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Precise electrochemical prediction of short tantalum oxide nanotube length

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ABSTRACT

While the thickness of compact oxide films formed on valve metals can be easily predicted from the anodization constant and applied voltage, a similar predictive method is not available for oxide nanotubes (NTs) formed on these substrates. This is due to the unknown anodization charge efficiency, oxide flow from pore base to walls during anodization, and the unknown characteristics of the oxide, such as density and porosity. Here, we report a simple and precise method to predict the length of short (50 to 1000 nm), adherent Ta oxide NTs, formed by the anodization of polycrystalline Ta in sulfuric acid solutions containing HF at concentrations significantly lower than normally used for long NT growth. It is shown that the NT length can be calculated from the total anodic charge passed during anodization, demonstrating that factors such as anodization charge efficiency and oxide density are independent of the HF concentration and anodization time. The very useful and versatile correlation of anodization charge density and Ta oxide NT length allows for the calculation of NT length using only charge measurements and eliminates the need for electron microscopy examination of each sample. This work also opens the door to many new applications for which short metal oxide NTs, having lengths accurately but simply gauged just from the anodization charge density passed, are of great interest.

1. Introduction

There is a significant amount of interest in nanoporous and nanotubular materials, due to their high surface area, ease of fabrication, and their many practical applications. As an example, nanoporous valve metal oxides (e.g., Al,[1] Zr,[2–4] Ti,[5–7] Nb,[8] and Ta [9–13] oxides), produced by electrochemical anodization, have received significant attention recently due to their many applications in biosensors,[14–17] catalysis,[18] waveguides,[19] and photoelectrochemical applications.[20–22] Medical devices, such as pacemaker electrodes and orthopedic and dental implants, have been fabricated from porous oxide coated Ta [23] and Ti[24], dating back to the mid-1900s,[25] providing a long history of the biocompatibility of these materials.

In addition to not eliciting a foreign body response, Ta is well-suited for biological applications, primarily because it is chemically inert (does not catalyze reactions in the body and does not dissolve in harsh environments, such as the bloodstream). This results from the protective air-formed oxide that is stable over a wide pH range.[23] Recent work employing nanostructured metal oxides as implantable biosensors has shown that these surfaces are also very resistant to fouling by protein adsorption.[24,26] These attributes, along with the potential for miniaturization, make Ta oxide nanotubes (NTs) a promising material for incorporation in an implantable biosensor, work that is currently ongoing in our group in a parallel project.

As previously reported, ordered surface arrays of Ta oxide NTs can be formed by the anodization of Ta at 15 V in 16 M H_2SO_4 + 3 M HF.[9] Ta oxide NTs, which have independent walls and voids between neighboring NTs, differ from porous Ta oxides (formed using different anodization conditions, such as lower sulphuric acid concentration[13]), in which the walls surrounding pores are shared by adjacent pores. The NTs are believed to form via two competing reactions, the anodic oxidation of Ta (reaction (1)), forming Ta oxide, and the dissolution of the oxide, caused by fluoride ion attack (reaction (2)).[9,10]

$$2Ta + 5H_2O \rightarrow Ta_2O_5 + 10H^+ + 10e^- \quad (1)$$

$$Ta_2O_5 + 10H^+ + 14F^- \rightarrow 2(TaF_7)^{2-} + 5H_2O \quad (2)$$

In the absence of fluoride ions, a compact Ta oxide film is formed (reaction (1)), and it is widely accepted that the thickness of this

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film is directly related to the potential applied (via the anodization constant, which is ~1.9 nm/V for Ta).[27] This type of simple relationship is useful for quickly determining the thickness of compact oxide films formed on Ta and on other valve metals, and also for determining the anodization voltage required to form a compact oxide of a desired thickness. Although a similar relationship exists for the determination of the pore diameter in porous oxide and nanotubular films at valve metals,[28] a simple approach for the prediction of NT length has not yet been reported.

The thickness of the layer of NTs is known to be dependent on the anodization time,[9,10] with many applications demanding high aspect ratio NTs for use as semiconductors,[29] catalyst supports,[18] etc. However, there has been little work done to form short NTs (< 300 nm) or to understand how to precisely control their thickness for use in a variety of other applications. As an example, short NTs, 50-100 nm in length, could serve as ideal nano-vesicles for an enzyme (e.g., glucose oxidase) and redox mediating nanoparticles, producing a selective and sensitive glucose biosensor, of direct relevance to parallel work underway in our group.[30]

Currently, anodization of Ta in the standard 16 M H_2SO_4 + 3 M HF solution gives NTs > 1000 nm in thickness in only 20 seconds. Therefore, in order to form a nanoarray of nanotubes that are as short as 50 nm, anodization times of less than one second would be needed, but the procedure would then be very difficult to control reproducibly. For this reason, the rate of NT growth must be lowered in order to precisely control the length of short NTs during their formation. It has been suggested [13] that lowering the concentration of fluoride ions in the anodization solution should achieve this goal, likely because the chemical etching of Ta oxide by fluoride ions (reaction (2)) is the slow step in the formation of Ta NTs.

Here, it is shown that the rate of Ta oxide NT growth can be deliberately slowed down by using HF concentrations as low as 0.15 M and by employing easily controlled anodization times ranging from 2 seconds to 4 minutes, thus reproducibly forming Ta oxide NTs down to 50 nm in length. Most importantly, it is shown that the anodization charge density provides an excellent indication of NT length, whereas NT length depends on the anodization time and solution composition in a very complex manner. Although a correlation of the anodization charge and the resulting NT length has previously been alluded to (without an exact relationship given) in the case of Ti anodization,[31] to our knowledge, our work represents the first report of the precise tuning of metal oxide NT length by tracking (and controlling) only the charge passed during the anodization process. The facile conversion of the charge to NT length, even when the NTs are very short, also minimizes the need for costly and time-intensive cross-sectional imaging analysis.

2. Experimental Methods

2.1. Materials

H_2SO_4 (95-98%), acetone, and isopropanol (all ACS reagent grade) were all purchased from EMD Chemicals, while HF (48-51%, ACS reagent grade) and Ta foil (99.95%, 0.127 mm, annealed) were purchased from Alfa Aesar. All solutions were prepared with deionized water (Corning Mega-Pure system) and all chemicals were used as received without further purification.

2.2. Electrochemical Methods used for Ta anodization

Ta samples (typically 10 mm x 5 mm) were cut from as-received Ta foil (Alfa Aesar, 0.127 mm thick, 99.95% purity) and were rinsed sequentially with acetone, isopropanol, and deionized water. After drying, samples were anodized using a Princeton Applied Research 263A potentiostat for 5 to 300 seconds at 15 V vs. a Pt gauze counter electrode. The anodization solution consisted of 16 M H_2SO_4 and 0.2 to 1.1 M HF, which was stirred thoroughly during and after preparation until it had cooled to room temperature.

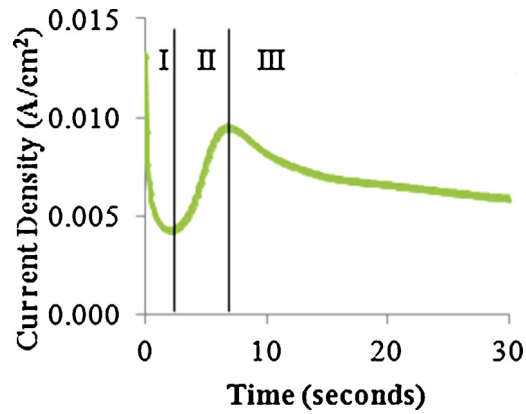

Fig. 1. Current-time behaviour observed during the anodization of Ta at 15 V in 16 M H_2SO_4 + 0.6 M HF, showing three distinct stages.

Anodization was performed in a polytetrafluoroethylene (Teflon) beaker, without stirring. The combined counter/pseudo-reference electrode (CE/RE) used was a Pt gauze cylinder, either 1.1 cm x 1.3 cm or 2.25 cm x 2.5 cm (6 or 22.5 cm^2 geometric area, respectively), with the Ta foil working electrode placed in the center of the CE to ensure a symmetrical field. Immediately after anodization, the samples were thoroughly rinsed with water and dried under a stream of nitrogen.

2.3. Surface Characterization Methods

To determine the length of the Ta oxide nanotubes (NTs) formed, cross-sectional field emission scanning electron microscope (FE-SEM) images were obtained. A brittle fracture, which would preserve the oxide/metal interface, could not be obtained with Ta foil, even when immersed in liquid N_2, due to the high degree of ductility exhibited by Ta. Therefore, anodized Ta samples were annealed in H_2 at 450 °C for 5 hours to convert the Ta substrate to Ta hydride, which is much more brittle, allowing it then to be fractured to obtain the cross-sectional images.

All samples were mounted on Al stubs using double-sided carbon tape and Ag paint, with the sample mounted perpendicularly to the stub such that the fractured oxide/metal interface was facing upwards. FE-SEM analysis (JEOL JAMP-9500F Field Emission Auger Microprobe, University of Alberta) was performed using an electron energy of 5 to 25 eV. The samples were imaged at several different angles by tilting the SEM stub, and NT length was determined only when the samples were positioned perpendicularly to the detector.

3. Results and Discussion

3.1. Effect of hydrofluoric acid concentration on Ta oxide nanotube growth rate

In an attempt to slow down the rate of Ta oxide nanotube (NT) growth and produce uniform arrays of short NTs (< 100 nm in length), HF concentrations down to 0.2–1.1 M were used, with the concentration of H_2SO_4 kept constant at 16 M. While monitoring the current density during anodization, three distinct stages are observed (Fig. 1, shown for the case of 0.6 M HF), similar to the behavior reported during porous Al oxide formation.[32–35] A