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Morphology characterization of TiO_2 nanotubes by scanning transmission electron microscopy

The titania nanotubes have become a very attractive material with potential applications in biomedicine, photocatalysis, energy etc. Their properties depend mostly on morphology which results from fabrication conditions. One of the simplest and most efficient method of TiO_2 nanotubes fabrication is electrochemical oxidation of Ti substrate. In this way, well-defined metal oxide nanotubes with controlled diameter and length can be produced. So far, all morphology investigations of titania nanotubes were based on SEM and TEM observations [1,2]. Both techniques give two-dimensional image of the structure of nanotubes and interface between nanotubes and metallic substrate. More information which allows for better understanding the growth mechanism of nanotubes might be taken from three dimensional visualization of the structure based on electron tomography imaging [3,4]. Therefore, in this work we used different methods of electron microscopy to fully characterize the structure of oxide layer fabricated on titanium substrate.

Based on this motivation, the TiO_2 nanotubes with 40-100 nm of diameter were prepared by titanium substrate anodizing method. After anodization, they were annealed at 450^{o}C to change amorphous structure of TiO_2 nanotubes into crystalline anatase one. FIB prepared specimens were analyzed using a Hitachi HD-2700 dedicated STEM (Scanning Transmission Electron Microscopy). Figure 1(a) shows the cross-section BF-STEM image of TiO_2 nanotubes layer on bulk titanium substrate. Higher magnification observations revealed the internal structure of the nanotubes (Fig. 1b). As can be seen the nanotubes are connected by bridges and their diameter is around 80 nm. High resolution investigations confirmed anatase structure of TiO_2 phase after annealing process (Fig. 1c).

In order to obtain three-dimensional structure information a high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) tilt series were recorded. 3D structure of nanotubes was reconstructed using conventional tomographic reconstruction algorithms. The segmentation process of reconstructed 3D structure allowed to show morphology of the nanotubes and connections between them (Fig.2). Additionally, it was revealed that during the growth process nanotubes of smaller diameter coalesce to one nanotube of bigger diameter. Three-dimensional imaging shows the structure elements which are not visible in 2D projections and provided information about nanotubes morphology changes during the growth process.

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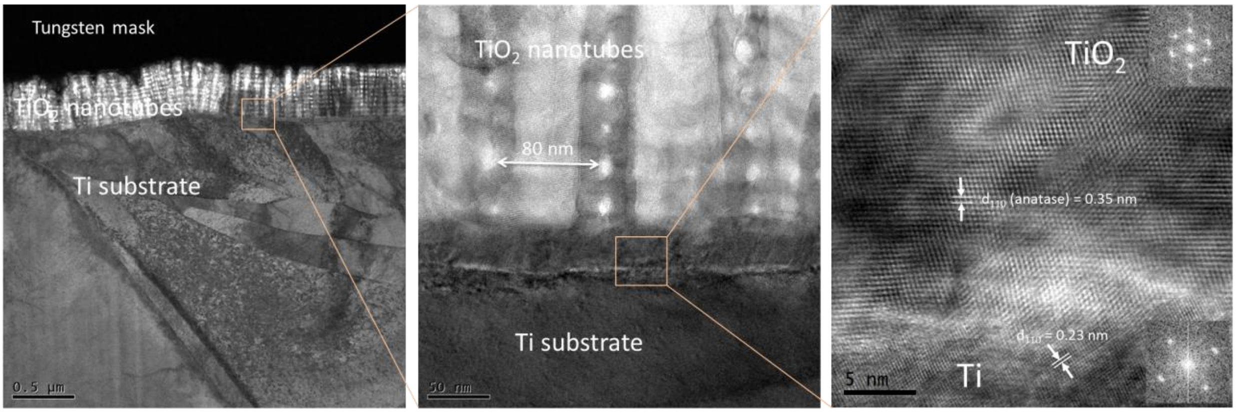

Figure 1. Cross-section STEM images of TiO_2 nanotubes on Ti substrate (a) Overview BF-STEM image of the prepared sample (b) BF-STEM image of TiO_2/Ti interface region with visible nanotubes walls (c) HR-STEM image of TiO_2/Ti interface

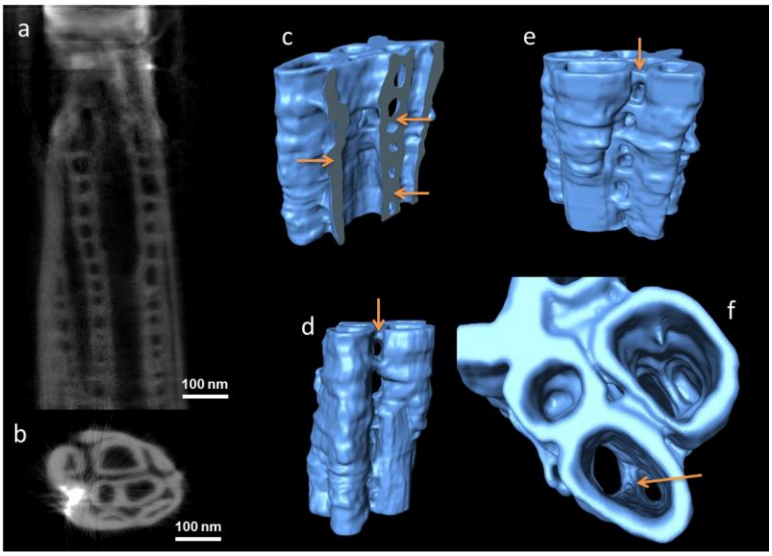

Figure 2. A tomographic reconstruction of TiO_2 nanotubes (a) Longitudinal slice view through the reconstruction (b) Cross-section of the reconstructed volume (c-e) The surface of reconstructed volume after segmentation of selected nanotubes with depicted bridges between nanotubes (f) The surface of reconstructed volume after segmentation of selected nanotubes with depicted place where nanotube split into two nanotubes.