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Cathodoluminescence of TiO_2 nanotubes prepared by low-temperature anodization of Ti foils

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ABSTRACT

We show that anodization of Ti sheets in an ethylene glycol and HF containing electrolyte at temperatures under 0 °C results in the formation of a self-arranged ordered porous structure at the top surface of the sample. This perforated surface structure initiates the growth of an ordered array of titania nanotubes. The inner diameter of nanotubes can be modified in a controlled fashion in the range from 10 nm to more than 250 nm through the change of the electrolyte temperature from −20 °C to + 50 °C. The spectral distribution of cathodoluminescence from a cluster of nanotubes clearly demonstrates the formation of resonator modes which are separated from each other by around 200 meV.

1. Introduction

Titania is widely used as a pigment, in sensors, electrocatalysis, and Grätzel-type solar cells. Titania nanotubes (TiO_2 NTs) exhibit better characteristics as compared to other titania nanostructures for application in photocatalysis, sensing, photoelectrolysis, photovoltaics, lithium ion batteries, and biomedical applications [1]. Titania nanotubes have been produced by a variety of methods, including anodization of titanium foils. Anodization is a relatively simple and cost-effective process which enables the growth of highly ordered TiO_2 NTs.

TiO_2 nanotubes with high aspect ratio were successfully fabricated by using anodization of Ti foils in ethylene glycol based electrolytes [2–4]. By tailoring the anodization voltage and the electrolyte composition, TiO_2 NTs with different inner and outer diameters can be produced, however, the spatial density of nanotubes is also changed in these processes.

It has been recently shown that the variation of electrolyte temperature allows the controlled modification of the inner diameter of the TiO_2 NTs in the range from several tens to hundreds of nanometers, while maintaining a nearly constant density and outer diameter [5]. The production of NT arrays with a controlled (e.g. modulated) inner diameter is of considerable interest for the elaboration of photonic crystals. In addition to traditional applications of titania nanostructures, it has been recently proposed to explore possibilities for photonic applications of titania nanotube arrays [6]. The calculations showed that the metallized TiO_2 NTs are promising for designing and manufacturing negative index materials [6]. Flat and concave lenses assembled from these nanotubes demonstrate good focusing properties at specific photon energies which are determined by the geometry of nanotubes and the metal used. The optical properties of TiO_2 NTs, particularly luminescence, are very important for photonic applications.

In this paper, we report on the cathodoluminescence microanalysis of TiO_2 NTs prepared by anodization of titanium foils in an ethylene glycol containing electrolyte. Some peculiarities of the TiO_2 NT formation at low electrolyte temperatures are discussed.

2. Experimental details

Ti foils (Sigma Aldrich, 99.7% purity, 0.25 mm thickness, $1.5 \times 1.5\ cm^2$ surface) were cleaned by sonicating in acetone, then rinsed in deionised (DI) water and dried with a nitrogen stream prior to electrochemical experiments. For anodization, a constant voltage source (Keithley 4200) with Pt as a counter electrode was used to apply a potential of 120 V for 2 h. The distance between counter and working electrodes was 1 cm. The electrolyte was prepared using 100 ml ethylene glycol, 10 ml H_3PO_4 and 1 ml HF. The experiments were carried out with the temperature of the electrolyte in the range from −20 °C to 50 °C. A JEOL 7001 F (Schottky) field emission scanning electron microscope (SEM) equipped with a Gatan XiCLone cathodoluminescence (CL) microanalysis system was used for morphological and CL characterization. The CL spectra have been excited with 10 keV accelerating voltage, and 10 nA current. Under these beam conditions,

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the estimated electron penetration depth for the bulk TiO_2 is ~750 nm, and majority of detected CL signal is generated in the top ~450 nm of the specimen. CL emission from the TiO_2 NTs is attenuated by the exposure to the electron beam, therefore to reduce beam induced effects the spectra have been collected from 10,000 μm^2 regions that have not previously been exposed to the electron beam.

3. Results and discussion

According to our recent results [5], anodization of Ti sheets in an ethylene glycol and HF containing electrolyte allows one to prepare TiO_2 NTs with controlled inner diameter. The diameter can be varied in a controlled fashion in the range from 10 nm to more than 250 nm through the change of the electrolyte temperature from −20 °C to +50 °C. The anodization process with the electrolyte temperature below 0 °C results in the production of closely packed TiO_2 NTs with a hexagonal transverse section, as shown in Fig. 1a.

An important feature of the Ti anodization process at electrolyte temperatures under 0 °C is the formation of self-arranged ordered porous structure at the top surface of the sample (Fig. 1b). In order to analyze the degree of order in the produced structures, we have generated numerically the diffraction pattern (DP) by taking direct Fourier transform (DFT) from the SEM image. Thus, a DP can be obtained by calculating the direct 2D Fourier transform from the pixel-arrays of SEM pictures [7].

The two-dimensional Fourier transform of the image in Fig. 1b is composed of a diffuse ring which is characteristic of polycrystalline domains of pores, i.e. for structures with short range order. Each pore at the surface represents an initial point for a follow-up growth of a titania nanotube. It is known [7] that a common feature of electrochemical processes related to the preparation of self-organized semiconductor or dielectric porous structures is the random initiation of pitting at the top surface followed by the in-depth ordering as a result of interaction between growing pores or tubular structures. As a result of this random initiation, a disordered nucleation layer is produced at the surface of the sample which has a strong influence on the whole porous structure. The nucleation layer consisting of crystallographically oriented pores is a prerequisite leading to the subsequent formation of self-arranged 2D single crystals of pores. One should remove the nucleation layer in order to evidence the buried ordered network of pores. In contrast, the nucleation layer imaged in Fig. 1b demonstrates short range order, in spite of the fact that no crystallographically oriented pores can be produced during the electrochemical oxidation of the titanium foil. We believe that the observed phenomenon is due to the anodization at the low electrolyte temperature.

The CL emission from the closely packed TiO_2 NT array is characterized by a broad (possibly multi-component) low intensity emission between ~1.5 and 4 eV which may be associated with oxygen vacancy type defects [8] and/ or the radiative recombination of the self trapped exciton [9] The resultant panchromatic cathodoluminescence image of the nanotube array is nearly homogeneous (Fig. 2b) demonstrating similar low emission intensity from the cap layer as well as from the closely packed nanotubes underneath. Note that our experiments were not sensitive for the polarized CL emission.

However, when the individual nanotubes are cleaved from the closely packed array, the CL intensity is significantly enhanced, as illustrated in the panchromatic CL image of Fig. 3b. This CL enhancement is likely to be due to the formation of resonators inside of the isolated TiO_2 NTs. Whispering gallery modes (WGM) propagation due to total internal reflections are well established within the visible spectral range in ZnO resonators with hexagonal cross section and transverse dimensions down to several hundreds of nanometers [10,11]. The refractive index of TiO_2 is dependent on the wavelength [12], porosity [13] and crystal structure [9,12] and ranges between n~2 and 2.6 at ~500 nm.

Taking into account that the refractive index of TiO_2 is similar to ZnO (n~2 at ~500 nm), the WGM can also easily propagate in TiO_2 NTs provided that the ratio of the inner to the outer nanotube diameters is less than ¾, which is clearly the situation in the case of our nanotubes (e.g. see Fig. 1a). The resonator modes can not propagate when the nanotubes are closely packed since there is no air gap between the nanotubes (see Fig. 2).

The microresonator effect can also occur inside a cluster consisting of several TiO_2 NTs. The emission from such a cluster cleaved from the nanotube array is shown in Fig. 3d. Emission from this cluster is much more intense than that of the closely packed nanotubes.

The spectral distribution of emission from the cluster presented in Fig. 4 clearlydemonstrates the formation of resonator modes. There are two possible explanations for the formation of these modes: (i) the emission represents a superposition of modes produced in individual nanotubes, and (ii) the modes are produced in a microresonator formed in the cluster. The first suggestion is less probable, since the nanotubes are not well separated. In addition, the energy separation between the modes observed is around 200 meV,

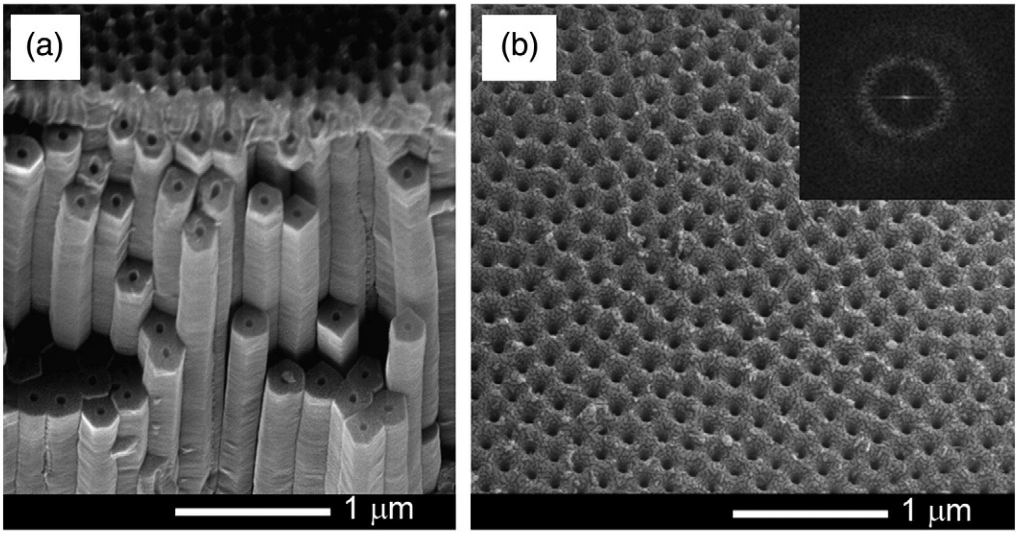

Fig. 1. (a) SEM secondary electron image of TiO_2 NTs produced by anodization of Ti sheets with the electrolyte temperature of −5 °C. (b) SEM SEI of the nucleation layer. The insert shows the two-dimensional Fourier transform.