

Photon-Enhanced Crystallization Kinetics and In Situ High Temperature Conductivity Studies in Ultra-Thin $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ Films

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Abstract and Introduction:

Solid oxide fuel cells (SOFCs) have drawn attention for electrical power generation because of their low emissions, high efficiency, and flexibility in fuel sources [1]. SOFCs typically operate at temperatures at or above 700°C, creating issues with thermal stress, material selection, and device packaging [2,3]. Efforts are being made to reduce SOFC operating temperatures to between 200°C and 600°C utilizing thin film device structures, reducing many of the impacts of the aforementioned factors [4]. However, reduced operating temperature may also decrease the ionic/electronic conductivity and decrease oxygen reduction reaction rate at the cathodes [5]. Thus, it is critical to advance synthesis routes for high performance cathodes with superior electrical conductivity [6,7].

$\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_y\text{O}_{3-\delta}$ has been explored as a possible cathode material for use in SOFCs [8]. LSCF exhibits mixed ionic and electronic conductivity and high electrocatalytic activity [9]. Synthesis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ by RF-sputtering has been shown to produce functional films with crystallization temperatures in the vicinity of 450°C without producing interfacial reaction products with yttria-stabilized zirconia (YSZ) [9,10].

La = Lanthanum
Sr = Strontium
Co = Cobalt
Fe = Iron
O = Oxygen

The interaction of energetic UV photons with oxygen can produce oxygen radicals or ozone, dramatically increasing oxygen reactivity on surfaces and enhancing oxygen incorporation into thin films [11]. In this paper, we demonstrate that photo-excitation during crystallization leads to enhanced oxygen incorporation into a prototypical perovskite oxide that in turn results in a significant improvement in the high temperature conductivity. Further, utilizing *in situ* conductivity measurements, we show an enhancement in crystallization kinetics arising from photo-excitation.

Experimental Procedure:

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ thin films were RF-sputtered from a stoichiometric target (AJA International) onto single crystalline YSZ substrates. Sputtering was carried out in

5×10^{-3} Torr of argon plasma starting from a base pressure of 3×10^{-8} Torr with a gun power of 60 W. *In situ* high temperature conductivity studies were also performed on 60 nm thin LSCF films on similar substrates with platinum electrodes in air. Photon sources in-built into the probe station enable *in situ* exposure while heating experiments as well as electrical conductivity. The temperature was continuously monitored using thermocouples. LSCF films were characterized by x-ray diffraction (XRD).

Results and Discussion:

In order to examine the crystallinity of LSCF films annealed at 450°C, low angle XRD was performed at an incident angle of 1°. The results of the scans, seen in Figure 1, indicate that both the films annealed with and without UV are crystalline after annealing to 450°C. XRD peaks appear around two-theta 33°, 41°, and 47°, corresponding to the LSCF peaks (110) (104), (202), and (024) respectively [12]. No additional peaks are observed for the films annealed under UV irradiation, indicating that no un-desirable reactions between the LSCF and the YSZ substrate have occurred. The location of the 33°

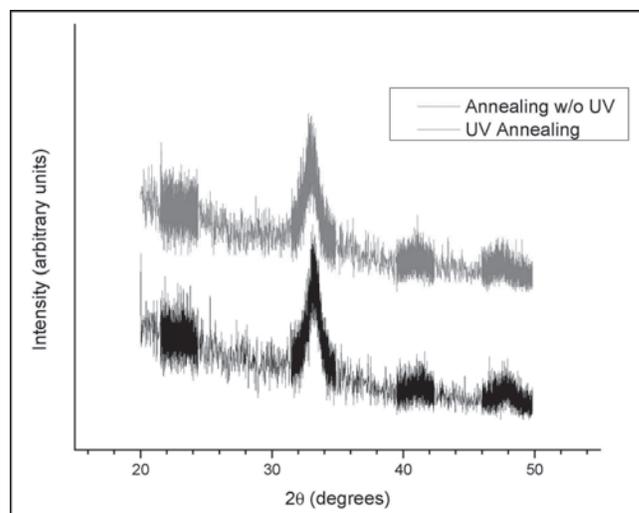


Figure 1: XRD profile of LSCF films annealed at 450°C.

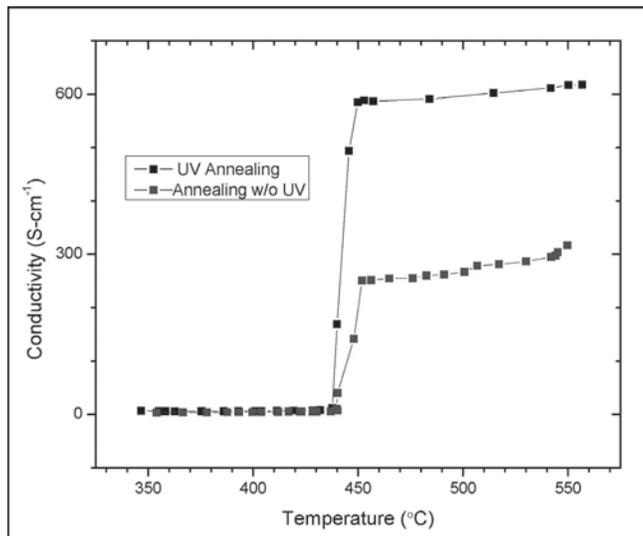


Figure 2: LSCF in-plane electrical conductivity vs. temperature.

two-theta peak is 0.1° higher for the film crystallized under UV irradiation compared to the film annealed without UV, indicating a slight decrease in the average lattice parameter of the LSCF thin film. Enhanced oxygen incorporation during annealing could possibly decrease the overall oxygen deficiency in the film, reducing the number of oxygen vacancies [11].

In situ conductivity studies were performed on LSCF thin films during and prior to the onset of crystallization. Sample temperature was held at 450°C for 40 minutes to observe LSCF conductivity changes with time. Film resistance was calculated via linear regression to tabulate in-plane LSCF conductivity. Upon crystallization, a conductivity increase of approximately 100x can be observed, serving as a suitable *in situ* probe of the structural evolution. The onset temperature for this change in conductivity is $\sim 440^\circ\text{C}$ in films crystallized both with and without UV assist as observed in Figure 2. The conductivity of the LSCF films measured 248 S-cm^{-1} and 588 S-cm^{-1} at 450°C after 50 minutes for samples annealed with and without UV irradiation respectively. Upon increasing temperature to 557°C , conductivities measured 320 S-cm^{-1} and 618 S-cm^{-1} in films annealed without UV irradiation and with UV irradiation respectively.

Figure 3 shows the evolution of in-plane conductivities for LSCF films annealed both with and without UV at 450°C . With time, the film conductivities annealed with and without UV approach a maximum asymptotically. The rate at which the films approach their maximum conductivity differs. The LSCF film crystallized under UV approaches its maximum conductivity at 450°C faster than the film crystallized without. This suggests that the crystallization rate of LSCF thin films is influenced by oxygen incorporation.

Conclusion:

We have demonstrated that UV assisted crystallization of RF-sputtered $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ thin films leads to higher in-plane electronic conductivity and more rapid

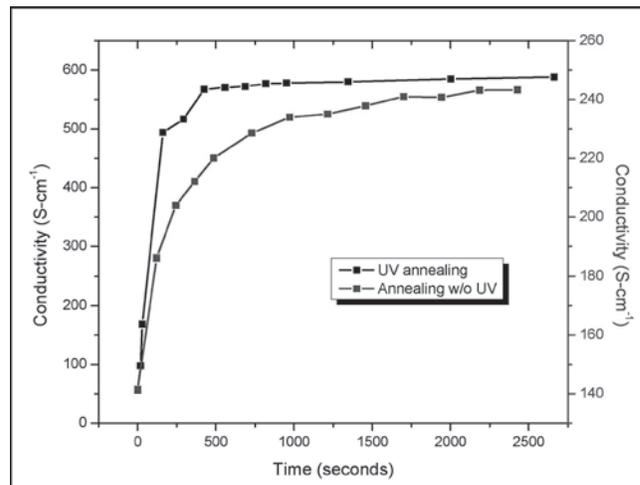


Figure 3: Conductivity vs. time during crystallization of LSCF films at $T \sim 450^\circ\text{C}$.

crystallization. A decrease in lattice parameter was observed in films annealed under UV irradiation, indicating increased oxygen concentration or decreased in oxygen vacancy concentration in the LSCF film due to the greater presence of oxygen radicals and ozone during crystallization. More rapid crystallization was also observed in films annealed under UV irradiation. The results indicate that UV enhanced crystallization of LSCF ultra-thin films could provide an increase in cathode performance.

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