

In Situ Solid Phase Crystallization of Functional Ceramics in the Transmission Electron Microscope

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Many interesting and technologically relevant materials are not at their true thermodynamic free-energy minimum but instead are kinetically stabilized [1]. Some of these metastable structures may demonstrate unique, and potentially improved properties over their thermodynamically stable counterparts. However, accessing metastable reaction products and controlling formation pathways to target them presents a formidable challenge. This is especially true for systems such as complex oxides, which often display diverse polymorphism [2].

We present a route for the formation of potentially novel, layered complex oxide structures formed from a solid thin-film amorphous precursor through rapid heating and quenching, whereby solid-phase crystallization (SPC) of 30-nm thick $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM82) pulsed-laser deposited (PLD) films is performed *in situ* in the transmission electron microscope (TEM). In contrast to solid-phase epitaxy (SPE) where the substrate imposes epitaxial constraints, LSM82 films are deposited on an amorphous Si_xN_y substrate such that the resulting phases are free of such constraints. This provides a very open phase space that affords plentiful opportunities to access unusual structures. Although the perovskite structure is the true equilibrium phase of bulk LSM82 under the given processing conditions [3], the exceptionally high free-energy starting film of this non-glass-former instead generates a tendency to adopt metastable or transition states upon crystallization. In accordance with Ostwald's step rule, those phases that develop first are likely those closest in free-energy to the far-from-equilibrium starting film [4]. As a result, the annealed LSM82 film has a surprising propensity to crystallize into layered structures which may be of interest in applications which require efficient charge transport, such as solid oxide fuel and electrolysis cells.

Multiple heat treatment schedules up to 900 °C were used to process LSM82 films. At higher temperatures, marked segregation of La and Mn occurs, followed by the formation of their respective oxides and an several other unidentified phases. However, isothermal treatment at intermediate temperatures dramatically reduces cation segregation and instead grows the nucleated layered structures and increases the crystallized fraction over time. Recently, amorphous-crystalline composites of some complex oxide films have been shown to expedite ionic charge transport which may provide a route to operate solid oxide fuel cells at lower temperatures without sacrificing performance [5]; thus, control over the crystallized fraction may prove to be an important and tunable parameter to tailor electrical behavior.

In conclusion, SPC from amorphous complex oxide thin-film precursors provides a unique route to access unique transition structures. Further, treating these films with isothermal anneals at the crystallization temperature can serve to crystallize the amorphous film into these structures while stifling cation segregation that leads to an uncontrollable branching into many nanoscale phases. Monitoring this process *in situ* in the (S)TEM allows for heightened control over the crystallized fraction, and makes it

possible to observe the interplay of the layered phase formation and orientation with respect to the film's morphological features. This study also demonstrates that under certain conditions, such as the annealing of thin-films where diffusion is expedited by the high fraction of surfaces, it may be not be possible to access equilibrium structures over reasonable timescales.

References:

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