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Polymer-Based Processing of Lateral Anionic Superstructures in Complex Oxide Films
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__Project Overview:__ The central objective of the project is to create lateral anionic superstructures and patterns in complex oxide films using a combination of a polymer-based fluorination reactions and lithographic techniques. In the first year of the project, we demonstrated feasibility of this approach by creating lithographically-defined superstructures of $SrFeO_{3-\delta}$ -based oxide and oxyfluoride stripes through fluorination of $SrFeO_{3-\delta}$ films using thermal decomposition of polyvinylidene fluoride (PVDF) over chromium hard masks. In the second year, we have been working to optimize the process by finding alternative hard mask materials and we have demonstrated that these improvements to the process enable transient/reprogrammable lateral structures in the films.

__Technical Research Progress:__ Patterned $SrFeO_{2.5}/SrFeO_{3-\delta}F_{\gamma}$ ($SFO_{2.5}$/SFOF) and $SrFeO_3$/SFOF superstructures with periodic length scales of 4-200 µm that display lithographically-defined phase coexistence have been synthesized using the process shown in Figure 1(a). The process starts by depositing $SrFeO_{2.5}$ thin films using molecular beam epitaxy; these films are then patterned through a combination of lithographic processes and topotactic fluorination. However, in the initial results obtained during year one, we observed a slight broadening of the x-ray diffraction peaks for the layers that were covered by the chromium hard mask. We hypothesized that some degradation of the underlying film was resulting from the high temperature deposition condition of the Cr film. To mitigate this problem, we have investigated the feasibility of various other materials as a hard mask. We have found that Cu can serve as an excellent mask material. To illustrate this, uniform layers of Cr and Cu were deposited on $SrFeO_{2.5}$ films, and the metals were subsequently removed using standard etch processes for these respective metals (ceric ammonium nitrate solution for Cr and ferric chloride solution for Cu). As shown in Figure 1(b), the 002 diffraction peak for the film exposed to Cr is significantly suppressed after the Cr etch, while the presence of Cu and subsequent Cu etch does not alter the 002 diffraction peak of the $SrFeO_{2.5}$ film.

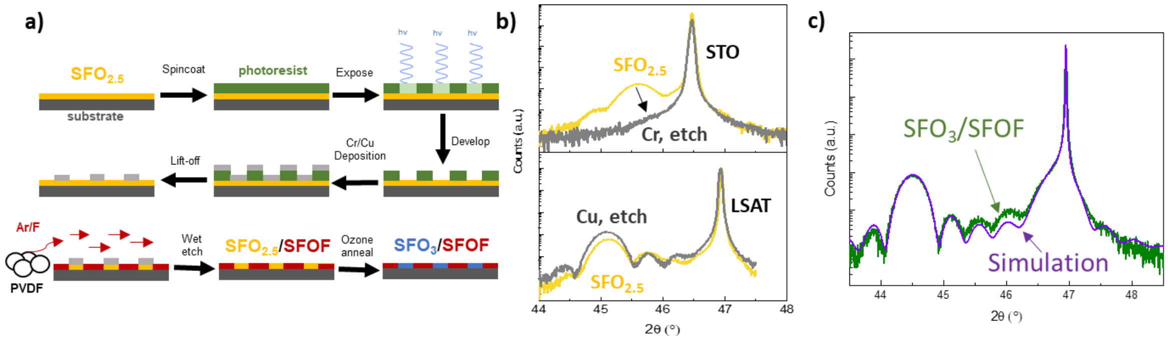

Figure 1. (a) Schematic of the process combining photolithography with topotactic fluorination to synthesize lateral anionic patterns in oxide films. (b) X-ray diffraction data of the 002 reflection from $SFO_{2.5}$ films in the as-grown state (yellow curves) and the same film (gray curves) following deposition and subsequent etching of Cr (top panel) and Cu (bottom panel). While the Cr deposition and etching clearly leads to film degradation, the diffraction data from the film exposed to Cu deposition and etching shows no changes in crystalline quality. (c) X-ray diffraction data taken from a lateral SFO_3/SFOF superstructure. The green curve shows the data and the blue curve shows the simulation. The SFOF 002 peak is near 44.5°, while the SFO_3 002 peak is slightly to the left of the large substrate peak near 46.6°. The presence of both SFO_3 and SFOF reflections with similar peak widths confirms the crystalline quality of both constituent layers within the superstructure.

By utilizing Cu hard masks instead of Cr, we were able to mitigate the film degradation and prepare fully oxidized SFO_3/SFOF superstructures, which we were unable to realize using the Cr hard mask. Figure 1(c) shows experimental x-ray diffraction data from a SFO_3/SFOF superstructure compared with a simulation calculated assuming distinct SFO_3 and SFOF layers. The agreement between the experimental data and simulation is excellent, with approximately the same coherence length (or layer thickness) obtained for both SFO_3 and SFOF, indicating that crystalline degradation has been avoided. These SFO_3/SFOF structures are promising for hosting tunable anisotropy due to the dissimilar functional properties of SFO_3, which is an opaque conducting metal, and SFOF, which is a translucent insulator. The ability to fabricate SFO_3/SFOF also opens the door to adaptable or transient behavior. We have found that SFO_3 layers can be reduced to $SFO_{2.5}$ by simply heating the film at temperatures greater than 200°C. Conversely, $SFO_{2.5}$ can be oxidized to SFO_3 by exposing the film to ozone. We have found that heavily fluorinated SFOF layers (compositions close to $SrFeO_2F$) are stable during these processes and do not appear to lose F or incorporate O. Thus, the SFO_3/SFOF can be smoothly converted to $SFO_{2.5}$/SFOF, simply by heating as shown in Figure 2. The sample can be transformed back to SFO_3/SFOF through exposure to ozone, without any additional patterning. Future experiments will determine the extent of electronic anisotropy in SFO_3/SFOF superstructures, which is anticipated to exceed that of $SFO_3/SFO_{2.5}$ superstructures.

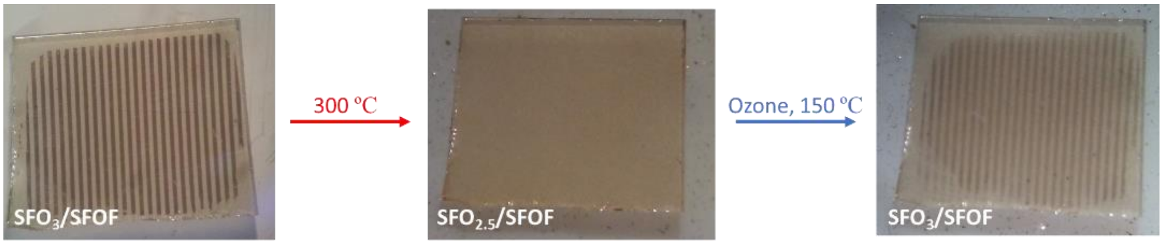

Figure 2. Optical microscopy images of the same sample demonstrating the ability to reversibly convert a SFO_3/SFOF superstructure to $SFO_{2.5}$/SFOF and back to SFO_3/SFOF without additional patterning. The stripes are not visible in the $SFO_{2.5}$/SFOF superstructure (middle image), as both $SFO_{2.5}$ and SFOF are transparent with similar optical band gaps.

Having demonstrated successful fluorine-based patterning, we have also studied the effect of fluorine content on electronic transport in $SrFeO_{3-\delta}F_\gamma$ films to better understand how to tune electronic anisotropy in the superstructures. By increasing the temperature of the fluorination reaction to increase the fluorine concentration, we have achieved a variation of conductive behavior [Figure 3(a)] ranging from nearly metallic conductivity in SFOF reacted at 170°C to highly insulating behavior in SFOF reacted at 250°C (not shown due to its resistance being too high for our instruments to measure). Thus, by tuning the initial fluorination condition, we should be able to better control the degree of macroscopic electronic anisotropy in the superstructures. We are currently exploring the use of resonant X-ray reflectivity and nuclear Rutherford backscattering spectrometry as routes to quantify the fluorine stoichiometry within the films as a function of reaction temperature. Unexpectedly, we have observed that the presence of small concentrations of fluorine (we estimate $F < 0.2$) within the SFOF films significantly alters the kinetics of film oxidation. As shown in Figure 3(b), *in situ* resistance measurements performed during an ozone anneal at 85°C reveal that lightly fluorinated films exhibit a decrease in resistivity with a time constant 3.5 times faster than that of unfluorinated $SFO_{2.5}$. The accelerated kinetics could potentially be used in decrease transformation times in transient lateral superstructures. Work is ongoing to provide an understanding of the mechanism by which small F concentrations appear to dramatically alter the oxidation kinetics. Additionally, in the final year of the project we will fabricate patterned structures beyond stripes, for example, exploring lattices of dots that could result in interesting macroscopic optical or magnetic properties.

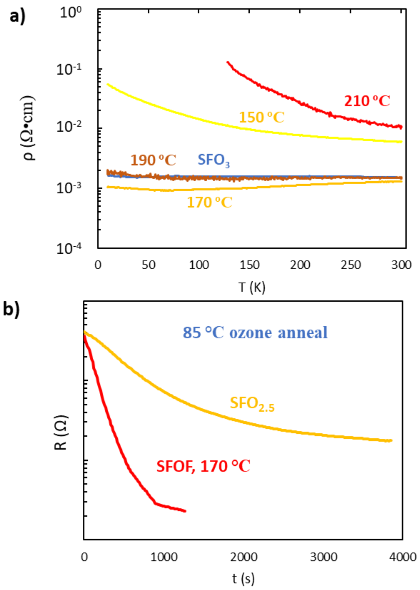

Figure 3. (a) Temperature dependent resistivity from SFOF films reacted at different temperatures. The F content increases with increasing temperature, resulting in more insulating behavior. (b) The presence of small concentrations of F in SFO leads to more rapid changes to resistance upon ozone exposure.

<u>*Impact of Research*</u>: The grant has enabled the May group to move into a completely new direction, that of laterally patterned heterostructures. External federal funding will be pursued over the next year to ensure continuity of the project now that feasibility of the general approach has been demonstrated. This PRF grant has fully funded the work of PhD student Ben Lefler in his role as research assistant at Drexel University. The basic scientific understanding of how to controllably create laterally-patterned materials with highly anisotropic properties may find applications in photonic crystal development, transient or reprogrammable plasmonics and other optical devices.