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Influence of fluoride content on the anodic formation of TiO₂ nanopores/nanotubes in Ti films

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Abstract : The formation of nanostructured TiO₂ oxides in the form of nanotubes or nanopores grown on Ti films was investigated. Ti thin films were deposited by radio-frequency (RF) magnetron sputtering on silicon substrates and then anodized. Anodization was performed in glycerol electrolytes containing 0.6 wt.% and 1.2 wt.% ammonium fluoride (NH₄F) with an applied potential from 20 to 60 V. The morphology and structure were identified by means of scanning electron microscopy (SEM) and X-ray diffractometry (XRD).

The effect of fluoride concentration on the forma-

tion of nanotubes or nanopores prepared on Ti thin layer have not been understood, besides most of the works are focused on Ti sheet.

We show in the present work that a simple parameter as the NH₄F content in the electrolyte can turn the morphology from porous to tubular. It can allow an understanding of the mechanism of formation of pores/tubes and its practical impact.

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Keywords : RF magnetron sputtering; TiO₂; Anodic oxidation; Thin film.

INTRODUCTION

Highly ordered, vertically oriented TiO₂ nanotube-arrays fabricated by potentiostatic anodization of titanium have been found to possess a variety of advanced applications, including their use in sensors^[1-5], dye sensitized solar cells^[6-8], hydrogen generation by water photoelectrolysis^[9], photocatalytic reduction of CO₂ under outdoor sunlight^[10], and supercapacitors^[11,12]. Furthermore, the nanotube arrays have demonstrated great utility in biomedical related applications including biosensors, mo-

lecular filtration, drug delivery, and tissue engineering^[13-15].

However, most of the works have been focused on the anodization of titanium foils, which limits the application of such a material in functional microdevices (e.g. dye-sensitized solar cells or electrochromic devices)^[16,17]. Recently, some researchers have successfully developed the technology to grow the nanotube arrays from thin titanium films using anodization on a variety of substrates including glass^[18-20], conducting glass (FTO, ITO)^[21], and silicon^[22-24], but anodization of thin films is a

much less well-known process than foils due to its specific complications.

In the case of Ti thin films using conventional deposition methods, is possible to obtain by anodization different microstructures like nanopores or nanotubes^[25-27].

It is well known that the TiO₂ nanostructures grown by anodization strongly depend off the morphology of the Ti film deposited on substrate. Some authors claim that the columnar structure in Ti thin film is essential for the nanotubes formation by anodic oxidation^[24]. Another ones affirm that the crystallographic orientation of the Ti thin film is critical for the nanotubes obtention, but there have been cases in which the Ti thin film structure was columnar and nanopores were obtained instead of nanotubes. As well it was reported the growth of nanotubes from Ti thin film with different crystallographic orientation^[26].

In this paper, we will discuss the effects of fluoride contents on the formation of pores/tubes in TiO₂ films, in order to optimize the fabrication process and finally to improve their properties.

EXPERIMENTAL PROCEDURE

Deposition of a Ti thin film on a Si substrate

Ti films were deposited by RF magnetron sputtering on p-type Si (100) wafer with 300 nm layer of SiO₂. The substrate was heated at 500°C. Target of 99.9% Ti was used as the material source. The chamber pressure was maintained at 0.5 Pa during the deposition process. Sputtering was carried with a pure gas argon flowing of 8 cm³/min. The distance between the target and the substrate was 14 cm and the sputtering power was 150 W using RF power supply. Under these conditions, the deposition rate was 2.9 nm/min and a 600 nm thick Ti film was obtained after 210 min.

Fabrication of TiO₂ nanostructure

The anodization was conducted in a two electrode electrochemical cell with a platinum foil as cathode and silicon substrate with titanium film as anode at a constant potential.

Before anodization the specimens were

degreased in acetone and isopropanol using an ultrasonic bath during several minutes and then rinsed in deionized water (DI) and dried with a nitrogen stream.

The growth of the nanostructure has been obtained in a glycerol solution with different NH₄F concentration ranging from 0.6 wt.% to 1.2wt.% at room temperature. All electrolytes were prepared from reagent grade chemicals. The solution was stirred^[28] using a magnetic stirring bar (20 mm long) at 240 rpm for homogenization.

Anodization was performed applying a ramp during 3 min from 0 to the desire voltage (20, 30, 40, 50 and 60V) and finally holding the voltage constant during 30 min using 2612A Keithley system sourcemeter. The distance between the two electrodes was kept at 2 cm in all the experiments. After the electrochemical treatment, the samples were immediately washed with deionized water and dried in nitrogen stream.

Finally, in order to convert the amorphous TiO₂ structure into a crystalline one, samples were annealed at 550°C for 2 h in air.

Characterization of Ti thin film and TiO₂

The samples of the Ti thin film and TiO₂ were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Scanning electron microscope (Zeiss Supra40 Gemini) was employed for the morphological characterization of the TiO₂ samples and analysis of pictures were performed by ImageJ. XRD patterns were recorded with a diffractometer (PANalytical model Empyrean) equipped Cu K α ($\lambda=0.15418$ nm) using a generator voltage of 40 kV and current of 40 mA.

RESULTS AND DISCUSSION

Composition and microstructure of the titanium thin films

Figure 1 shows the SEM top images of Ti film deposited by RF magnetron sputtering at 500°C. The film has rough granular structure, and some Ti grain coarse it was observed. The average grain size of the granular structure is 80 nm and Ti grain coarse is larger than 150 nm. Adhesion between Ti and Si

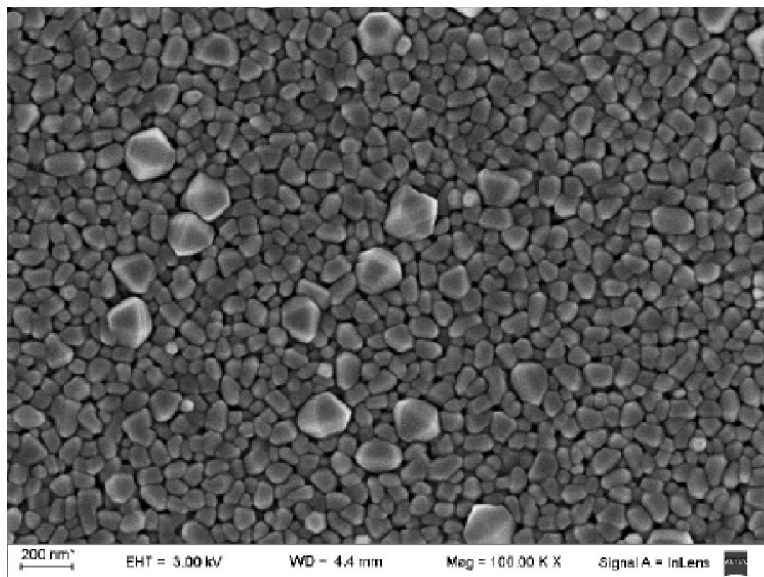


Figure 1 : SEM top views of Ti films deposited at 500°C

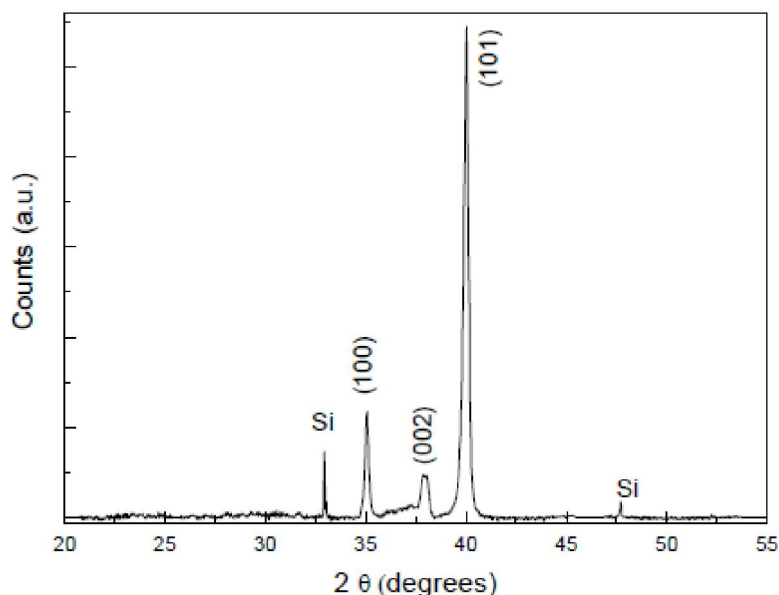


Figure 2 : XRD patterns of Ti films deposited at 500°C

substrate was found to be good. A peeling test indicated that not detachment was observed.

In Figure 2, XRD patterns of Ti deposited by RF magnetron sputtering at 500°C are shown. All of peaks are identified as hexagonal Ti (00-044-1294) at 2θ near 35°, 38° and 40° which correspond to the planes (100), (002) and (101), respectively. The relative intensity of the peaks indicates the presence of a polycrystalline microstructure without strong preferred orientation.

TiO₂ nanostructure thin films

The corresponding XRD patterns of TiO₂

nanostructure fabricated from Ti film at 60 V anodizing voltage after being annealed are shown in Figure 3. Typical peaks of anatase phase at 2θ near 25°, 37° and 48° are observed, which correspond to planes (101), (004) and (200), respectively. Also typical peaks of rutile phase at 2θ near 27°, 36°, 41° and 54° are observed which correspond to the planes (110), (101), (111) and (211), respectively. The peak at 2θ near 33° belongs to Si (200) plane of the substrate.

In summary, the structure consists of a mixed phase of anatase (01-086-1157) and rutile (00-034-

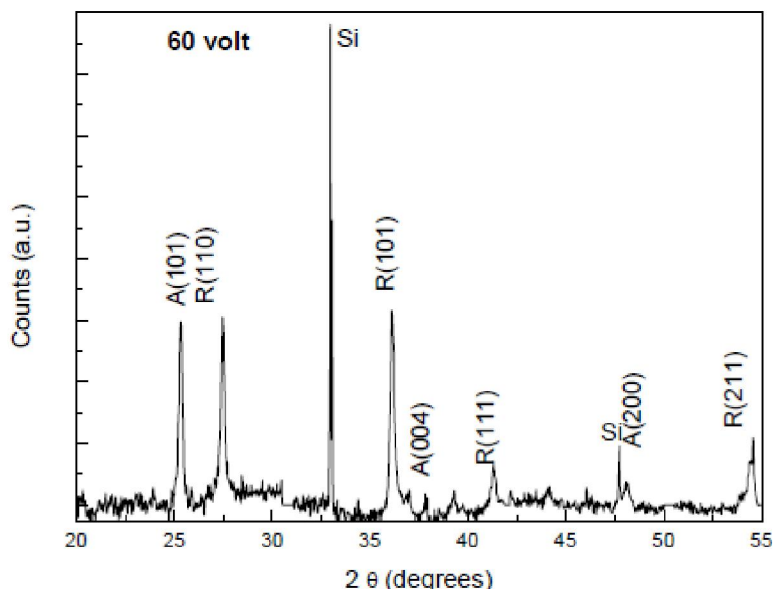


Figure 3 : XRD patterns of TiO_2 nanostructure prepared on Ti films

0180). According with the literature it is well known that there is a mixture of phases which depend strongly on heat treatment^[29,30] and of the substrate temperature during the deposition of the film^[31].

In order to find the appropriate conditions for the synthesis of TiO_2 nanotube arrays, we studied the effect of applied voltage while keeping the concentrations of NH_4F constant. Two sets of experiments were performed, one of them at 0.6 wt.% and the other one at 1.2 wt.% NH_4F in glycerol solution. Applied voltages were kept at 20, 30, 40, 50 and 60 V for 30 min durations.

Figures 4a, b, c show the SEM image of anodic TiO_2 at different potentials (20, 40 and 60 V) with 0.6 wt.% NH_4F solution. It can be seen a nanoporous structure, there are some grains with grains sizes well above the average. The pores are formed in the middle of the grains and the large grains can be formed over a pore. The pores have diameters of approximately 20 nm and average interpore distance of approximately 80 nm.

Figures 4d, e, f show the SEM image of anodic TiO_2 at different potentials (20, 40 and 60 V) with 1.2 wt.% NH_4F solution. At this concentration a nanotubular structure is obtained. The TiO_2 nanotubes are clearly seen uniformly distributed over the surface.

Figure 5 shows the size of nanotubes and wall thickness as a function of the applied voltage. When

voltage was raised from 20 to 60 V even larger diameter nanotubes were obtained, but wall thickness remained practically constant. It is well known that nanotubes diameters and wall thickness greatly depend on applied voltage^[32]. Although the diameter increases with the voltage applied, in this case the size is limited by the grain size of deposited titanium.

Ordered porous or tubes layers could be grown depending on experimental details of the anodization process and the starting material. For the formation of TiO_2 nanotubes or nanopores it is essential that steady state conditions between 1) oxide formation and b) metal dissolution can be established. The fluoride rich layer is considered to be the key-reason for the pore to tube transition and is a crucial condition for the formation of a tubular rather than a porous structure^[33-36]. Nevertheless, the first stages of nanotubular/nanoporous layers are very similar to the formation of barrier-layers.

When the concentration is 0.6 wt.% NH_4F nanopores are obtained but with 1.2 wt.% NH_4F nanotubes are formed. Probably at high concentration, the corrosion rate of titanium dioxide caused by the fluorine ion in the electrolyte is faster than the growth rate. The increasing concentration is the suitable condition for the nanotubes growth in the film. Therefore, the present work shows that a simple parameter as the NH_4F content in the electrolyte can

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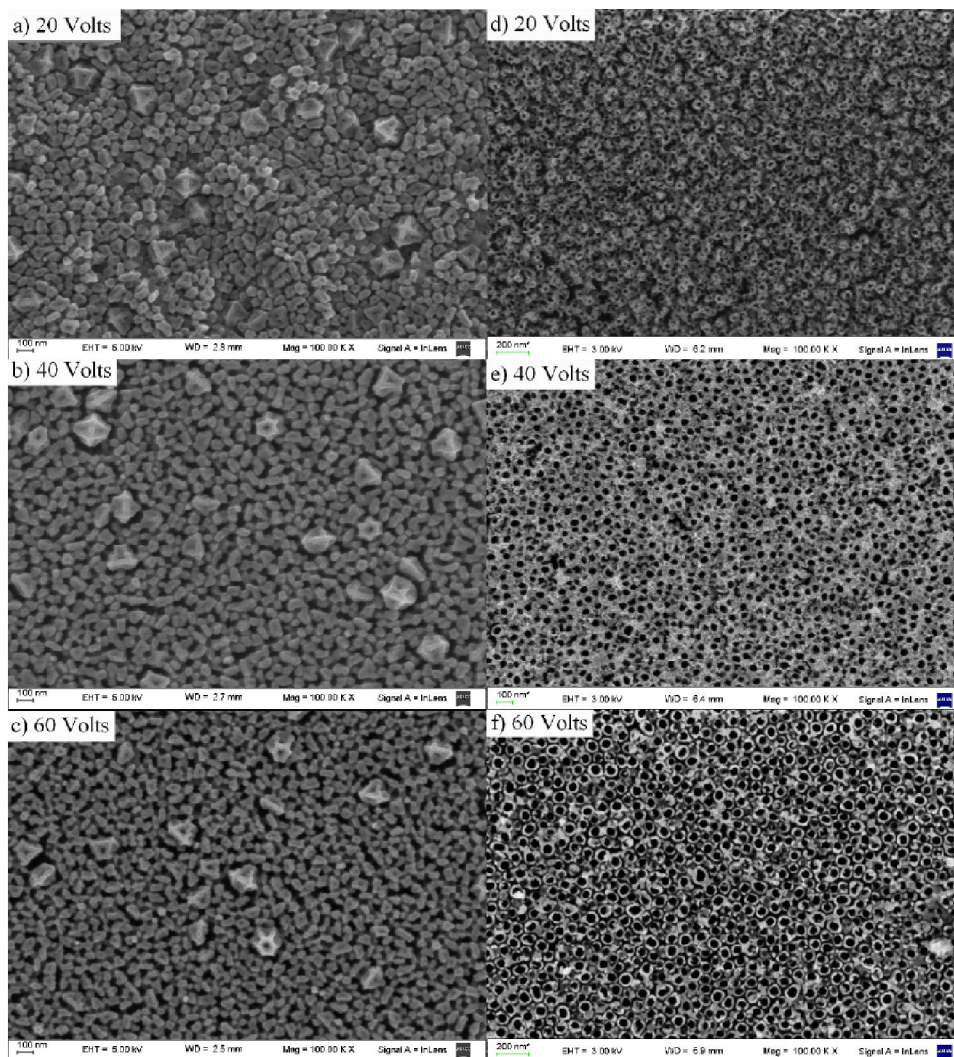


Figure 4 : SEM top images of TiO₂ structure prepared in glycerol electrolyte containing: 0.6 wt.% NH₄F (a) 20 V, (b) 40 V, (c) 60 V and 1.2 wt.% NH₄F (d) 20 V (e) 40 V (f) 60 V

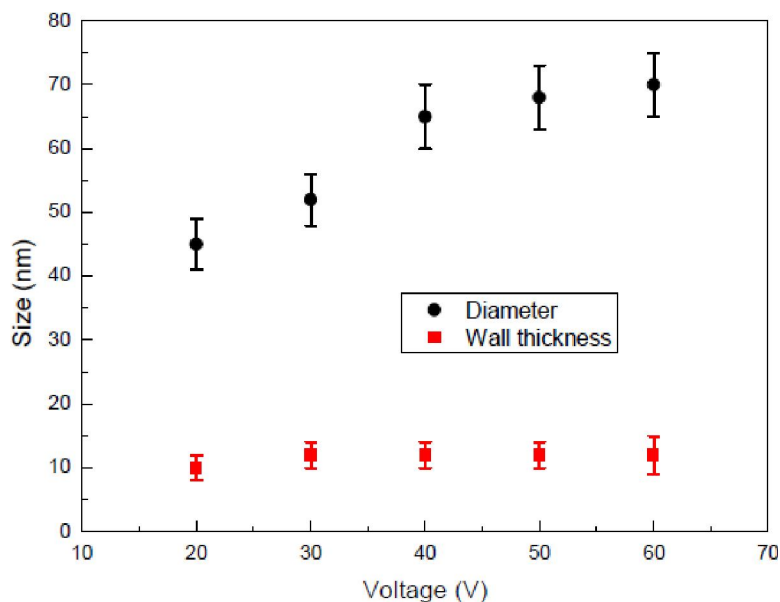


Figure 5 : Size of TiO₂ nanotubes grown on Ti films as a function of the applied voltage

turn the morphology from porous to tubular when the starting material is Ti thin film.

CONCLUSIONS

The present work shows the fabrication of ordered porous/tubes anodic TiO₂ arrays. These structures can be grown in glycerol/fluoride electrolyte in a specific range of NH₄F concentrations. At low NH₄F content a nanoporous morphology is obtained. The pore size is 20 nm and interpore distance of 80 nm independently of the voltage applied. Instead at high NH₄F content an entirely tubular morphology is obtained. At different anodization potentials ordered nanotube arrays with diameter size from 45 nm to 70 nm were fabricated. Probably the nanotube size is limited by the grain size of the titanium deposited by magnetron sputtering.

In summary, considerable parameters for the growth of the nanostructure is the grain size of the titanium thin film and the NH₄F concentrations.

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