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Synthesis of thick TiO_2 nanotube arrays on transparent substrate by anodization technique

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ABSTRACT

A vertically aligned transparent TiO_2 nanotube array (tTNA) of significantly enhanced tube-length 6.3 ± 0.3 μm was successfully synthesized on glass substrates by anodization technique with ammonium fluoride and ethylene glycol-based electrolyte. Prior to anodization, Ti metal was deposited on glass substrate by facing-target sputtering technique with various sputtering pressures at substrate temperature 420 °C to find out the relation between the structural properties of the Ti layer and the corresponding growth mechanism of the TiO_2 nanotube. The study revealed that structural properties of Ti metal layers and its adhesion to the glass substrate, which can be tuned by deposition parameters, play an important role in the process of tTNA formation.

1. Introduction

In the recent years, a vertically oriented, highly ordered titanium dioxide (TiO_2) nanotube array, prepared by anodization of titanium, has attracted huge attention [1–4] because it possesses unique properties, enabling a variety of advanced applications, including their use in photocatalysis, [5] solar energy conversion, [6–9], sensors, [10] in hydrogen generation by water photoelectrolysis [11] and in biomedical applications [12]. So far, the TiO_2 nanotube array has been prepared from titanium (Ti) metal foil [1–4] and the maximum height, 1000 μm, has been obtained by Prakasam et al. [13]. However, for effective practical applications, particularly in the fabrication of microscale devices, the transparent TiO_2 nanotube array (tTNA), grown on a transparent substrate compatible with photolithographic processing is very much desired. First successful preparation of tTNA of a thickness of 360 nm on fluorine-doped tin oxide (FTO) coated glass substrate was carried out by Grime's group [14,15], but later not much studies have been carried out on tTNA except few scattered efforts [6–9,16–18], where the maximum achieved height of the tTNA on a glass substrate is 2 μm. Recently, tTNA has been grown on FTO-coated substrate with high thickness-conversion ratio [19]. The successful preparation of tTNA of extended height largely depends on the characteristics of a Ti film from which tTNA is grown by anodization. The structural quality of a deposited Ti film and its adhesion to the substrate appear to be interrelated factors which can be optimized by the variation of sputtering pressure and substrate temperature. Although a dense compact structure is the most desirable property of the Ti film as an anodization substrate, however, the routes (increase of substrate temperature and decrease of sputtering pressure) that lead to such structure may also induce micro strain, which in turn reduces the adhesion property. Therefore, optimization of both adhesion and structural property is the key to achieve an ideal Ti substrate to produce tTNA of extended height.

In this present investigation, we represent a robust self-organized tTNA of appreciable enhanced height on glass substrate by anodization technique with ammonium fluoride and ethylene glycol as an electrolyte. Prior to anodization the Ti metal layer was deposited on a glass substrate by facing target sputtering (FTS) technique, which is a very effective technique for the deposition of high quality thin film. Because of its total plasma confinement, FTS system can achieve deposition, free from the damage, caused by γ electrons, O^- ions and high atomic mobility at the surface of the substrate. The Ti metal layer was deposited at a fixed elevated temperature of 420 °C with various sputtering pressures: 0.1 Pa, 0.5 Pa, 1 Pa, and 1.5 Pa. To the best of our knowledge, in this present investigation, the tTNA, prepared from the Ti layer that was prepared with sputtering pressure 1.5 Pa, is the highest (6.3 ± 0.3 μm) reported value on glass substrate.

2. Experimental details

The Ti layer on a glass substrate was deposited in two steps [4]. The first layer was deposited on the whole substrate and the second layer was deposited only on the half portion of the first layer while the other half was covered by a mask as depicted in the schematic diagram in Fig. 1 (inset 1). The detailed description of the FTS unit was

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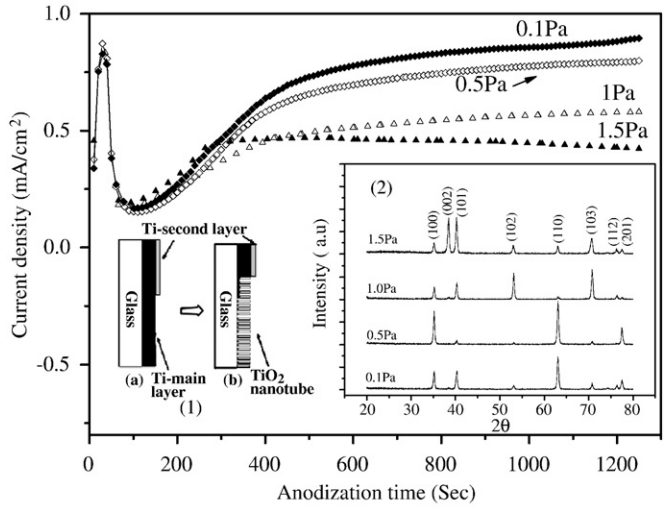

Fig. 1. Current-time behavior during anodization of Ti layers which are deposited on glass substrates at various sputtering pressures. (inset 1) Schematic diagram of (a) the Ti bilayer on glass substrate before anodization. (b) Transparent TiO_2 nanotube on the glass substrate after anodization. (inset 2) GIXRD patterns of Ti thin films, deposited on glass samples at various sputtering pressures.

given elsewhere [20]. The thickness of the Ti first layers for various sputtering pressures were in the range of 2.8–3.2 μm, measured with a mechanical surface roughness meter (Acretech, 1500 DX). Anodization of the sample was performed in a bath containing 0.25 wt.% NH_4F and water in ethylene glycol solution. Anodization was performed in room temperature under constant-voltage conditions using a source meter (Model-2400 Keithley Instruments, Inc) and the current response of the sample was monitored in real time using the same meter interfaced with a computer. The anodization voltage was ramped (2 V s^{-1}) from open-circuit potential to + 50 V versus Pt and held constant throughout the anodization process.

3. Results and discussions

The observation of nanotube formation from various Ti layers is described as follows. For the Ti layer deposited at 1.5 Pa, the whole anodization process successfully completed in 29 min and the sample became transparent. In the case of the Ti layer deposited at 1 Pa sputtering pressure, nanotube formation is evident but these samples never become homogenously transparent. It was noticed that the Ti layer starts pilling out during the anodization process of Ti layers deposited at 01. Pa and 0.5 Pa.

Fig. 1 shows the representative current transient, recorded during anodization of Ti layers in the ethylene glycol-based electrolyte. From the local minimum, observed in the anodization curve, the current increases slowly, which represents the enhanced rate of dissolution. This stage is followed by a steady state when anodization current reaches a saturation value. At this stage dissolution and oxidation of titanium reaches a kind of equilibrium which leads to maximization of formation of nanotube. Interestingly, only the Ti film, deposited with 1.5 Pa, shows a constant value of anodization current over a considerable time, but all other samples show a larger amount of dissolution which leads to enhancement of current.

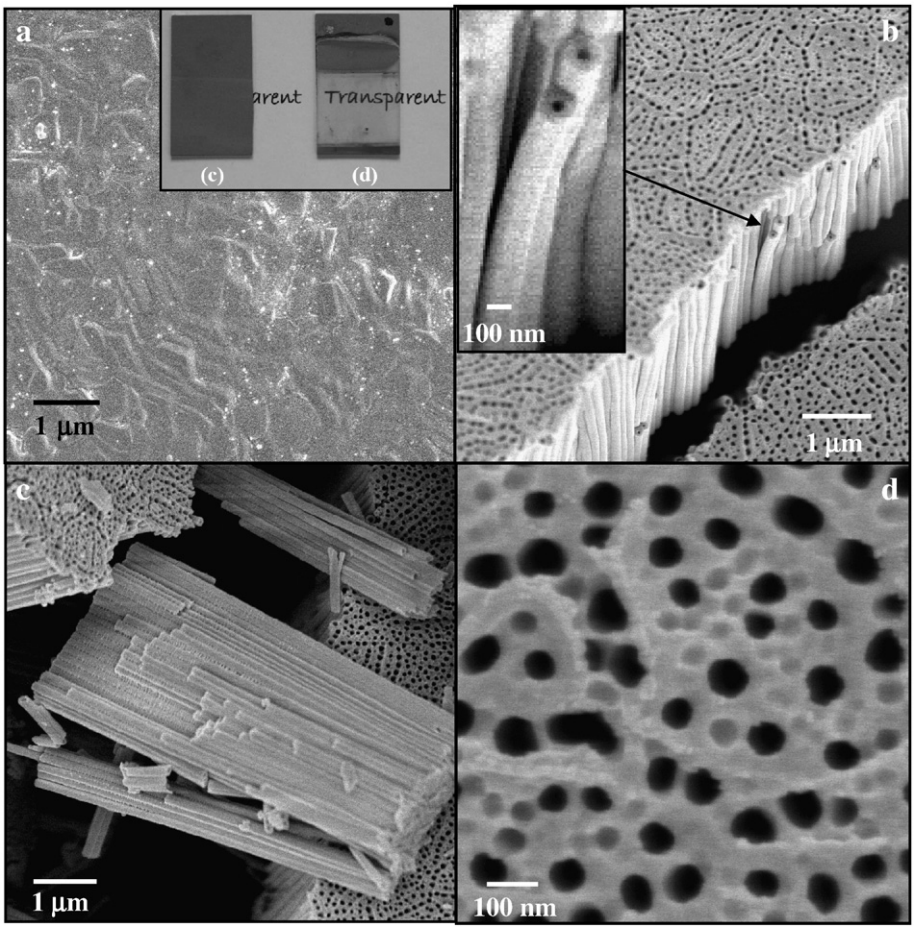

Fig. 2. FESEM (a) images of Ti layer surface (inset c). Photograph of Ti bilayer on glass substrate before anodization (inset d) transparent TiO_2 nanotube on the glass substrate after anodization.(b) tilted view of the transparent TiO_2 nanotube array. (c) side view of the transparent TiO_2 nanotube array (c) top view of the transparent TiO_2 nanotube array.