with a cap begins to grow, as shown in Figure 1d. In order to enhance the height of the Ti\textsubscript{x}W\textsubscript{y}O nanotubes, a higher voltage of 100 V was introduced in the second anodization process for 1s and 10s, and the results were shown in Figures 1e and 1f, respectively. The extra-fast growth for Ti\textsubscript{x}W\textsubscript{y}O nanotubes up to 118 nm in height has been achieved completely within 1 s because of a strong electrical field. Due to the dielectric breakdown effect, no distinct enhancement in height was observed after 1 s anodization. However, the nanotube wall thickness is apparently enlarged from \( \sim 8 \) nm to \( \sim 11 \) nm based on the continuous anodization for 10s. The tubular nanostructure for Ti\textsubscript{x}W\textsubscript{y}O is also confirmed by a TEM image in Figure 2. Hence, the vertical Ti\textsubscript{x}W\textsubscript{y}O nanotube arrays on Si substrates were successfully constructed after the self-assembled two-step anodization process.

First anodization: controllable morphology.—To investigate the effect of AAO pore size on Ti\textsubscript{x}W\textsubscript{y}O nanotubes, the various voltages applied in the first anodization were carried out from 10 V to 80 V followed by a 100 V-fixed second anodization process. For samples fabricated at 10 V and 20 V biases in the first anodization, only pillarated Ti\textsubscript{x}W\textsubscript{y}O nanostructures with the diameter of 18 nm and 25 nm are revealed, as shown in Figures 3a and 3b, respectively. Once the first anodization voltage applied at 30 V, Figure 3c shows that several Ti\textsubscript{x}W\textsubscript{y}O nanostructures start to exhibit tubular shapes of 29 nm diameter and wall thickness of 5.4 nm, accompanying most parts of nanorods still observed. The whole Ti\textsubscript{x}W\textsubscript{y}O nanostructures become completely tubular architectures for applied anodization bias voltages of 40 V, 60 V and 80 V, and the diameters of the nanotubes are 43 nm, 48 nm and 56 nm, with the wall thickness of 10.3 nm, 12.3 nm and 15.6 nm, respectively. The morphology of Ti\textsubscript{x}W\textsubscript{y}O nanostructures is relative to the controlling voltage in the first anodization process, and Figure 4a shows that the diameter as a function of voltage is 0.55 nm/V. From previous studies and literatures, it has been reported that during the anodization process the penetration behavior for Ti\textsuperscript{4+} and W\textsuperscript{6+} ions is in the outer part of AAO cell walls. Here, the tubular wall thickness of Ti\textsubscript{x}W\textsubscript{y}O nanostructures is also controlled by the thickness of the outer part of AAO cell walls, which is enlarged with an increase of voltages. Therefore, the 0.15 nm/V growth rate of the tubular wall thickness of Ti\textsubscript{x}W\textsubscript{y}O is observed when the first anodization bias is larger than 30 V, as shown in Figure 4a.

Figure 1. (a) The current diagram showing a two-step anodization process at a 40V-100V bias. (b) Plan-view and (c) cross-sectional SEM images showing the nanostructures without and with AAO templates, respectively, when the first anodization process is terminated at symbol A in (a). (d) A cross-sectional SEM image of Ti\textsubscript{x}W\textsubscript{y}O nanotubes showing the first anodization process interrupted at the current of 1 mA, labeled B in (a). A second anodization process is carried out for (e) 1s and (f) 10s to enhance the height of Ti\textsubscript{x}W\textsubscript{y}O nanotubes. The ratio for TiW alloys is Ti:W = 1:1.

Figure 2. A TEM image of the Ti\textsubscript{x}W\textsubscript{y}O nanotubes showing tubular structures.
Ti\(_{x}\)W\(_{y}\)O after first anodization treatment, and the nanorod structures were formed other than tubular structures.

**Second anodization: re-growth of Ti\(_{x}\)W\(_{y}\)O nanotubes.**—The re-growth mechanism of Ti\(_{x}\)W\(_{y}\)O nanotubes was studied using an enlarged voltage of 40 V to 117 V in the second anodization process, where the first anodization process is applied at 40 V-fixed voltage, as shown in Figure 5. Due to the restriction on the pore size of AAO, almost the same diameter of \(\sim 44\) nm is achieved in a 40 V-fixed first anodization process, shown in Figures 5a–5e. Figures 5f to 5j represent the cross-sectional SEM images of the Ti\(_{x}\)W\(_{y}\)O nanotubes fabricated in a second anodization process at 40 V, 60 V, 80 V, 100 V and 117 V for 20s, whose heights are 57 nm, 93 nm, 134 nm and 154 nm, respectively. The re-growth height as a function of voltage for the Ti\(_{x}\)W\(_{y}\)O nanostructures is 1.21 nm/V, shown in Figure 4b. Hence, the height of Ti\(_{x}\)W\(_{y}\)O nanostructures is enhanced certainly through the modulation of voltage in the second anodization process. Besides, the growth height of Ti\(_{x}\)W\(_{y}\)O nanotubes is confined by the non-conductive Ti\(_{x}\)W\(_{y}\)O metal oxide channel when the electrical field strength is less than 0.82 GV/m due to the dielectric breakdown effect,\(^{37,45}\) as shown in Figure 4b. The electrical field strength of dielectric breakdown for TiO\(_{2}\) and WO\(_{3}\) is 0.65 GV/m and 0.885 GV/m, respectively.\(^{31,34}\) Therefore, anodized WO\(_{3}\) nanostructures show a shorter height than anodized TiO\(_{2}\) nanostructures because larger electrical field strength is necessary for WO\(_{3}\) growth. In addition, no evident growth is found as the electrical field strength is less than that of dielectric breakdown.

**Component of the TiW layer.**—The Ti\(_{x}\)W\(_{y}\)O nanostructures fabricated through a different percentage of W in TiW alloys from 0\%, 25\%, 50\%, 75\% to 100\% (pure Ti, Ti\(_{3}\)W\(_{1}\), Ti\(_{1}\)W\(_{1}\), Ti\(_{1}\)W\(_{3}\) and pure W, respectively) was carried out in a two-step anodization process at a 40–100 V bias in Figure 6. Solidly pillared structures for TiO\(_{2}\) nanotubes are constructed from pure Ti metal, where Ti\(^{4+}\) ions (ionizing from Ti metal) migrate toward the TiO\(_{2}\) channel and penetrate in the outer part of AAO cell walls simultaneously, so that it becomes nanorod structures, corresponding to previous reports.\(^{34}\) Solid Ti\(_{x}\)W\(_{y}\)O nanorods are still acquired from the anodization on Ti\(_{1}\)W\(_{1}\) alloy. However, it is interesting that the tubular Ti\(_{x}\)W\(_{y}\)O nanostructures fabricated from the Ti\(_{1}\)W\(_{1}\) alloy are revealed. It is suggested that Ti\(^{4+}\) and W\(^{6+}\) ions migrating in the Ti\(_{x}\)W\(_{y}\)O channel anodized from Ti\(_{1}\)W\(_{1}\) alloy is terminated when the cap structures are accomplished and just pass through the outer part of AAO cell walls only, so that the tubular structures were formed. The tubular structures of the Ti\(_{x}\)W\(_{y}\)O and WO\(_{3}\) are also observed from the anodization on Ti\(_{1}\)W\(_{1}\) alloy and pure W metal, respectively. Hence, tubular Ti\(_{x}\)W\(_{y}\)O nanostructures can be prepared via the anodization process on TiW alloys, where the percentage of W in TiW alloys have to be more than 50\%. From the observation of SEM morphology, the similar diameter of 45 nm for the TiO\(_{2}\), WO\(_{3}\) and Ti\(_{x}\)W\(_{y}\)O nanostructures is exhibited based on the limitation of the pore size of AAO. Moreover, \(\sim 10.5\) nm tubular wall thickness of Ti\(_{x}\)W\(_{y}\)O and WO\(_{3}\) nanotubes, depending on the thickness of conductive outer part of AAO cell walls, is almost the same with each other at a fixed anodic voltage. Note that pillared WO\(_{3}\) nanorods fabricated using the same AAO-assistant anodization technology have been reported,\(^{31}\) whereas not for the WO\(_{3}\) nanotubes until in this study. The major discrepancy in this two studies is the pore size of AAO, where the blocking effect occurs in the smaller pore size to be the nanorod structures, mentioned above.

**Analysis of the composition profile.**—The Auger depth profiles, using Ar\(^{+}\) sputtering as an etching source, were explored on the analyses of AAO-removal Ti\(_{x}\)W\(_{y}\)O nanostructures fabricated from Ti\(_{1}\)W\(_{1}\) alloy, as shown in Figure 7. The relatively stable atomic ratio of \(\sim 45\%\) for Ti element is recorded within 50s Ar\(^{+}\) sputtering in the initial stage, whereas W element increases from 18\% to 35\%. This result may be attributed to an excellent migration capability for Ti\(^{4+}\) ions during the anodization process, compared with W\(^{6+}\) ions. A steady state is achieved with a \(\sim 40\%\) atomic ratio for both Ti and W elements after 100s Ar\(^{+}\) sputtering. However, due to preferential Ar\(^{+}\) ion bombardment, not only the Ti\(_{x}\)W\(_{y}\)O nanotube but also Ti\(_{1}\)W\(_{1}\) alloy layer in the valley contributes to the amount of Ti and W elements, resulting in high atomic ratio relative to O element of \(\sim 18\%\). The oxygen-rich phenomenon in the initial stage could result from the absorbed oxygen, bounder water, or incorporated oxygen-containing ions on the

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**Figure 3.** Plan-view SEM images showing Ti\(_{x}\)W\(_{y}\)O nanostructures fabricated in the first anodization process at (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V, (e) 60 V and (f) 80 V followed by a 100 V-fixed second anodization process. In order to observe the tubular structure, a 30min sonication vibration in a 0.1 wt% NaOH solution is used. The ratio for TiW alloys is Ti:W = 1:1.

**Figure 4.** (a) The diameter and wall thickness of the anodized Ti\(_{x}\)W\(_{y}\)O nanostructures carried out from 10 V to 80 V first anodization followed by a 100 V-fixed second anodization process. (b) The height of the Ti\(_{x}\)W\(_{y}\)O nanotubes was re-grown using a bias of 40 V to 117 V in the second anodization process, where the first anodization is applied at a 40 V-fixed voltage. The ratio for TiW alloys is Ti:W = 1:1.
Figure 5. (a)-(e) Plan-view and (f)-(j) cross-sectional SEM images showing Ti$_x$W$_y$O nanotubes fabricated in a 40 V-fixed first anodization process and then in the second anodization process at 40 V, 60 V, 80 V, 100 V and 117 V for 20s, respectively. The AAO template was removed completely in cross-sectional SEM images. The ratio for TiW alloys is Ti:W = 1:1.

Figure 6. The Ti$_x$W$_y$O nanostructures fabricated from TiW alloys with a different W percentage of (a) 0%, (b) 25%, (c) 50%, (d) 75% to (e) 100%, carried out at a 40 V-100 V bias in a two-step anodization process. A 30 min sonication vibration in a 0.1 wt% NaOH solution is used to partly remove AAO and Ti$_x$W$_y$O nanostructures.

top of Ti$_x$W$_y$O nanotubes. Besides, the Al element with ∼1.25% atomic concentration was always recorded in the Auger profile spectra during the Ar$^+$ sputtering process. The outer part of AAO cell walls is considered as a low ionic resistivity region due to physical defects, cation vacancies, anionic species, and bound water. Therefore, the penetration behavior for Ti$^{4+}$ and W$^{6+}$ ions into the outer part of AAO cell walls during an anodization process is proposed to be the growth path consistent with other anodic oxides.

Figure 7. Auger depth profiles for Ti$_x$W$_y$O nanotubes fabricated in a two-step anodization process at a 40 V-100 V bias was recorded to examine various atomic concentrations, where Ar$^+$ sputtering is used as an etching source. The AAO template was removed completely before examining. The ratio for TiW alloys is Ti:W = 1:1.

Figure 8a shows that 70% tube wall thickness is in the outer part of AAO cell walls and the other 30% is in AAO pores. In addition, based on the low quantity of 1.25% Al element, Al-O bonds in the outer part of AAO cell walls dissociate under the strong field. Then O$^{2-}$ ions could participate continuously in the anodization process with...
migrating Ti\(^{4+}\) or W\(^{6+}\) ions, and most of the Al\(^{3+}\) ions were expelled in the electrolyte and a few ones are injected into the growth.\(^{11,19,34}\)

**Growth mechanism of Ti\(_x\)W\(_y\)O nanotubes.**—Figures 8b and 8c show the schematic diagram of Ti\(_x\)W\(_y\)O nanotubes growth mechanism. When the AAO barrier layer contacts the TiW alloy layer, a few part of underling TiW alloy is ionized, and Ti\(^{4+}\) and W\(^{6+}\) ions start to migrate outward to the AAO barrier layer in a strong electrical field more than 0.82 GV/m, dielectric breakdown strength. Meantime, O\(^{2-}\) ions migrate inward to the bottom. Then based on the reaction of Ti\(^{4+}\) and W\(^{6+}\) ions with O\(^{2-}\) ions, the root-like Ti\(_x\)W\(_y\)O nanostructures are constructed in the AAO barrier layer during the first anodization process, as shown in Figure 8b. After that, AAO barrier completely contacts TiW alloy layer and a void may be formed at the oxide/metal interface due to violent evolution of oxygen bubbles arising from tungsten metal in an oxidation reaction. The similar situation has been reported by Al-coated Au and Pt metals, ITO/glass materials, and W\(_6\)O\(_5\)\(\cdot\)2H\(_2\)O arrows. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).