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Atomic-Level Fabrication of Crystalline Oxides in STEM

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Manipulation and control of the matter at the atomic level is one of the ultimate goals in nanoscience. The demonstration of atomic manipulation of xenon atoms by STM [1] was one of the seminal achievements in this direction. Beyond the obvious impact of demonstrating the smallest artificially fabricated structure, this opened the possibilities for the fabrication of novel atomic structures including quantum corrals,[2] standing electronic waves,[3] atomic switches,[4] molecular cascades for atom based computing,[5] and quantum holographic devices.[6] While the STM and non-contact AFM approaches are limited to material surfaces, an alternative paradigm for nano-patterning in bulk material is offered by electron beams. E-beam lithography in scanning electron microscope (SEM) geometry[7] has been demonstrated to fabricate three dimensional structures at the nanometer scale. However atomic-level fabrication is only expected with highly energetic e-beams in (scanning) transmission electron microscope ((S)TEM). Recently in-situ fabrication of metallic nanowires of 2D MoS_2 and $MoSe_2$ materials have been demonstrated. However, there are very few reported studies of fabricating bulk material in (S)TEM. For several materials it has been shown that an amorphous area several tens of nm in size can be converted into a polycrystal[8] or single crystal.[9] Recently, atomic rearrangements in amorphous materials have been reported.[10] These observations suggest that (S)TEM beam can in principle be used to achieve sub-nanometer level bulk nanofabrication.

In this work, we demonstrate atomic-level sculpting of 3d crystalline oxide nanostructures from metastable amorphous precursor in a scanning transmission electron microscope (STEM). $SrTiO_3$ nanowires can be fabricated epitaxially from the crystalline substrate following the beam path. This method can be used for producing crystalline structures as small as 1-2 nm and the process can be observed *in situ* with atomic resolution. Two interesting observations are made, as shown in Figure 1: Firstly, there is a certain threshold electron dose required, beyond which the crystallization is not observed. Secondly, the nucleation of the crystal preferably happens at the interface between the amorphous film and the crystalline substrate, and the new crystal grows epitaxially. Assuming an unphysically low thermal conductivity of the amorphous $SrTiO_3$ material, Joule heat induced by electron beam was estimated to be at most 50K, which is still too low to be responsible for the phase transformation. The energy transfer is thus likely to be knock-on in nature. Atomistic molecular dynamics (MD) simulations verified the feasibility of beam-induced crystallization if the high-energy excitation is applied in the vicinity of the amorphous-crystalline interface.

We further demonstrate fabrication of arbitrary shape structures via control of the position and scan speed of the electron beam. Combined with broad availability of the atomic resolved electron microscopy platforms, these observations suggest the feasibility of large scale implementation of bulk

atomic-level fabrication as a new enabling tool of nanoscience and technology, providing a bottom-up, atom-by-atom, complement to 3D printing. [11]

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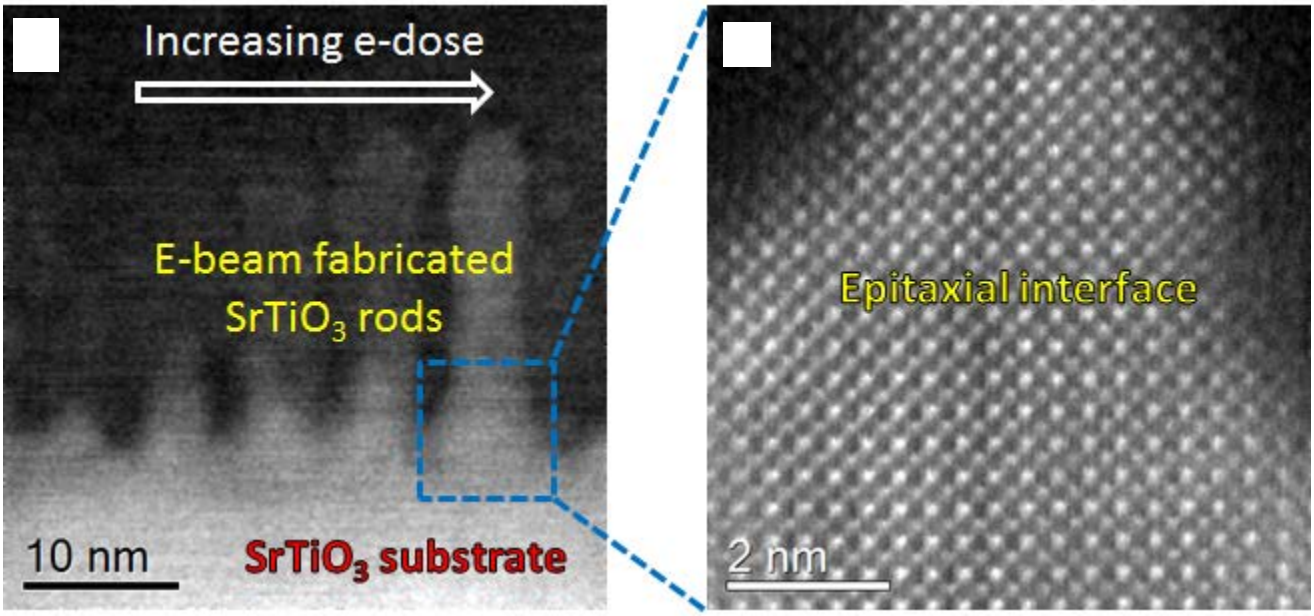

Figure 1. HAADF-STEM images of the e-beam fabricated epitaxial $SrTiO_3$ rods. (a) A lower magnification HAADF image of a series of $SrTiO_3$, demonstrating the effect of electron dose and the importance of the substrate. The formation of the SrTiO3 rods is more complete with higher electron dose. However for the left most rod, which was grown using the lowest electron dose, there is still growth near the interface. (b) A higher magnification HAADF image of the region highlighted in (a), showing the epitaxial character of the growth.

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