doi:10.1017/S1431927611009317
Microsc. Microanal. 17 (Suppl 2), 2011

A Real Time Observation of Phase Transition of Anatase TiO_2 Nanotubes into Rutile Particles by *in situ* Joule Heating Inside Transmission Electron Microscope

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It has been demonstrated that some properties of TiO_2 are very sensitive to its structure. Since the anatase phase is chemically and optically active, it is suitable for catalysts and supports [1]. Usually, the anatase phase can be transformed into rutile via post-annealing [2], because anatase is thermodynamically unstable. This anatase-to-rutile phase transition, which is dependent upon annealing temperature, induces the variation of the optical properties in TiO_2 films [3]. Therefore, the post–annealing should be a controlled process in order to make desirable properties of a TiO_2 film for various applications. In view of this, we have taken a new approach to synthesize rutile nanoparticles. Here, we report the phase transition of anatase TiO_2 nanotubes into nanometer size rutile particles via *in situ* Joule heating inside a high resolution transmission electron microscope (HRTEM). The Joule heating experiment was carried out by using a special scanning tunneling microscopy holder from "Nanofactory Instruments" in a JEM 4000FX TEM, operated at 200kV. When the TiO_2 nanotube was in contact with the STM tip, the Joule heating experiment was conducted by applying a constant bias voltage. Fig. 1a shows a TiO_2 nanotube contacted on both ends and free standing in high vacuum (10-6 Torr), inside the TEM. Under 10V bias, the current, *I*, starts to increase gradually with time, *t*, and reaches a maximum value of 12 µA in a period of 180 sec, as shown by the *I* vs *t* plot (Fig. 2). Fig. 1(b) shows the image of the TiO_2 nanotube undergoing the heating at constant bias voltage of 10V for 180 sec. On increasing the bias voltage to 20V, it was observed that the current increased drastically to a maximum value of 20 µA in a time period of 130 sec and then started to decrease gradually with the further breaking of the nanotube, while at the same time the nanometer diameter titania underwent a solid state reaction and grew into a bigger crystal of 20-25 nm (as shown in the image of Fig. 1c). On increasing the bias heating voltage to 30V, the current increased slightly from 13.75 µA to 15 µA in a time period of 30 sec. Due to this increase in current at this stage, some of the rutile particles formed agglomerates of around 100-200 nm and finally the nanotube structure collapsed. In conclusion, we have shown for the first time, the anatase nanotube dissociation and their phase transformation to rutile in real time. The anatase nanotubes under Joule heating dissociate to small particles (~10-20 nm) of anatase at low bias voltage (≤10V). At an intermediate bias range, between 10V and 20V, the anatase nanoparticles transformed to rutile. The size of the rutile nanoparticles can be controlled by the applied bias voltage. Under the bias heating condition with 30V, the rutile particles agglomerate into large particles with sizes range up to 200nm. It is known that thermodynamic stability of different phases of TiO_2 is size dependent [4-6] and thus by controlling the size of the particles, we can control the properties of the TiO_2 used for various applications.

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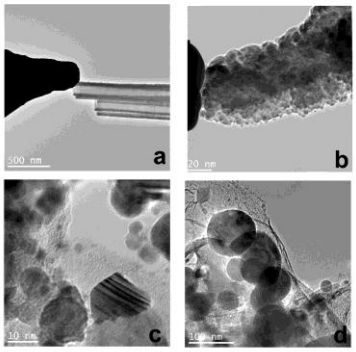

Fig. 1

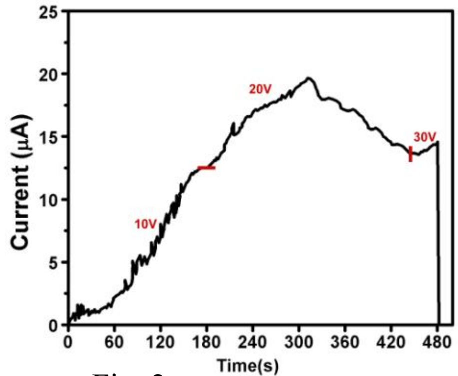

Fig. 2

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