Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

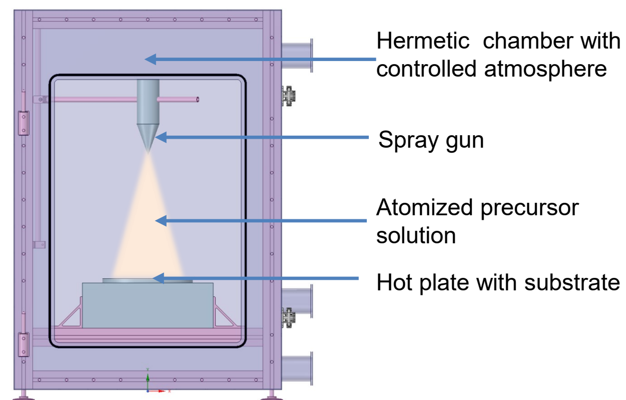

Figure SI 1: Schematic of spray pyrolysis deposition chamber

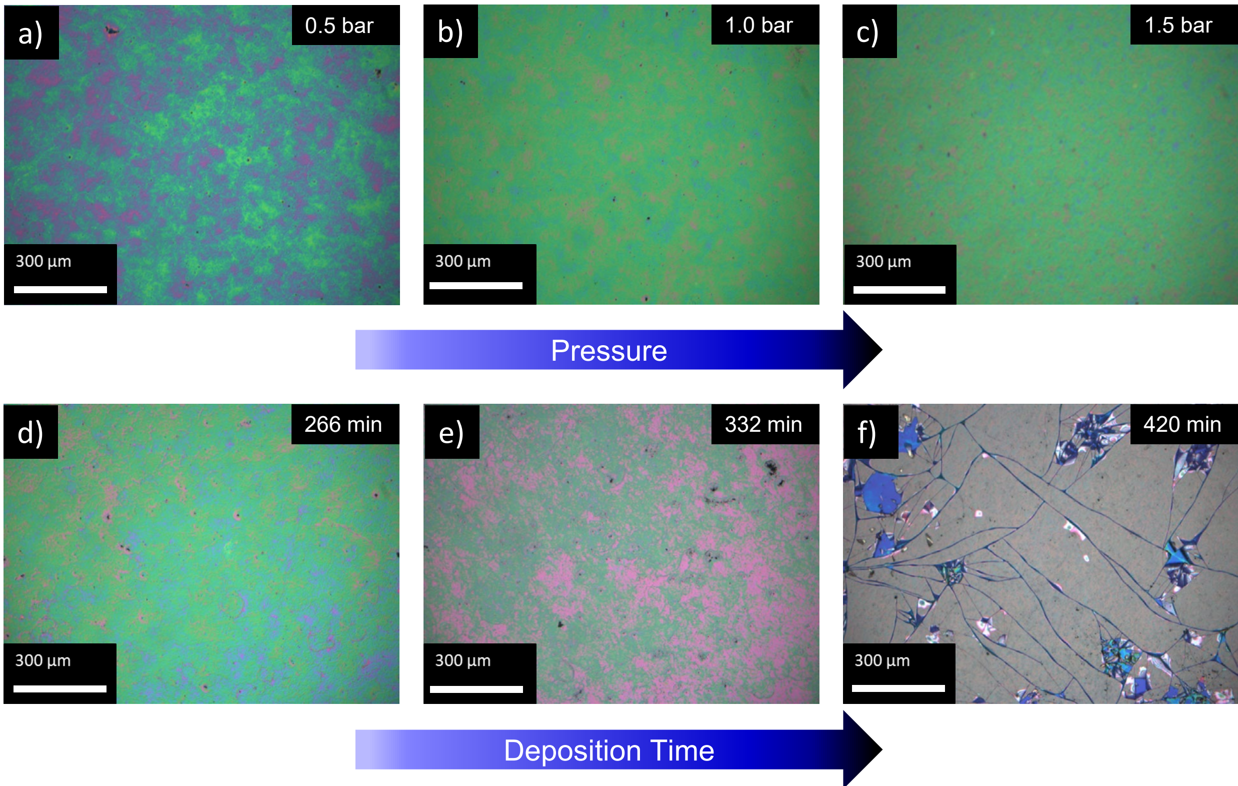

Figure SI 2: Optical micrograph of films deposited at an air pressure of a) 0.5 bar, b) 1.0 bar, and c) 1.5 at otherwise fixed deposition conditions. Optical micrograph of films deposited at d) 266 minutes, e) 332 minutes, and f) 420 minutes at otherwise fixed conditions (with the exception of a being deposited at 0.6 bar and the others at 0.4 bar)

Spray Pyrolysis Optimal Processing Parameters:

The first step in this deposition analysis were to determine the optimal processing parameters towards depositing homogeneous, crack-free films. Figure SI 2 displays optical micrographs of films deposited at varying spraying air pressures (a-c), but otherwise identical deposition conditions, and for different durations (d-f), also at otherwise identical conditions. Increasing the air pressure from 0.5 to 1.0 bar resulted in more homogeneous films, as seen in Figure 1d-f. At higher pressures, the droplet size of the precursor decreases, allowing for more uniform films as seen by the even color distribution in the optical micrograph. In contrast, at lower pressures, droplets are larger, creating an inhomogeneous morphology as can be seen from the color pattern where individual droplet residues can be seen, causing color changes due to large thickness irregularities. The films deposited at 1.0 and 1.5 bars of air pressure only show slight morphology deviations, so a 1.0 bar pressure was used for subsequent depositions. The impact of spraying duration also proved to be critical towards depositing high-quality films. It was seen that spraying for 7 hours at a flow rate of 3 mL/hr resulted in cracked films (Figure SI 2 f). Generally, it was observed that longer depositions of thicker films resulted in cracked films whereas shorter depositions with otherwise identical deposition conditions led to intact films. This implies that

there exists a critical film thickness, above which crack formation becomes favorable over dense, crack-free film deposition.

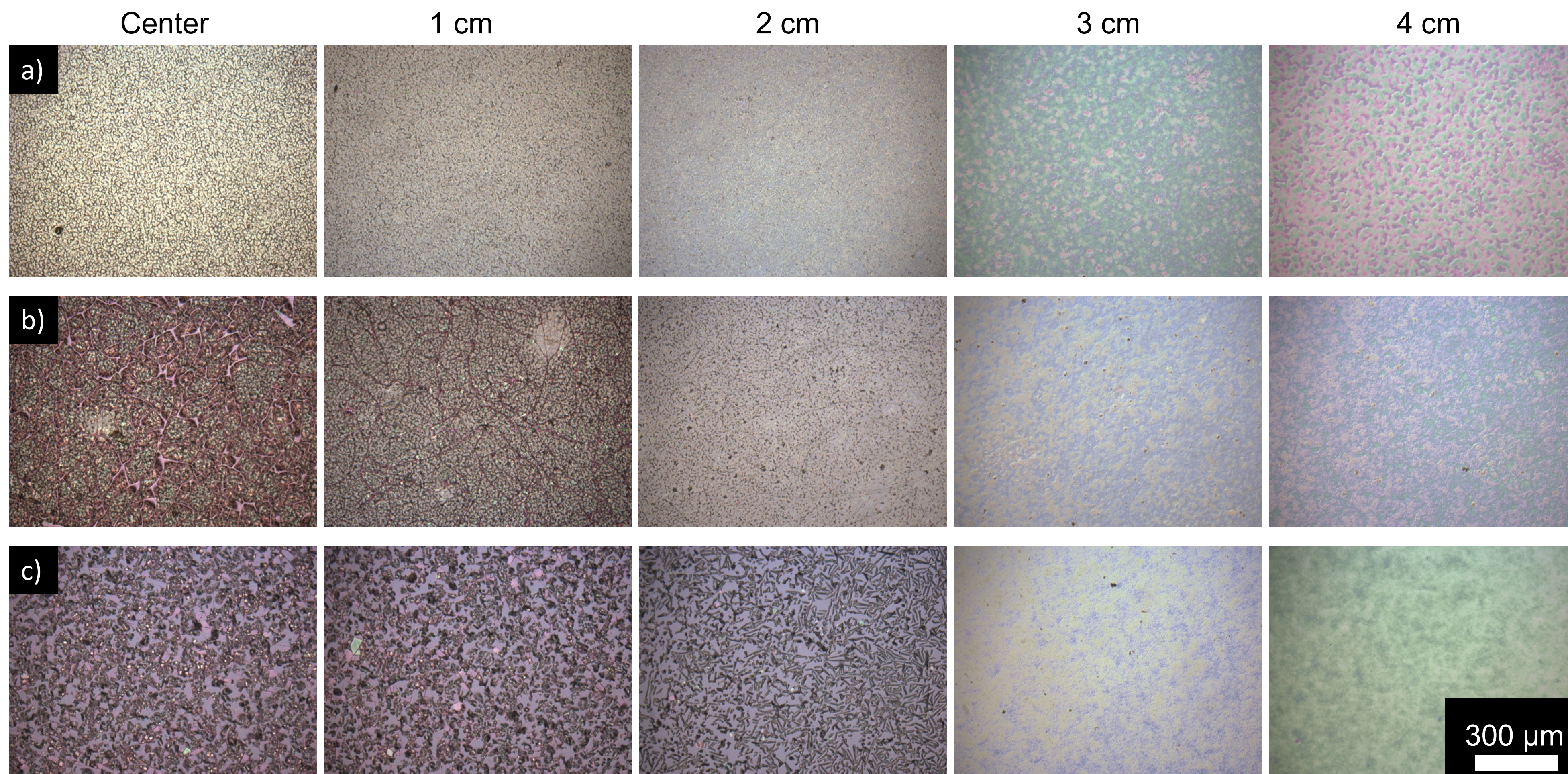

Figure SI 3: Micrograph of film along wafer from left to right: center, 1-4 cm from the center deposited at a) 350 C, b) 400 °C, and c) 450 °C

Energetics of Crack Formation:

SI Eqn. 1 provides a generalized expression of the energetics of the crack formation:

$$\Delta U_{crack} = 2\gamma a - \Delta U_{released\ strain} \qquad \textbf{SI Eqn. 1}$$

where ΔU_{crack} corresponds to the total internal energy difference associated with the formation of a crack, and $\Delta U_{released\ strain}$ corresponds to the internal energy difference of releasing strain energy through the crack formation. γ represents the surface energy, a the crack length, and the factor of 2 is present because cracking forms two surfaces. We can see that if the amount of released strain energy is greater than the surface energy term, the formation of cracks becomes energetically favorable

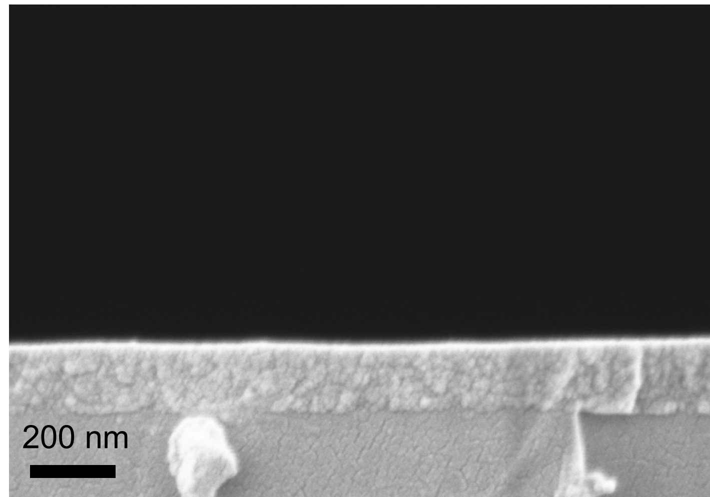

Figure SI 4: Cross section of CeO2 film deposited at 1 bar, 500 °C, for 210 minutes, at 3 mL/hr flow rate, 20 cm working distance, 3 cm offset.

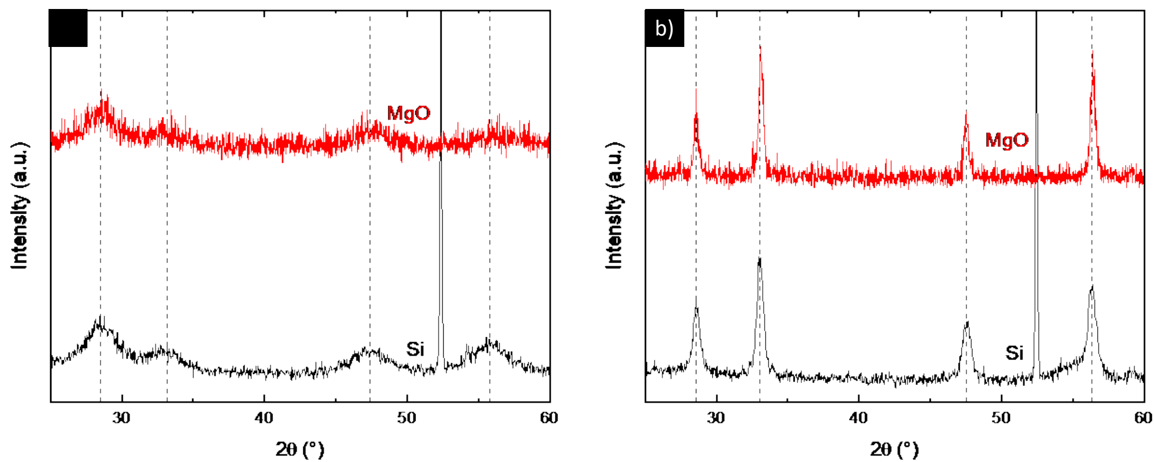

Figure SI 5: XRD of ceria films deposited at 450 °C on Si/Si3N4 substrates and MgO substrates a) as deposited and b) after annealing at 800 °C. Peak intensity was normalized to the (111) peak. Peak position and relative intensity remain the same between the different substrates.