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Electrochromic properties of anodically grown mixed V_2O_5–TiO_2 nanotubes

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ABSTRACT

Mixed V_2O_5–TiO_2 nanotube arrays were fabricated by self-organizing anodization of different Ti–V alloys. The mixed oxide nanotubes show switchable V-oxidation states and strong cathodic coloration. Already a low V content of ≈0.2 at.% significantly increases the electrochromic switching properties. Using a sample with 3 at.% V, very high electrochromic contrast can be established and a significantly lower switching onset voltage than for pure TiO_2 nanotubes is observed. At high V contents, although charge storage is increased, the improvement of contrast is diminished due to the strong background color of the sample.

1. Introduction

In recent years, TiO_2 nanotube arrays grown by self-organizing anodization have been extensively studied and have been explored in numerous functional applications such as in photovoltaics [1], photocatalysis [2], biomedicine [3], and electrochromic devices [4]. A particular advantage for many applications is that the oxide structures grow vertically aligned on a Ti metal substrate and therefore the structures can directly be used as electrodes. The geometry of the nanotube arrays can be controlled by tailoring the electrochemical conditions such as electrolyte concentration, pH, applied voltage and electrolyte composition [5,6]. In order to improve the functional properties of TiO_2 nanotube arrays, various methods have been explored to mix or dope TiO_2 nanotubes with other functional materials, for example: doping of the nanotubes with C, N or metal ions [7–9]; modification of TiO_2 nanotubes with semiconductor quantum dots [10]; filling the TiO_2 nanotubes with other metal or metal oxides [11]; introducing other low dimensional oxide nanomaterials into the TiO_2 nanotube arrays [12].

A most direct approach to fabricate mixed oxide nanotubes is the anodization of a suitable Ti alloy. This allows to quantitatively control and introduce a specific functional property into TiO_2 nanotube arrays or even to achieve synergistic effects. In very recent works, TiO_2–WO_3, TiO_2–MoO_3, TiO_2–Nb_2O_5 nanotube arrays, or even more complex TiO_2–Nb_2O_5–Ta_2O_5–ZrO_2 nanotube arrays were fabricated using anodization of corresponding Ti alloys and were explored for various applications [13–17]. From a functional material viewpoint, one of the most interesting transition metal oxides is V_2O_5, as it possesses a very high ion intercalation ability which can be exploited for Li ion batteries and electrochromic devices [18–21]. However, attempts to grow pure self-organized nanotube layers of the oxide fail due to the low stability of the vanadium oxide in virtually any anodization electrolyte. In the present work, therefore we grow V_2O_5–TiO_2 mixed oxide nanotubes and explore them for electrochromic switching.

In this context particularly interesting is that both compounds, TiO_2 and V_2O_5, are recognized as efficient electrochromic materials due to their strong reversible field-assisted ion (H^+ or Li^+) intercalation behavior [22,23]. Moreover, for the mixed oxide powders, synergistic electrochromic properties have been reported [24,25]. In other words, V_2O_5 is expected to enhance the electrochromic performance of TiO_2.

2. Experimental

Ti–V alloy plates (Ti: V = 99.8: 0.2 at.%, 97: 3 at.% and 82: 18 at.%, provided by the Central Institute for New Materials and Processing Technology, University of Erlangen, Germany) and titanium foils (0.1 mm, 99.6%, Advent Materials) were used as substrates. Samples of each material were ground and polished to a mirror finish before use, followed by sonicating in acetone, isopropanol and ethanol, respectively. After rinsing with deionized (DI) water and drying in nitrogen, substrates were anodized under self-organizing conditions to grow oxide nanotubes. Electrochemical anodization was carried out at room temperature in a solution of ethylene glycol (EG, Riedel-de Haën, 99.5%) with 0.2 M HF (40 vol.%, Merck). The anodization was conducted at 60 V for different durations to grow 1 μm long nanotubes using a high-voltage power source PE 1530 (Philips) and a conventional two-electrode configuration with platinum gauze as counter electrode. After anodization, the samples were soaked in

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ethanol for overnight and then washed with DI water followed by drying in a nitrogen stream.

Thermal treatments of the samples were carried out using a Rapid Thermal Annealer (Jipelec JetFirst 100) at 450 °C for 3 h in air with a heating/cooling rate of 5 °C min^{-1}. A field-emission scanning electron microscope (Hitachi FE-SEM S4800) equipped with an Energy dispersive X-ray (EDX) spectrometer was used to investigate the morphology and composition of the samples. X-ray diffraction (XRD) analysis was performed by an X'pert Phillips PMD with a Panalytical X'celerator detector using graphite-monochromized CuKα radiation. The composition and the chemical state of the samples were characterized by X-ray photoelectron spectroscopy (XPS, PHI 5600, Perkin Elmer).

Electrochemical and electrochromic measurements were carried out in a classical three electrode set-up: For this, the nanotubes on the metal substrates were used as working electrode, a platinum plate served as a counter electrode, and Ag/AgCl (3 M KCl) electrode in Haber-Luggin capillary served as a reference electrode. Both cyclic voltammograms and chronoamperometric measurements were performed on an Autolab PGSTAT 30 Potentiostat/Galvanostat (Ecochemie, The Netherlands). Reflectance measurements were carried out with a fiber optic illuminator (tungsten halogen lamp, LS-1, Ocean Optics, El Dorado Hills, CA, USA).

3. Results and discussion

Fig. 1 shows the morphologies of nanotube arrays formed on different Ti–V substrates, namely, Ti, Ti-0.2 at.% V (Ti0.2 V), Ti-3 at.% V (Ti3V), Ti-18 at.% V (Ti18V). The layers were all grown by anodization of the alloys in an electrolyte composed of ethylene glycol with 0.2 M HF. In every case, ordered nanotube arrays with a layer thickness of 1 ± 0.1 μm and an average tube diameter of 120–130 nm were obtained. The nanotube length was controlled by the anodization duration, namely, 15 min for Ti, Ti0.2 V, Ti3V, and 20 min for Ti18V. It can be seen from the top-view images in Fig. 1e that a thin porous layer is present on the top of the nanotubes, which is an initiation layer formed at the beginning of the anodization process. Under the initiation layer, highly ordered nanotube arrays are present as shown in Fig. 1f. After annealing the as-prepared amorphous nanotubes at 450 °C for 3 h, the originally amorphous

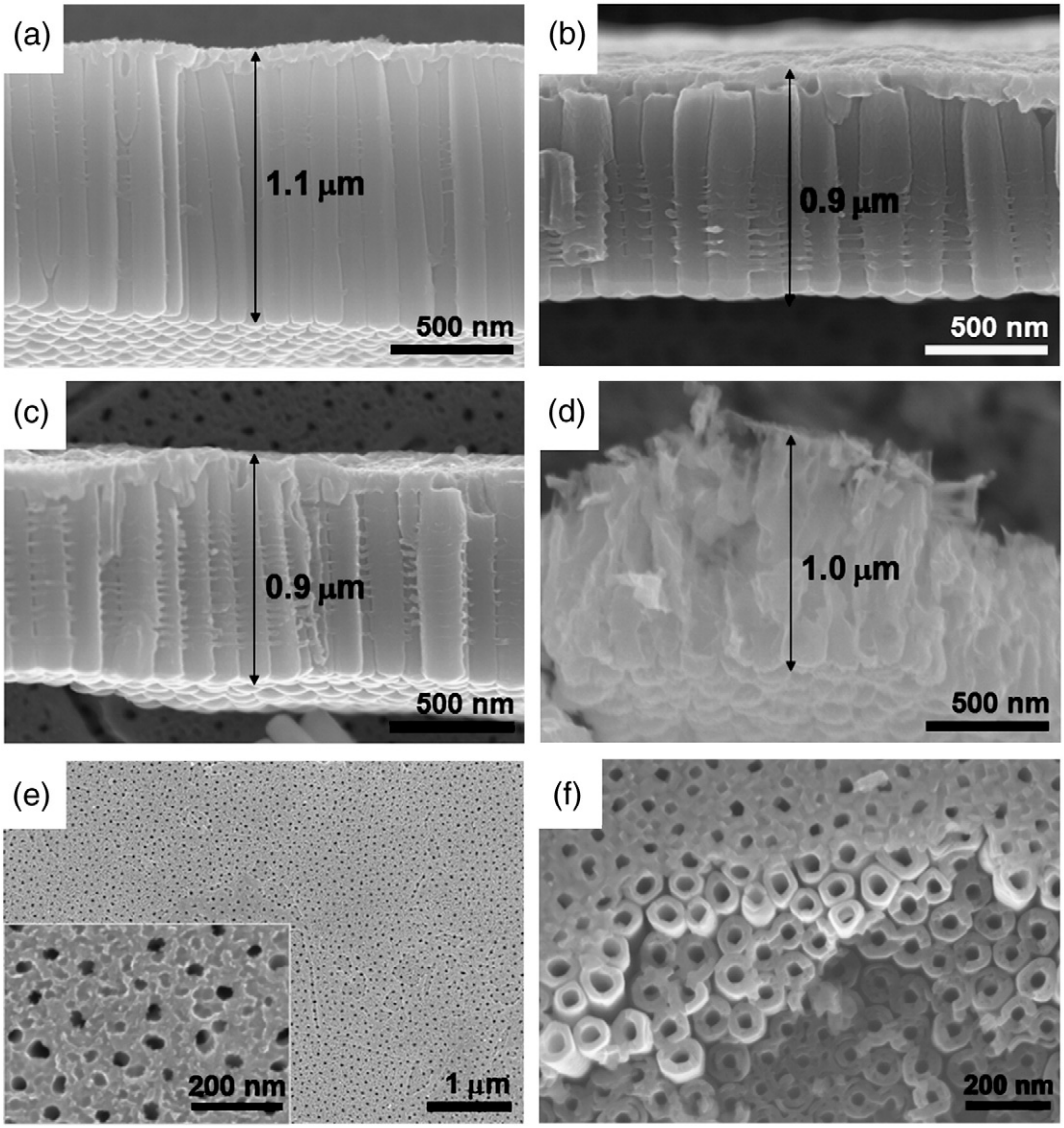

Fig. 1. Cross-section SEM images of ordered nanotube arrays on different substrates: (a) Ti, (b) Ti0.2V, (c) Ti3V, and (d) Ti18V prepared by anodization in an electrolyte composed of ethylene glycol with 0.2 M HF at 60 V for 15 min (Ti, Ti0.2V, and Ti3V) and 20 min (Ti18V), respectively. Top-view SEM images of the as-prepared nanotubes: (e) with initiation layer on the surface and (f) highly ordered and aligned nanotubes underneath the initiation layer.