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# Electron-Beam Induced Crystallization of $Al_2O_3$ Film Generated from Inorganic Aqueous Precursors

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The various metastable polymorphs of alumina have received wide attention because of their industrial applications as catalysts, catalyst supports, wear abrasives, and structural composites [1]. Most alumina samples prepared with deposition processes, however, have amorphous structures [2]. Understanding the microstructural evolution of these amorphous materials is critical to controlling the formation of desired structures and properties.

Here a high-speed and environmentally benign technique [3], i.e., spin-coating a water-based solution with $Al_{13}$ precursor on a $SiO_2$/Si substrate, is applied to generate $Al_2O_3$ film. Compared with conventional film-deposition techniques (e.g., chemical vapor deposition, sputtering, atomic layer deposition) in high-vacuum and high-temperature system, the inorganic-aqueous-precursor technique requires no vacuum and only modest processing temperatures. It expands the number of transformation paths available to the system and hence the menu of thermodynamically feasible phases. In this talk, an FEI Titan 80-300 TEM is applied to directly investigate the transformation of the deposited precursors into the metastable phases.

TEM observation reveals the porous amorphous structure of the original $Al_2O_3$ film, as shown in Fig. 1(a). After exposing the film under electron beam for tens of seconds, the small pores coalesce and form larger pores [Fig. 1(a)-(c)]. The further radiation induces the crystallization of amorphous $Al_2O_3$ [Fig. (d)-(f)]. High-resolution TEM images clearly show the heterogeneous nucleation. That is, the nucleation preferentially occurs on imperfections such as the edge of large pores [Fig. 2(a)] and the interface between $SiO_2$ and $Al_2O_3$ [Fig. 2(b)]. At such preferential sites, the effective surface energy is lower, thus diminishing the free energy barrier and facilitating nucleation. The Fast-Fourier Transformation (FFT) and selected-area electron diffraction pattern of the crystallized film match the crystal structure of $\gamma$-$Al_2O_3$.The fraction of crystal structure increases as the radiation time increases. The rate of crystalline product depends on the composition of the precursors. Addition of phosphate into the Al precursor postpones the electron-beam-induced crystallization, while the addition of Zn accelerates crystallization. The thermodynamics and kinetics of the observed amorphous-to crystalline transition will be addressed in the presentation. This work provides a nanoscale view of transforming sets of small reactive precursors into dense or porous solids. The experiments and analyses could be extended to the formation mechanisms of other films deposited from inorganic aqueous precursors.

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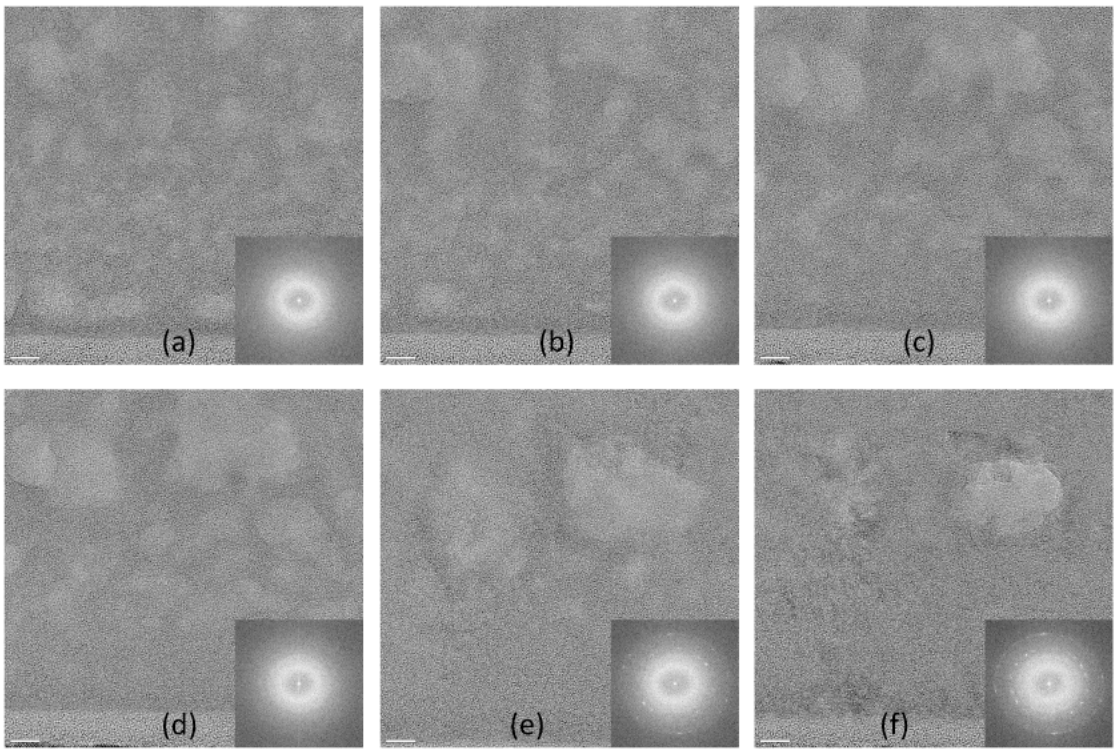


Figure 1. High-resolution TEM images of the as-deposited amorphous Al2O3 film (a), and subject to electron beam radiation at 300 kV for 20 s (b), 40 s (c), 70 s (d), 240 s (e) and 490 s (f). The insets are FFTs of high-resolution TEM images.

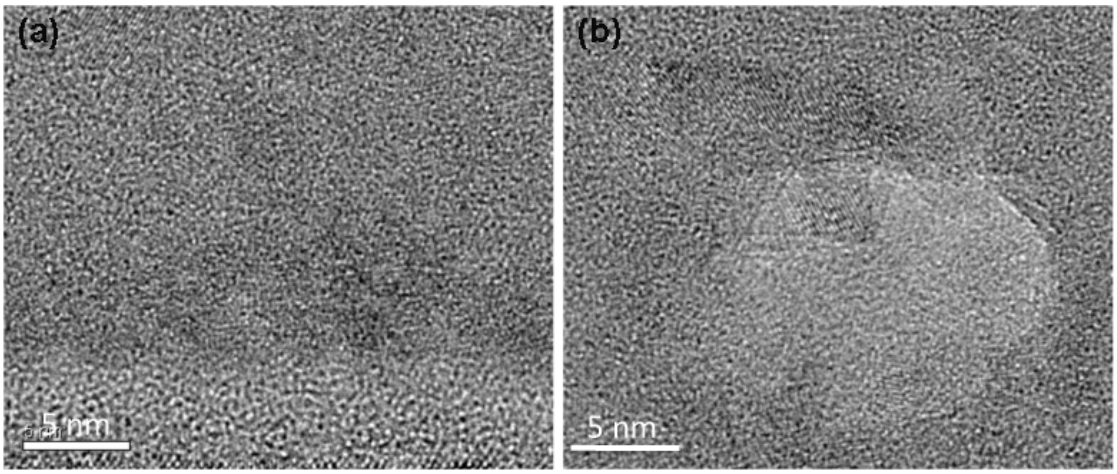


Figure 2. High-resolution TEM images indicate that nucleation prefers to occur on imperfections such as the edge of large pores (a) and the interface between $SiO_2$ and $Al_2O_3$ (b).

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