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Nitrogen doped anodic TiO_2 nanotubes grown from nitrogen-containing Ti alloys

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ABSTRACT

N-doped TiO_2 nanotubes were produced by anodization of a TiN alloy. The alloy was prepared to contain approximately 5 at.% of N from high-purity Ti and TiN powders using an arc-melting and consisted of a two-phase structure with different N-contents. Anodization of the alloy in fluoride-containing electrolyte results, under optimized conditions, in the growth of an ordered TiO_2 nanotube layer on both phases. On the N-rich phase significantly smaller nanotubes are grown while on the low N-concentration phase nanotubes with larger diameter were formed. However, XPS and photoelectrochemical measurements demonstrate successful nitrogen doping of the resulting nanotube layers, which leads to a significant visible photoresponse from this material.

1. Introduction

Since the work of Fujisima and Honda [1] in 1972 it is well established that TiO_2 can act as a photoactive material or photocatalyst due to the semiconductive nature of anatase with a band gap energy $E_g \sim 3.2$ eV [2]. Due to its comparably high band gap energy, photoinduced processes typically require UV light irradiation ($\lambda < 380$ nm). This does not allow an efficient use of solar energy as the UV part amounts only to about 2–3% of the solar spectrum. To enhance efficiency of the solar light conversion in the visible range, considerable efforts have been taken to engineer the band gap by doping of the electrode with suitable species.

Asahi et al. [3] reported that improved photocatalytic activity of TiO_2 under visible light irradiation can be achieved by nitrogen doping. Thereafter also transition metals or other non-metals have been introduced into TiO_2 layers and a visible response of a various magnitude has been reported for the different approaches [4–6]. However, up to now, still the most efficient procedure to narrow the band gap energy of TiO_2 is nitrogen doping. This can be achieved by sputtering TiO_2 surfaces in nitrogen-containing gas mixtures [3], annealing in NH_3 gas [7] or by chemical routes during the precipitation of TiO_2 nanoparticle mixtures [8]. These processes were mainly applied to produce N-doped TiO_2 nanoparticulate layers. Over the past few years another route of producing highly defined TiO_2 morphologies, i.e., ordered nanotube layers has attracted considerable interest [9].

Recently, we showed that these organized TiO_2 nanotube layers can be doped with carbon in acetylene [10] or with nitrogen using ion implantation [11,12] and in NH_3 [13,14] gas streams. These organized TiO_2 nanotubes structures offer the advantage of combining a well defined nanostructure with a "high surface area".

In the present work, we investigate an alternative doping approach, i.e., using a TiN alloy as substrate in the anodization process with the idea to directly incorporate the nitrogen into the growing anodic TiO_2 tubes and, therefore, to create a visible range photoresponse.

2. Experimental

A nitrogen-containing titanium alloy (TiN alloy) was prepared from high-purity Ti and TiN powders by using an arc-melting apparatus equipped with a turbo molecular pump. The TiN alloy contains nominally 5 at.% of N.

The alloy ingot was sawed into slices and prior to anodization the surface of the alloy was polished with abrasive paper and diamond particle slurries successively to a final finish of 1 μm diamond paste. For comparison titanium foils (0.1 mm thickness and 99.6% purity) were used and treated identically. The substrate surfaces were degreased by sonicating in acetone, isopropanol, and methanol, rinsed with deionized (DI) water and dried in a nitrogen stream.

Nanotubular oxide layers and compact oxide layer were produced on these alloy plates anodization using a conventional three-electrode configuration with the platinum gauze as a counter electrode and a Haber-Luggin capillary with Ag/AgCl (1 M KCl) reference electrode.

To obtain nanotubes, a glycerol + water (50:50 vol%) + 0.27 M NH_4F mixture was used as an electrolyte. Anodization was carried out at 20 V for 2 h, after the potential was ramped from open

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circuit potential (OCP) to 20 V with a sweep rate of 500 mV/s. To obtain a compact oxide TiO_2 film, anodization was carried out at 20 V for 3 min with a sweep rate of 100 mV/s in 1 M H_2SO_4 electrolyte. Then the samples were rinsed with DI water and dried in a nitrogen stream. All the experiments were carried out at room temperature.

For morphological characterization of the samples, a field-emission scanning electron microscope was used. The cross-section images were taken from cracked layers after scratching the sample surface. Energy dispersive X-ray analyzer fitted to the SEM chamber was used for determining the composition. The composition and the chemical state were characterized by using X-ray photoelectron spectroscopy. X-ray diffraction analysis was used for determining the crystalline structure of the samples.

To convert the nanotube layers into anatase, the samples were annealed at 450 °C for 1 h with a heating and cooling rate of 30 °C/min using a rapid thermal annealer.

Photoelectrochemical characterization was carried out with a set up consisting of a 150 W Xe arc lamp as an irradiation source and a cornerstone motorized 1/8 m monochromator. Phototransient spectra were acquired in 0.1 M Na_2SO_4 at 500 mV.

3. Results and discussion

Fig. 1 shows SEM images of the TiN alloy surfaces before (a) and after anodization (b–e) in the F-ion containing electrolyte. For comparison a sample of pure titanium (f) was anodized under the same conditions. The insets show SEM cross-sectional images of the respective structures. In some parts of Fig 1a and b, there are some scratch marks that served for alignment of the sample locations to perform SEM and EDX measurement at the same places before and after anodization. As shown in Fig 1a, the alloy has a two-phase surface structure with lighter and darker regions. After anodization, the two-phase structure can even more clearly be seen in Fig 1b. In the darker region (Fig 1c) typical TiO_2 nanotube layers with approximately 650 nm thickness and 80 nm diameter were grown. In the lighter region porous layers with a thickness of 530 nm but only a diameter of 20 nm were produced. Fig 1e shows the border between these two regions. For the anodized pure titanium the tube length is about 850 nm and the diameter is about 100 nm (Fig 1f) i.e., overall the tubes on the anodized TiN alloy have lower thickness and a smaller diameter (the latter particularly apparent in the brighter phase).

Fig. 2a shows EDX spectra of different regions for the TiN alloy before and after anodization. As can be seen for the sample before anodization, there are mainly the two elements of the alloy (Ti and N) detected while after anodization, also oxygen is detected reflecting the oxide growth. An evaluation of several spectra revealed that the phase providing a small (20 nm) nanotubes diameter contained significantly more nitrogen (15–18 at.%) than the phase where 80 nm tubes were grown.

Evidently, the morphology of the tubes is very sensitive to the N-content in the alloy substrate. Different N-contents also in the tubes (not only in the substrate) was confirmed by AES measurements on the two different tube morphologies. While fully quantitative evaluation of the AES results turned out to be difficult, the peak shapes clearly indicated a higher N-content in the tubes grown on the N-rich substrate phase.

In order to obtain the information on the amount and chemical state of the nitrogen in the oxide nanotubes XPS characterization of the tube layers was carried out. Fig. 2b shows the XPS spectrum acquired for the TiN alloy before and after anodization. In the sample before anodization the main XPS peak for nitrogen 1s is located at a binding energy of 396 eV and a smaller peak at 400 eV is apparent. After anodization a new peak at 402 eV is the dominant feature while still smaller peaks of 400 eV and 396 eV can be detected. Generally the literature ascribes the peak at 400 eV to N_2 present physisorbed on TiO_2 surfaces [15,16]. The peak at 396 eV corresponds to nitride forms, i.e., can be ascribed to Ti–N binding in the substrate. The peak at a binding energy of 402 eV can be ascribed to titanium–oxy–nitride (Ti–O–N) compounds that were in literature several times identified as being an active TiO_2 doping species [17,18]. Quantitative evaluation yield of the XPS data of the tube surface indicates that 2 – 3 at.% of N is being present as Ti–O–N in the nanotubes.

Fig. 2c shows the XRD spectra for the anodized TiN alloy and the anodized pure Ti, i.e., surfaces that both carry nanotube structures. The data are given for samples after annealing in air at 450 °C for 1 h. It is evident that in both cases an anatase TiO_2 structure can be identified. The as-anodized samples are amorphous – this typically leads to a low photoresponse. However, these tubes can easily be transformed by annealing to an anatase structure with a high photoresponse in the UV range [19].

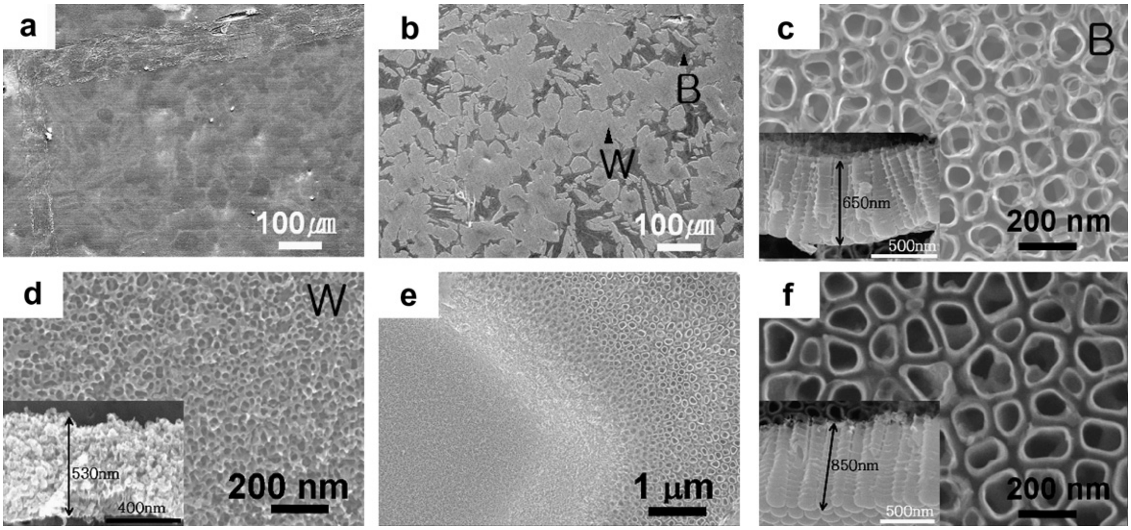

Fig. 1. SEM top-view images of the TiN alloy before (a) and after anodization (b). High magnification for the black (c) and white (d) regions in (b). (e) Border between black and white regions. (f) Anodized pure titanium at the same conditions. The insets show the cross-section images of the corresponding regions and samples.