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In-situ TEM Characterization of Nucleation and Growth of Nanopatterned Oxides

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Functional oxide ceramics have been attracting much attention for years due to their scientific and technological significance. In the recent decade, advanced nanofabrication techniques provide the capability of fabricating ceramic nanostructures with precise size and shape control, which has brought new vitality to the field of traditional ceramics [1,2]. Further development of oxide nanostructures requires fundamental understanding of the new phenomena and behavior induced by shrinking their dimension down to nanoscale under spatial constraints.

Nucleation and (grain) growth are fundamental to any phase transformation, including conversion of liquid precursor to glassy/amorphous- to eventual solid-state form; as the sol-gel [3,4]. This is particularly important in emerging nanostructures and nanoscale patterns, where spatial and dimensional constraints are expected to significantly alter the local thermodynamic and kinetic conditions. Further, a detailed understanding of the early stage of such phase transformation is critical for manipulation and tailoring of "internal" microstructure of nanostructures and nanopatterns. However, despite the universal acknowledgement and significance, relevant early stage studies of nucleation and growth are rarely reported due to the challenges in building an effective test-bed, compatible with measurements tools and techniques.

In the present study, $CoFe_2O_4$ (CFO) nanodots were fabricated using "soft" electron beam lithography (soft-eBL), a nanopatterning approach recently developed in our group [5,6]. Soft-eBL is a flexible and convenient technique for patterning site-specified, shape-controlled and three-dimensionally confined solid-state nanostructures on diverse substrates. It synergistically combines the top-down with bottom-up method. By using sol-gel as precursor, oxide nanostructures prepared by soft-eBL are readily appropriate for *in-situ* studies of nucleation and growth phenomena.

Transmission electron microscopy (TEM) was applied to quantitatively characterize the nucleation and growth behavior of CFO nanodots, which were patterned on both electron transparent SiN_X membranes and MgO single-crystal substrates. Electron diffraction and other analytical techniques (EDS, EELS) were utilized to identify the phase and chemical composition of early-stage nuclei. Dark field images were taken for providing statistical information of size distribution of the nuclei (small crystallites) in CFO nanodots. By employing a heating sample holder, evolution of small nuclei could be monitored *in-situ* and in real time, to enable unambiguous study of the thermodynamics and kinetics of nucleation and growth (See Fig. 1).

The preliminary results reveal that the activation energy for grain growth of CFO nanodots is notably different than both CFO thin films and bulk materials [7]. We speculate that the increased intrinsic hydrostatic pressure due to the larger aspect ratio of nanodots and modulated strain field induced by the substrate may be responsible for these changes. Moreover, the CFO nanodot patterned on MgO substrate eventually grows into epitaxial single crystal. Heterogeneous nucleation and preferentially grain growth are observed and regarded as the key pathway for single-crystal conversion. Given the versatility of soft-eBL approach and *in-situ* TEM technique, the proposed strategy should be applicable to other oxide materials. We believe such studies will facilitate elucidation of the behavior of constrained ceramic nanostructures with significant implications for their technological applications.

References:

[1] V. Nagarajan, R. Ramesh *et al.*, , *Nature Materials,* 2 (2003) 43
[2] Z.W. Pan, *et al.*, *Science*, 291 (2001) 1947
[3] R. W. Schwartz*, Chem. Mater*., 9 (1997) 2325
[4] T. Sun, V.P. Dravid *et al.*, *Phys. Rev. B*, 77 (2008) 205414
[5] Z. Pan, V.P. Dravid, et al., Nano Lett., 6 (2006) 2344
[6] Z. Pan, V.P. Dravid, et al., Small, 2 (2006) 274
[7] M.J. Iqbal, Mah Rukh Siddiquah, Journal of Alloys and Compounds 453 (2008) 513–518
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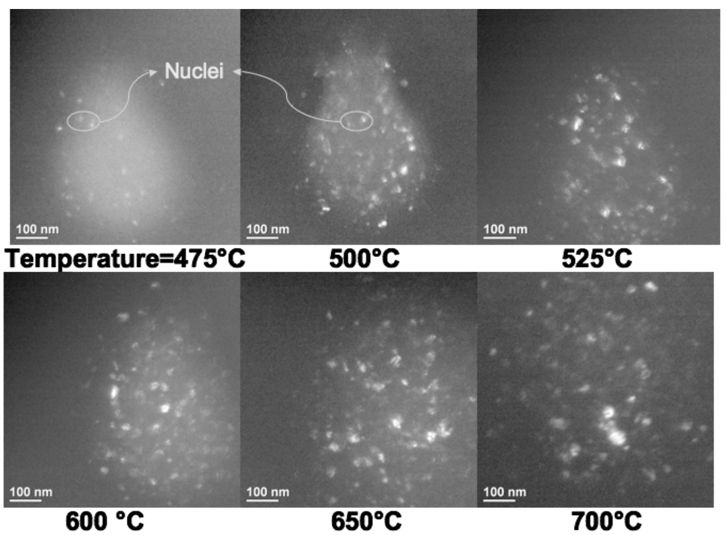

Figure 1: Dark Field Images of CFO nanodot (250nm) at different temperatures. Scale bar = 100 nm.

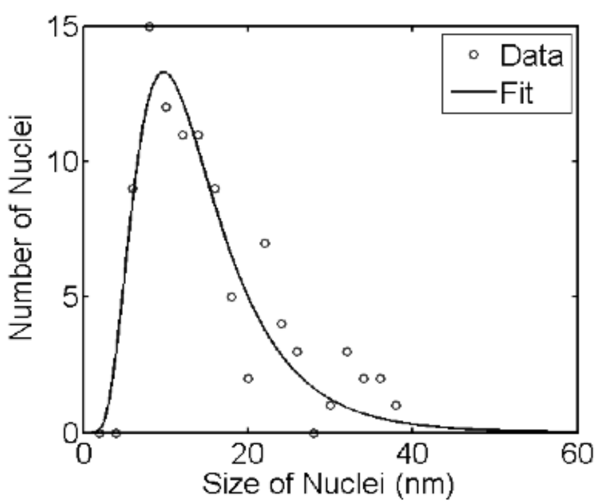

Figure 2: Lognormal fit of the nuclei size distribution at one temperature and the average nuclei size at this temperature (e.g. as shown here, nuclei in CFO nanodot at 600°C).

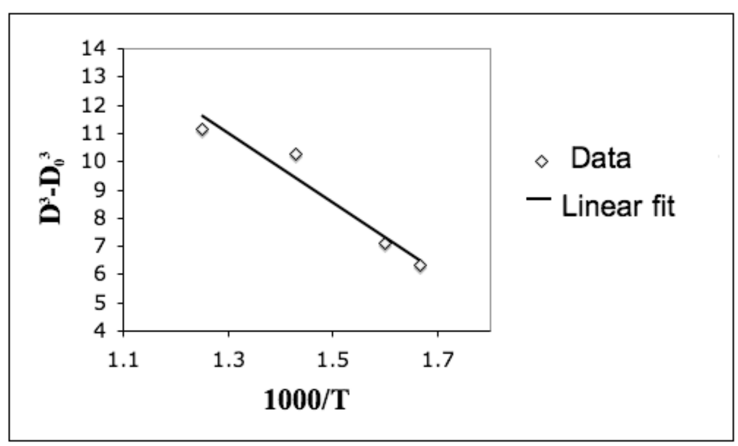

Figure 3: Activation energy calculated from the data (e.g. activation energy for a 150 nm CFO nanodot: Slope=–2.75= -1000*Ea/K_B, Ea ≈ 0.24 eV).

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