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Shifting Through Phase Fields: $CaAl_4O_7$ on Sapphire

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The earliest stages of reactions between ceramic materials are of interest as oxides find more applications in thin-film form [1-2]. Even small interactions with the substrate or other materials can become important in determining the properties of the films. This study is aimed at monitoring the interfacial reactions of calcium di-aluminate ($CaAl_4O_7$) thin-films with α-Al_2O_3 substrates as a function of temperature.

Samples were prepared from a basal-plane alumina substrate with an optically polished surface. A polymerized organic-inorganic complex route was used to synthesize pure crystalline $CaAl_4O_7$ (CA_2) powders as the source of the film material [3]. Approximately 100 nm thick CA_2 films were deposited on sapphire substrates by pulsed laser deposition (PLD) at 900°C in an oxygen ambient atmosphere. All reaction couples were heat treated in air at 1300°C and 1400°C for various times after deposition. Atomic force microscopy (AFM, DI Nanoscope III) and scanning electron microscopy (SEM, Hitachi S900 FEG) were used to monitor the microstructural changes of the films. Cross-sectional transmission electron microscope (TEM) samples were prepared by focused ion-beam (FIB, FEI Dual Beam) using self-supporting samples. The interfaces between the films and the substrates were examined by TEM (FEI Technai G2 30 FEG).

Fig. 1a and b are height-mode AFM images of the films heat treated at 1300°C for 1 hour and for 4 hours. Besides having the grainy microstructure, the film starts to retract from the substrate surface due to the densification during film crystallization. Hexagon on hexagon epitaxy of the film on c-plane sapphire can be seen in the image which suggests the formation of $CaAl_{12}O_{19}$ (CA_6) (Fig. 1b). Dewetting of the film is well pronounced for the samples heat treated at 1400°C for 1 hour and for 4 hours (Fig. 1c-d). In Fig. 1d formation of the hexagonal phase can be seen clearly.

Montages of the cross-sectional TEM images of the CA_2 films heat treated at 1300°C and 1400°C for 1 hour are shown in Fig. 2a and b. While the film heat treated at 1300°C is continuous and containing small grains, the same film dewetted the surface after the heat treatment at 1400°C. As shown in Fig. 2c, an interfacial reaction occurred between the film and the substrate at both heat treatment temperatures. The reaction layer at the interface was identified as γ-Al_2O_3 from the fast fourier transform (FFT) of the image. There is a perfect epitaxy between the interfacial layer and the substrate. CA_6 phase was formed by the transformation of the metastable γ phase. Although it is believed that dewetting of the film occurred in solid-state by the formation of the interfacial layer, the exact dewetting mechanism is still under investigation.

References

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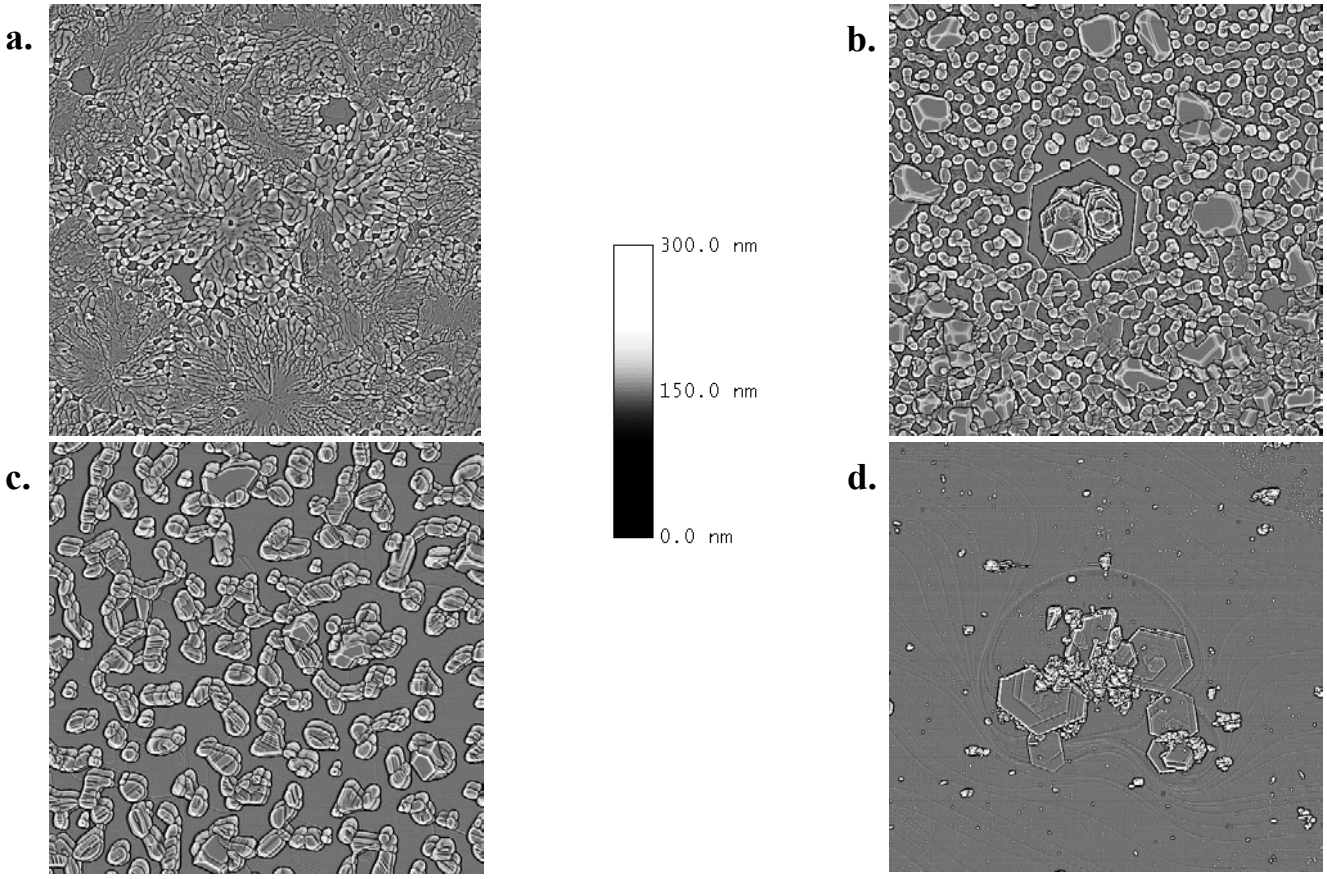

Fig. 1. Height-mode AFM images of the films heat treated at a) 1300°C for 1 hour, b) 1300°C for 4 hours, c) 1400°C for 1 hour, d) 1400°C for 4 hours. All scans are 20μm × 20 μm

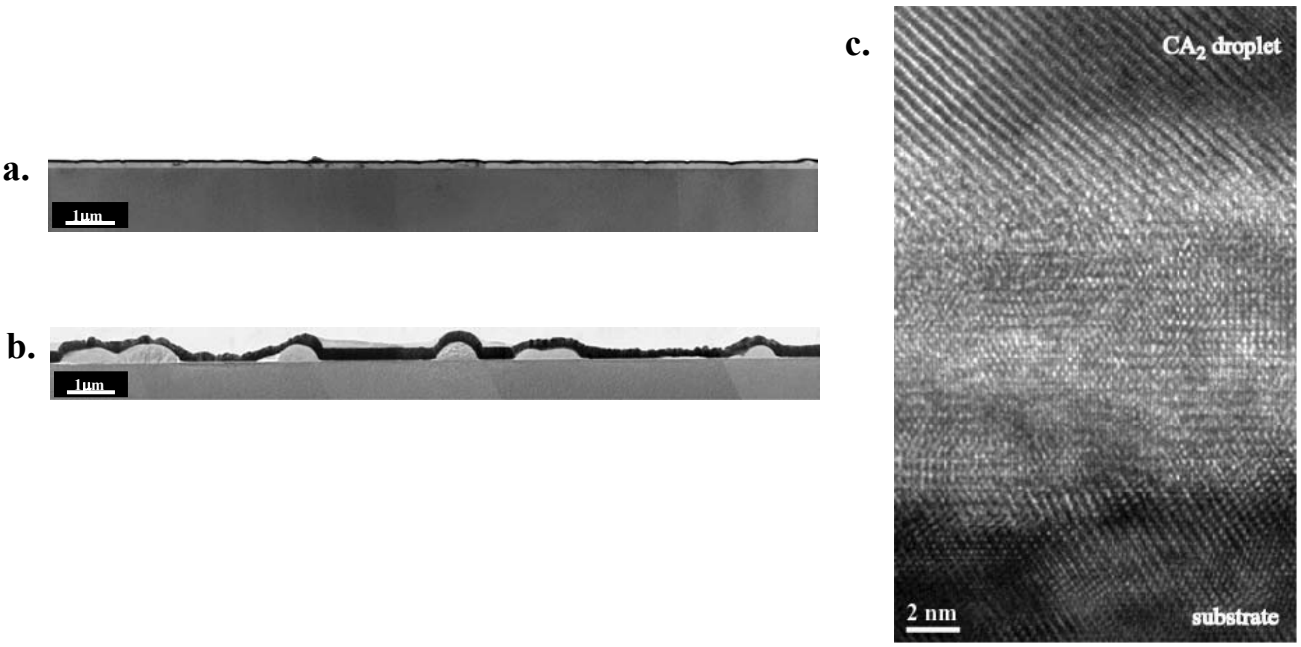

Fig. 2. Montages of the cross-sectional TEM images of the films heat treated at a) 1300°C for 1 hour, b) 1400°C for 1 hour, c) high resolution TEM image of the film heat treated at 1400°C for 1 hour.

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