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Ferroelastic Domain Organization in Solution-Grown HfO_2 Nanorods

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Hafnia (HfO_2) is a technologically important hard material with a relatively high dielectric constant and wide band gap [1]. However, the basic properties of HfO_2 have been little studied in the literature due to its close resemblance to zirconia in chemical properties. In the bulk, the monoclinic (space group: $P2_1/c$) phase represents the thermodynamic minimum; phase transformation to a distorted fluorite tetragonal (space group: $P4_2/nmc$) phase is induced upon heating to 1720°C. [2] The symmetry-lowering tetragonal to monoclinic phase transition in HfO_2 closely parallels the better studied phase transition in ZrO_2 and is believed to be Martensitic and athermal in nature. The transformation is thought to proceed through a diffusionless process wherein bond distances and angles are altered without disrupting the atomic connectivity within the lattice with preservation of a mirror plane symmetry element. Similar to ZrO_2, this tetragonal to monoclinic phase transformation in HfO_2 is strongly anisotropic being most pronounced along the *a*- and *c*-axes and negligible along the crystallographic *b*-axis. This anisotropic expansion induces a substantial shear strain within the materials that can be variously accommodated.

One approach by which this transformation strain can be relieved in this symmetry-lowering transition is by formation of periodic sequences of twin variants. The system seeks to establish a balance between compensating for macroscopic strain and the inevitable energetic penalty for establishing a new interface (the twin boundary). In other words, by forming a sequence of periodic domains separated by a coherent twin boundary, the structural integrity of the material can be retained and the macroscopic strain can be relaxed without extensive deformation or crack propagation. Evidence for formation of twinned domains has been reported in HfO_2 polycrystalline samples [3] thin films [4] and nanorods [5].

However, periodic organization of twinned domains along 1D nanorods has not thus far been evidenced in either thin films or bulk ceramic grains. In this study, we demonstrate the organization of ferroelastic domains that create a nanoscopic stripe pattern within colloidal HfO_2 nanorods.

An extended non-hydrolytic sol-gel synthetic route was developed to increase the length of the HfO_2 nanorods. Seed nanocrystals were synthesized from a condensation reaction between 2 mmol $HfCl_4$, 2 mmol of hafnium-*tert*-butoxide, and 10 g of TOPO and the mixture was heated for 2 h at 340°C. At the end of the 2 h reaction time, an additional 0.5 mmol of hafnium-*tert*-butoxide was added to the reaction vessel every 15 min for 10 h. Subsequently, the reaction mixture was cooled to 60°C, and the nanocrystals were recovered and purified as descripted in [6]. A JEOL-2010 electron microscope, operated at 200 kV, was used for high-resolution transmission electron microscopy (HRTEM) image and for acquiring selected-area electron diffraction (SAED) patterns.

Figure 1A shows a low-magnification TEM image of the HfO_2 nanorods and the inset shows the size distribution histogram. The nanocrystals are on average 2.9 ± 0.5 nm in width and 31.9 ± 10.7 nm in length with some nanorods approaching lengths of ca. 60 nm. SAED pattern shown in Figure 1B and

XRD pattern (not shown) of HfO_2 nanorods confirm the monoclinic phase of HfO_2 The reflections indexed to (200) plane is much narrow and sharp suggesting (100) preferential growth planes for the nanorods.

The HfO_2 nanorods are characterized by distinctive domains that span the diameter of the nanorods. The HRTEM image shown in Figure 1C indicates that the domains correspond to twin variants that form a sequence along the nanorods long direction and are organized as bands across the nanorods. Such organization of twin-related variants has been observed across all >90% of the HfO_2 nanorods. In every instance (of ca. 100 nanorods that have been surveyed), the twin boundaries extend across the entire width of the nanorod. As the length of the nanorod increases, the number of twinning planes also increases. Nanorods that are under 10 nm in length have at most three different domains (two coherent twin boundaries) in the same nanocrystal. As the length increases to 20 nm, 3-6 twin variants are observed in each nanorod. Upon increasing the length to 45 nm, as many as 10 different twin variants can be stabilized within a single HfO_2 nanorod. The twins unfailingly occur along the (100) plane; we do not observe any evidence of perpendicular twinning, multidirectional twinning, or twinning along any other crystallographic direction. The individual twins have a width of only a few lattice planes entirely uncharacteristic of bulk HfO_2.

The presence of an invariant mirror plane is characteristic of a Martensitic transformation and suggests that the array of organized twin variants is formed to accommodate the shear strain when an initially tetragonal (austenite) HfO_2 nanorod undergoes a phase transformation to the monoclinic (martensite) phase upon cooling. This quasi-periodic "bar-code"-like twin domains are ascribed to being a result of dimensional confinement. The high density of twin boundaries and their organization along the length of the nanorods in a pattern reminiscent of domains in shape-memory alloy materials [7] is most unusual for non-metallic nanostructures and points to remarkable mechanical properties that can be realized in nanoscale ceramics.

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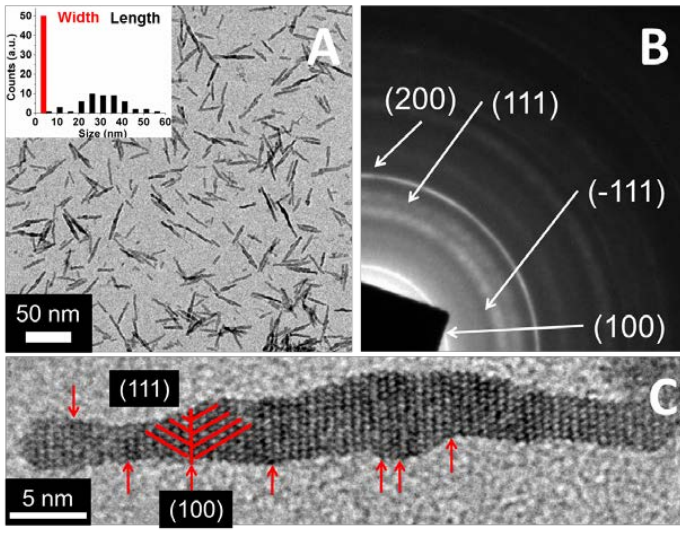

Figure 1 A) Low-magnification TEM image of HfO_2 nanorods. The inset depicts a histogram showing the distribution of width and length for the nanorods. B) Indexed SAED pattern. C) A HRTEM image of an individual HfO_2 nanorod. Arrows indicate the (100) twin plans. Red lines highlight the (111) lattice fringes as they cross the twin plane.

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