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Long-Range Hexagonal Arrangement of TiO_2 Nanotubes by Soft Lithography-Guided Anodization

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ABSTRACT

Long range hexagonally ordered TiO_2 nanotube arrangements have been synthesized by employing a novel strategy consisted of combining the well-known Laser Interference Lithography technique together with electrochemical anodization methods. By properly tuning the fabrication parameters that make match between both techniques, TiO_2 nanotube arrays having near 32 nm of inner diameter, wall thickness around of 25 nm and 210 nm of lattice parameter were anodically grown on pre-patterned Ti foils over large sample surface areas, typically of several squared centimetres in size. This opens the possibility to the development of new types of functional devices based on self-organized morphologies of anodic TiO_2 nanotubes, requiring both high spatially ordered and defect-free nanotube arrangements.

1. Introduction

During the last decade, TiO_2 nanotubes have received great attention in several research fields due to their unique tubular geometry together the exciting electronic and photochemical features exhibited by this oxide. The excellent biocompatibility [1], chemical and mechanical robustness [2–4], wide energy band gap [5], large specific surface area together with high catalytic and photocatalytic activities [6] exhibited by this multifunctional material make TiO_2 nanotubes useful for a wide range of applications, covering from dye-sensitized solar cells [7–10], water splitting for H_2 production [11–15], photocatalytic decomposition of hazardous wastes [16–19], gas sensors [20–23], drug delivery [24] and orthopaedic prosthesis [25,26], or inclusive for magnetics and diluted magnetic semiconductors [27,28], among others. Novel synthesis strategies couple titania nanoparticles or nanotubes to 1D photonic crystals of titania nanotube and found a significant increase of the power conversion efficiency of dye-sensitize solar cells [29,30]. Also matching the surface plasmon resonance wavelength of gold nanoparticles to the photonic band gap of a titania nanotube film resulted in an enhancement of the photoelectrochemical water splitting performance [14,31].

The origin of the excellent physicochemical properties of TiO_2 nanotubes, and particularly of its unusual photocatalytic activity is not well fully understood. There is a controversy on whether the geometrical structure or the crystalline nanotexture of the nanotubes prevail. Liu et al. showed, based on a theoretical kinetic model, that the geometrical parameters of TiO_2 nanotube arrays (tube length, inner diameter and tube wall) have a strong impact on their photocatalytic activity [32]. Other studies point out that the crystallographic facets exposed in the nanotubes wall significantly affect their photocatalytic and photochemical properties. In particular, the enhancement of the presence of the more reactive {001} crystal facets of anatase respect to the more thermodynamically stable {101} facets is demonstrated in such nanostructures, with improvement of the performance of TiO_2-based solar cells or in the photocatalytic decomposition of waste materials [33,34].

The possibility of synthesizing films of self-aligned TiO_2 nanotubes displaying a rather uniform and well controlled geometry by means of the inexpensive and flexible electrochemical anodic oxidation method, i.e. titanium anodization [5,35–38] has made this material widely accessible and applicable in many fields. Furthermore, continuous and increasing research efforts have allowed a deep understanding on the electrochemistry and mechanism of TiO_2 nanotubes growth [39–45], thus enabling a

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high control degree on the geometrical parameters of the resulting nanotubular anodic titanium oxides [5,15,46–49].

Thus, in the last years, there is an increasing interest in the development of TiO_2 nanotubes with superior uniformity of the geometrical and crystallographic parameters, coupling different properties as respects to their photocatalytic, photonic and electronic properties in order to obtain significant enhancements of the efficiency of TiO_2-based devices [50]. The investigation of novel synthesis strategies based on electrochemical anodization of Ti and allowing for an improvement of the uniformity and control degree of the nanotubes morphology, namely their diameter, wall thickness and spatial periodicity, over large surface areas can enhance the performance of current applications of TiO_2 nanotubes and may also give rise to novel uses of this highly functional material [51]. In this regard, a two-step anodization process has been employed in order to enhance the ordering degree of the TiO_2 nanotube array [52,53]. This method, based on the spontaneous nanotubes self-ordered growth during the anodic oxidation of Ti, allows for an improvement of the spatial arrangement of the resulting nanotubes, despite the fact that a long-range hexagonal ordering of the nanotubes was not achieved by this technique. The use of high purity starting Ti foils has also been demonstrated to exert a strong impact on the final hexagonal arrangement of the TiO_2 nanotubes grown by the two-step anodization method [52].

Alternatively, Focused Ion Beam (FIB) has also been employed to define a hexagonal array of nanometric concavities on the surface of a Ti substrate, which act as seeds for the nucleation of TiO_2 nanotubes in a further anodization step [54,55]. By this guided self-assembly method, an almost perfect hexagonal geometry was obtained in the TiO_2 nanotube arrays. However, the limitation in the maximum areas that can be effectively patterned by FIB (of only few squared microns in size) and the expensiveness of this technique make it not suitable for practical applications [56]. On the other hand, nanoimprinting of Ti by using metallic molds allows a high-throughput formation of ideally ordered pretexturing patterns that can generate highly ordered porous or nanotubular TiO_2 over a large sample area by adopting appropriate anodizing conditions [57].

In this work, we report on a novel combination of Laser Interference Lithography (LIL) and electrochemical anodization techniques that allows for guiding the spatially ordered growth of TiO_2 nanotubes arranged over large surface areas. This combined approach has been effectively demonstrated in the case of Al_2O_3 nanoporous films grown by the aluminum anodization technique in a previous work [58], and it is now adapted to anodic titania nanotube films as a proof of concept of the flexibility and suitability of this combination of nanofabrication techniques. Briefly, the process involves the use of LIL to pattern a photoresist layer with a highly regular hexagonal pattern of holes using a three-beam configuration [59]. The interpore distance is here the main parameter to control. Next the periodic structure is fully transferred into a second layer of SiO_2, which will work as a hard mask during the first stages of the anodization. A clean titanium surface is hence exposed at the bottom of the holes generated in the SiO_2 layer. During the subsequent anodization process, the hard mask forces the nucleation of the pores at the desired positions, resulting in a perfectly-ordered cellular array of TiO_2 nanotubes grown over large surface areas. It also prevents the oxide dissolution, which usually takes place at the cell junctions of the fluoride-rich layer typical of titanium anodization processes, assuring the coalescence of the whole structure [60]. The formation of a periodically ordered and high aspect ratio nanotube arrangement within TiO_2 could be achieved by properly tuning the more appropriate anodizing conditions for the nanotubes growth. These combined processes allow for the fabrication of hexagonally ordered TiO_2 nanotubes over a large area of the sample surface, thus enabling the expansion of the application fields of research for the anodized TiO_2 nanotube arrays requiring high spatially ordered and defect-free tube arrangements.

2. Experimental

Disc shaped high purity Ti foils (99.6 +%, Goodfellow, 2.5 cm in diameter) were mechanically polished up to a mirror-like finishing. The Ti substrates were then cleaned by ultrasonication in acetone, isopropanol and ethanol. Some of the polished substrates were directly anodized at room temperature ($20 \pm 2\,^{\circ}C$) in ethylene glycol based electrolytes containing 0.3 wt.% of NH_4F and 1.8 wt.% of H_2O, without any pre-patterning step, at several anodization voltages ranging between 30 V and 120 V.

A second batch of polished Ti substrates were lithographically patterned by means of a Laser Interference Lithography (LIL) setup described in detail elsewhere [58]. The layer stack employed for the LIL patterning is schematized in Fig. 1(a) and it consists of a SiO_2 protective layer deposited by means of sputtering (30 nm) and two spin-coated layers: a 70 nm of antireflection coating (DUV 112 from Brewer Science), together with a 200 nm of a high resolution positive photoresist (UV2000 from Microresist Technology). The hexagonal pattern was produced in a single exposure by using a 266 nm of wavelength CW laser, in a 3-beam configuration LIL setup and controlling the energy dose. The 3-beam LIL setup is based on the work of de Boor et al. [59], and consists of two mirrors, placed at an angle of 120 to each other, being both perpendicular to the sample plane. In this setup, the three incident waves (direct laser beam and two reflected waves) have wave vectors with 120° symmetry, leading to the hexagonal pattern of dots onto the sample surface. After the laser beam exposure, the photoresist layer was developed employing an alkaline solution to reveal the photo-lithographically printed hexagonal pattern in the photoresist layer. Afterwards, the pattern was transferred to the Ti substrate by a combination of Reactive Ion Etching (RIE) steps. Firstly, an O_2 plasma (25 mTor, 25 sccm, 75 W) was employed to transfer the hexagonal pattern to the organic ARC layer. Secondly, a CHF_3 plasma (transfers it in the SiO_2 layer and exposes in these sites the Ti substrate. Finally, the sample is exposed again to an O_2 plasma etching to remove the remaining organic coatings.

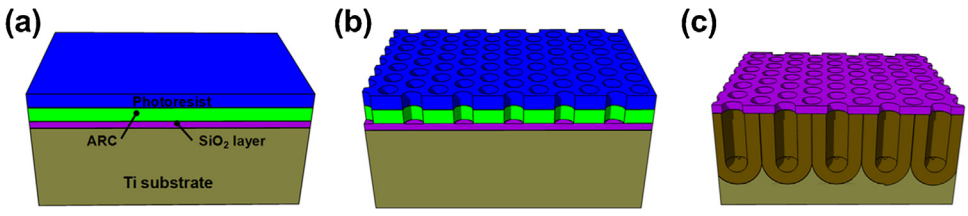

Fig. 1. Schematic drawing of the procedure followed in the fabrication of the patterned Ti substrate employed for the guided self-assembly growth of highly ordered TiO_2 nanotube arrays. a) layer stack b) after LIL exposure and first plasma etching c) after second and third plasma etching and subsequent Ti anodization.