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Direct Observation of Hafnia Structural Phase Transformations

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The continued miniaturization of electronic device components such as metal oxide field effect transistors has pushed the semiconductor industry to replace silicon dioxide with high-κ dielectrics as the gate material. Hafnia is a wide band-gap and high dielectric constant material that is thermally stable on Si substrates, making it an attractive candidate to replace SiO_2 as the gate dielectric material in such devices [1]. The tetragonal phase of hafnia, occurring at 1720°C, is desired for device application due to its larger band gap and high permittivity in comparison to the monoclinic phase [1,2]. However, due to the displacive nature of the structural phase transformation, quenching the tetragonal phase to room temperature leads to a reversion back to the monoclinic structure [2]. It has been shown that the tetragonal phase of ZrO_2, an isomorph of HfO_2, can be stabilized with respect to the monoclinic phase at room temperature below a critical size of about 15-30 nm. It is estimated that the critical size for stabilization of tetragonal HfO_2 is much smaller, at about 4-10 nm, thus making it more difficult to stabilize [3]. This is illustrated schematically in Figure 1a. Since the tetragonal phase of hafnia is more important for technological applications than the monoclinic phase, it is of utmost importance to find a way to stabilize the tetragonal phase at low temperature [1]. Here we observe directly the monoclinic → tetragonal structural phase transformation of an individual hafnia nanorod with atomic resolution, using *in situ* scanning transmission electron microscopy (STEM).

High aspect ratio, monoclinic hafnia nanorods were grown *via* a nonhydrolytic sol—gel synthesis. The monoclinic nanorods contain multiple twin boundaries on the (100) planes [3]. These twin planes are believed to develop to accommodate strain during the tetragonal to monoclinic phase transformation upon cooling during synthesis. Shown in Figure 1b, when heated *in situ* in the STEM at 600 °C – over 1000 °C below the bulk transition temperature – we can observe an atomic-scale structural phase transformation from the monoclinic phase to the tetragonal phase, and upon slow cooling we observe reduction of the nanorods to hafnium metal. The phase transformation nucleates at a twin boundary and propagates one lattice plane at a time *via* a transformation dislocation. The high-energy twin planes as well as surface energy effects arising from size-confinement combine to depress the transition temperature by more than 1000 °C and prevent the tetragonal to monoclinic transformation. Using these *in situ* techniques, we are able to study the transformation mechanism in real time, providing crucial information necessary to stabilizing tetragonal HfO_2 nanocrystals near room temperature. [4]

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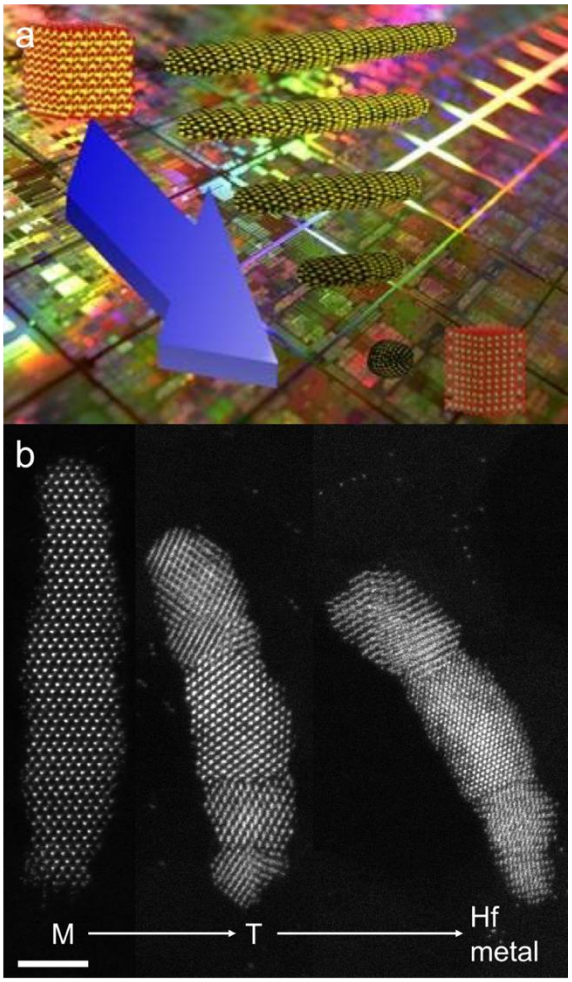

Figure 1. (a) Cartoon schematic demonstrating size confinement of hafnia nanocrystals stabilizing the tetragonal phase. (b) STEM images of a monoclinic nanorod undergoing a structural phase transformation to tetragonal HfO_2 upon heating and then hafnium metal when cooled *in situ*. Scale bar = 5 nm.

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