Functional Materials

MS.3.P081

Controlled morphological transformation of hollow oxide nanostructures upon *in situ* annealing in a transmission electron microscope

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Hollow oxide nanostructures are materials with a high technological potential for applications in various fields ranging from nano-optics, catalysis, sensing, energy storage, microreactors to drug delivery. Currently, there is an interest in the development of methods to fabricate hollow oxide nanostructures of a wide variety of materials [1]. Among these hollow structures, oxide nanotubes are considered as potential building blocks for nanoelectronics. Up-to-now, the majority of the synthesis methods produce oxide nanotubes which suffer from short length and poor organization. Recently, a fabrication method of highly organized ultra-long metal oxide nanotube (length-up to several centimeters) based on the thermal oxidation of metal nanowire arrays selectively grown on nanograting template structures has been developed [2]. Figure 1 shows scanning electron microscope images of highly organized copper oxide nanotubes as-prepared on a nanograted silicon substrate. This route, based on the nanoscale Kirkendall effect, is also extendable to periodic zero-dimensional hollow nano-objects [2].This novel fabrication method yields oxide nanotubes in a planar configuration and opens-up the way to further nanodevice construction and characterization.

In this contribution we present an extensive structural study of the morphological transformation of oxide nanotubes upon *in situ* annealing in a transmission electron microscope. Based on this, the role of oxygen on the fundamental mechanisms occurring during the formation of such oxide nanotubes will be discussed. These results show the structural transformation and copper ions diffusion inside an oxide nanotube due to the effect of heating.The experiments were performed to temperatures higher than 600°C and done using a dedicated Gatan 652 heating holder. Figure 2 (a) shows a TEM bright-field image of periodic Cu nanoparticles created inside an oxide nanotube. Figure 2 (b) is the corresponding TEM dark-field image. Further *ex situ* studies using spatially resolved scanning transmission electron microscopy in combination with electron energy-loss spectroscopy revealed the chemical nature of the Cu based surrounding core-shell structure.

1. Fan, H. J. *et al.* Monocrystalline spinel nanotube fabrication based on the Kirkendall effect. *Nature Mater.* 5, 627-631 (2006).
2. El Mel, A. A. *et al.* Highly ordered hollow oxide nanostructures: The Kirkendall effect at the nanoscale. *Small*, in press.DOI: 10.1002/smll.201202824
3. Chun, S R *et al.* Joining copper oxide nanotube arrays driven by the nanoscale Kirkendall effect. *Small*, in press.DOI: 10.1002/smll.201202533

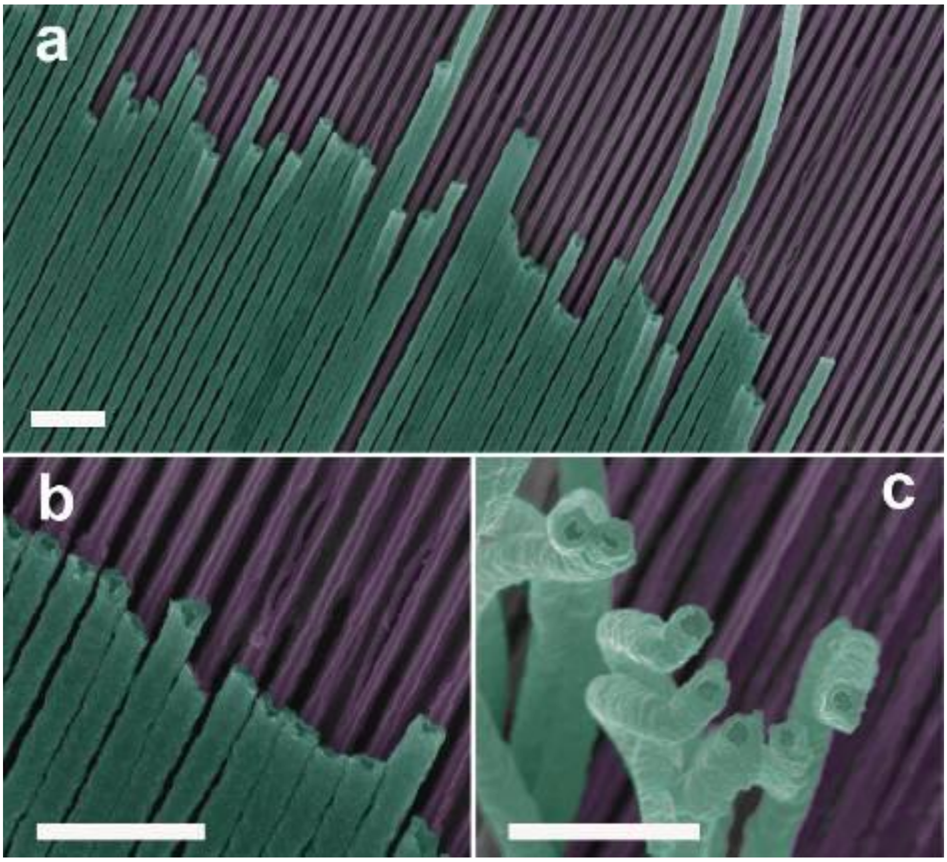

Figure 1. (a,b) False colored SEM micrographs of highly organized copper oxide nanotubes as-prepared on the nanograted substrate. c) SEM micrograph of oxide nanotubes disengaged from the silicon substrate. Scale bar: 1µm.

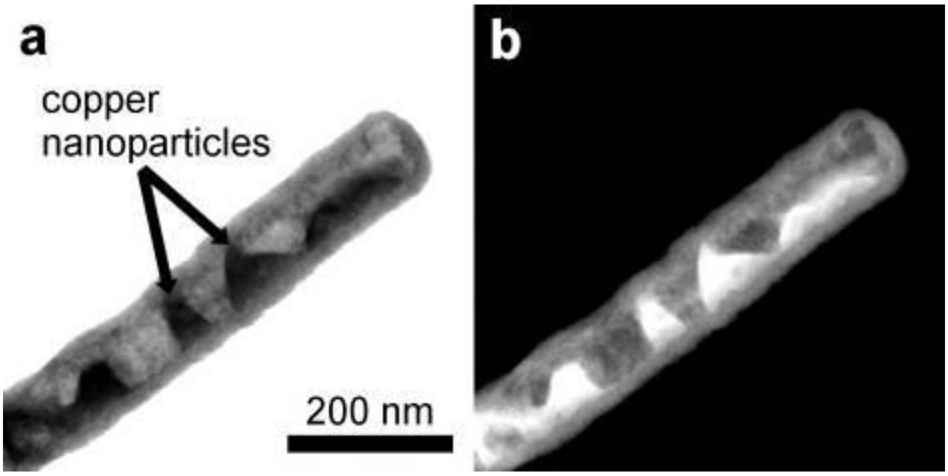

Figure 2. (a) TEM-bright field image of periodic Cu nanoparticles created inside an oxide nanotube (b) Corresponding TEM