Cross-Sectional TEM of the Ferroelectric Dielectric and ZnO Semiconductor in Field-Effect Transistors

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Field-effect transistors (FETs) are critical components to any electronic device we use today, behaving as current regulators and switches. These components are typically made up of 4 layers: a gate electrode, a gate dielectric, a semiconductor, and source/drain contacts. In many of the FETs made in our lab and other labs, SiO_2 is a standard gate dielectric. Based on their dielectric constant, different gate dielectrics can lead to lower turn-on voltages, resulting in lower power consumption devices. One of the gate dielectrics we are currently investigating is polyvinylidene fluoride trifluoroethylene (PVDF-TrFE) which is a ferroelectric polymer. Due to its ferroelectric nature, PVDF-TrFE films can be poled in different directions, leading to very different device performances using a pentacene derivative as the organic semiconducting layer.[1]

The goal of this research was to observe and measure the differences in film structure between 3 samples, each with a different poling condition, utilizing cross sectional TEM. Cross sections of these samples were obtained via trenching and polishing in the Scios FIB-SEM. The poling conditions were: vertically poled only, vertically poled with subsequent lateral poling at 200V, and vertically poled with subsequent lateral poling at 400V. We expected to observe a region of laterally poled (L-poled) film at the bottom interface with aluminum with the remaining film being vertically poled (V-poled) all the way to the top surface, as these samples were L-poled along the bottom interface.

The September quarterly report ended with determining the nature of a contrasted region within PVDF-TrFE dielectric films for application in FETs. Upon imaging an additional cross-section in the Tecnai F30 TEM, it was determined that the change in film morphology is a result of both the poling technique for PVDF-TrFE films and beam interaction with the sample (Figure 1). In the vertically and laterally poled films, which we call textured poled, the contrasted region near the Al interface is present upon initial imaging. However, in films which are not poled, this contrasted region is initially absent but appears after a short time. After some analysis, we observe this region quickly increases in thickness with prolonged exposure to the electron beam (Figure 2). In addition, this phenomenon also occurs in textured poled films, which we realized after going through previously taken TEM images. While not as dramatic, the textured region increases from 35 nm initially to 60 nm in most regions of the cross-section after prolonged beam exposure (Figure 3). Theoretical simulations have agreed well with what we see experimentally, in that a certain thickness of the film will arrange itself differently than the remainder of the film based on the poling voltage magnitude.[2]

Aside from the PVDF-TrFE films, we also focused on ZnO thin films for application in FETs and photodiodes. ZnO is an intrinsic *n*-type semiconductor that can be partnered with organic polymer semiconductors, which tend to be *p*-type, for the realization of *p*-*n* junctions in photodiodes and other devices. Previous work has shown a short UV-Ozone treatment on

solution processed ZnO films can significantly improve their semiconducting properties in devices.[3]

Over the previous year, new processing conditions have been developed to further improve charge transport. The impact has been seen in thorough FET measurements and diode measurements. In FETs, ZnO films were spin-cast on SiO_2 dielectrics, pre-baked at 100 °C, UV-Ozone treated for 60 seconds, and annealed at 275 °C. These will be referred to as "treated" ZnO films. Similarly, "non-treated" films were spin-cast and then annealed at 275 °C. When compared to non-treated ZnO films, the treated films yielded devices with nearly 3 orders of magnitude higher charge carrier mobility and On/Off current ratios of an order of magnitude higher, important device metrics in FETs. This UV-Ozone treatment increases the Zn-O bind strength and fills Oxygen vacancies within the lattice, lowering the density of defects.[4, 5] This is also observed in transfer measurements where the existence of charge trapping sites is more prevalent in the non-treated films.

Due to these new processing conditions and the improvement in device characteristics, changes in the nanostructure were sought out to be observed. Cross-sectional TEM images were taken of both treated and non-treated ZnO films. Initial treated and non-treated films display randomly oriented crystalline grains and nearly identical grain sizes. An example of a cross-section can be seen in figure 4. Quantifying the difference has proven to be difficult due to the grains being roughly 7-8 nm in diameter, too small for Electron Backscatter Diffraction (EBSD) and Transmission Kikuchi Diffraction (TKD). Thus, future work on this project will involve controlling grain sizes in ZnO films.

Despite the similarities in the ZnO film cross-sections, additional insight was gained regarding modification of the film surface. Since these ZnO films are solution processed, the surface can be textured through a dynamic annealing method.[3] By allowing the film to rest at room temperature after spin casting, the surface morphology can be better controlled to be more planar or more textured (figure 5). This texturing does not play a role in FET performance, but it can drastically alter hybrid organic-inorganic photodiode performance.

Lastly, a brief mention of the perovskite films which our lab has been developing since February 2019 through chemical vapor deposition (CVD). We have been working with Chris Arendse from University of Western Cape in South Africa to assemble the instrument and grow methylammonium lead iodide ($MAPbI_2$) films. Initially, the lead iodide film is grown on glass, which is later converted to $MAPbI_2$. With our first films, SEM was conducted to observe the grain size in PbI_2 films grown at different distances within the tube furnace (Figure 6). Work here is still being done to optimize film growth.

As of August 2019, the Excellence in Electron Microscopy Award has aided us in two publications [2, 5] while one regular journal article and one review article are in preparation, both of which intend to use images obtained at the Mizzou Electron Microscopy Core. We thank Tommi White, Xiaoqing He, Dave Stalla, and Deana Grant at the EMC for their assistance with these projects and for funding this work. We look forward to utilizing the facility and the EM Excellence award again in the future.

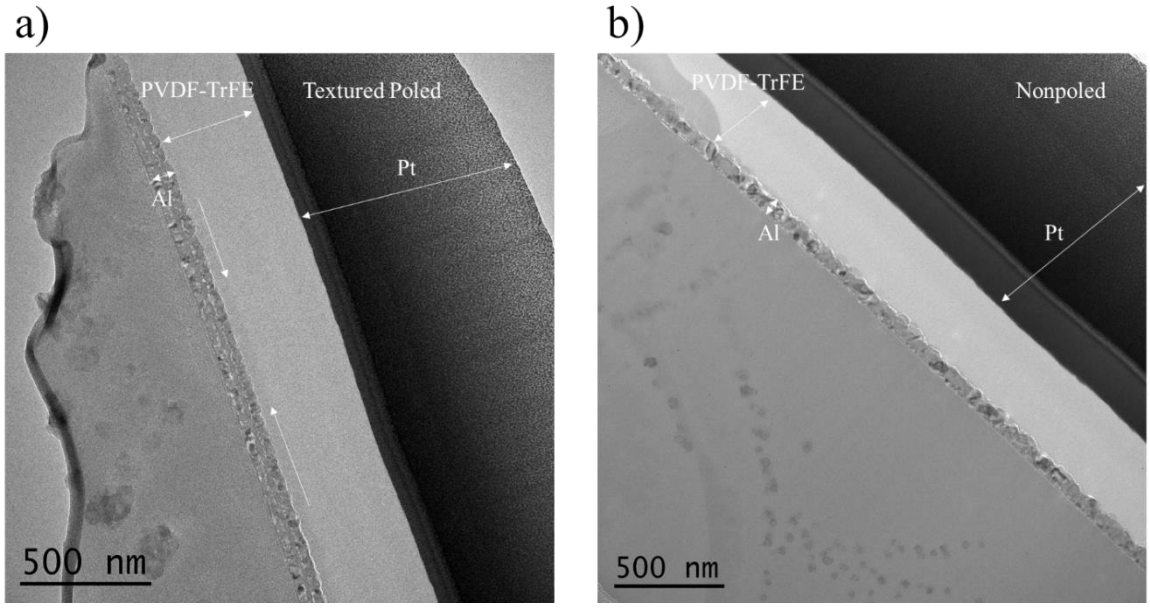

Figure 1. a) Textured poled PVDF-TrFE film at 2.1 μm HFW. The textured region is roughly 30nm thick upon intitial imaging, near the Al interface and marked with arrows. b) Nonpoled PVDF-TrFE film at 2.5 μm HFW. Aside from the textured region in the upper-left corner, the majority of the film at the Al interface does not initially show any texturing.

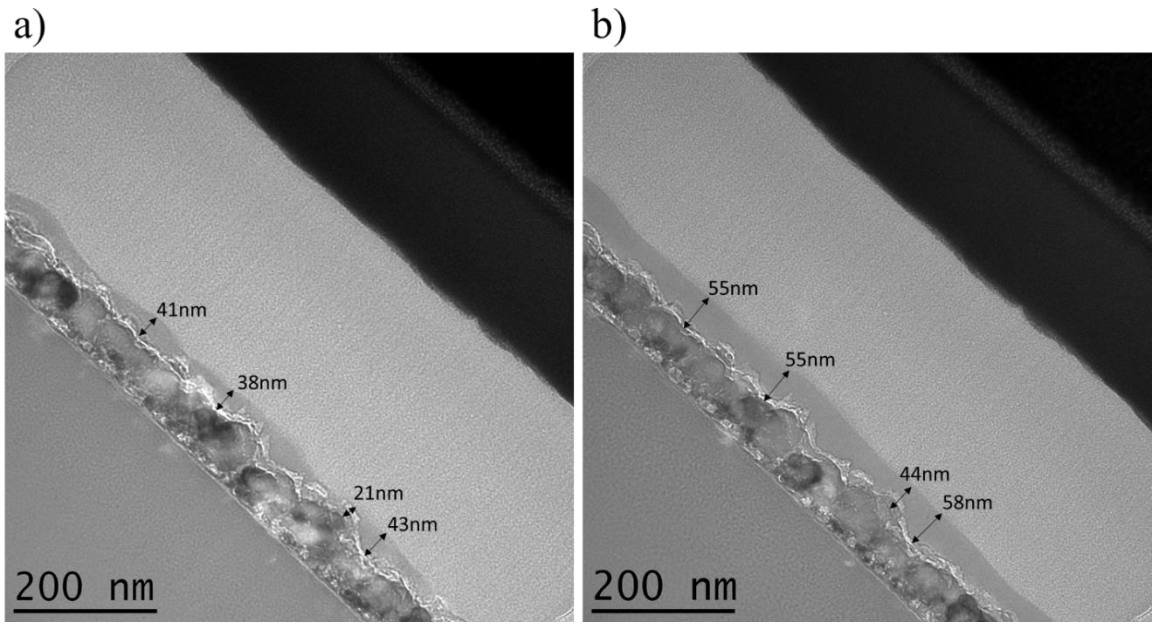

Figure 2. Cross sectional TEM images of a nonpoled PVDF-TrFE film at 793.7 nm HFW. Across many locations along the cross-section a) limited exposure to the electron beam resulted in a textured region of variable thickness. b) 60 seconds of continuous exposure on the same area results in a localized increase of the textured region. Further exposure to the beam results in the textured region saturating towards 60 nm.

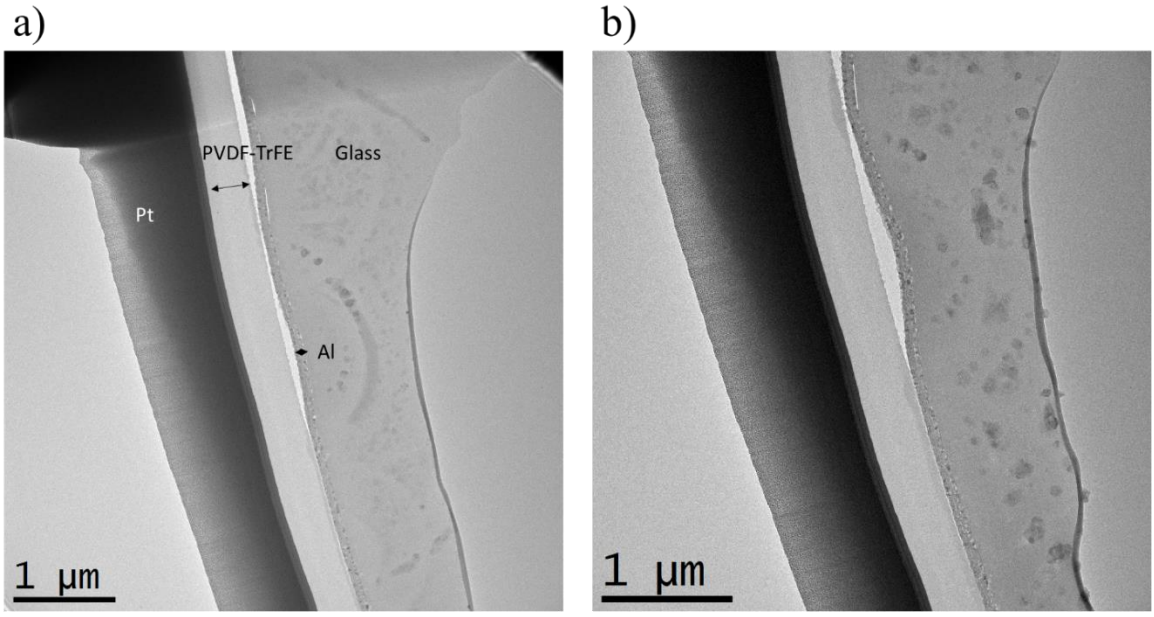

Figure 3. a) Textured poled PVDF-TrFE film at 5.4 um HFW. This was one of the first few images taken of the cross-section. The textured region to the left of the Al interface is 35 nm thick. b) After an hour and a half of taking images, the final image of the same cross-section shows a thicker, 60 nm textured region in the lower half of the image.

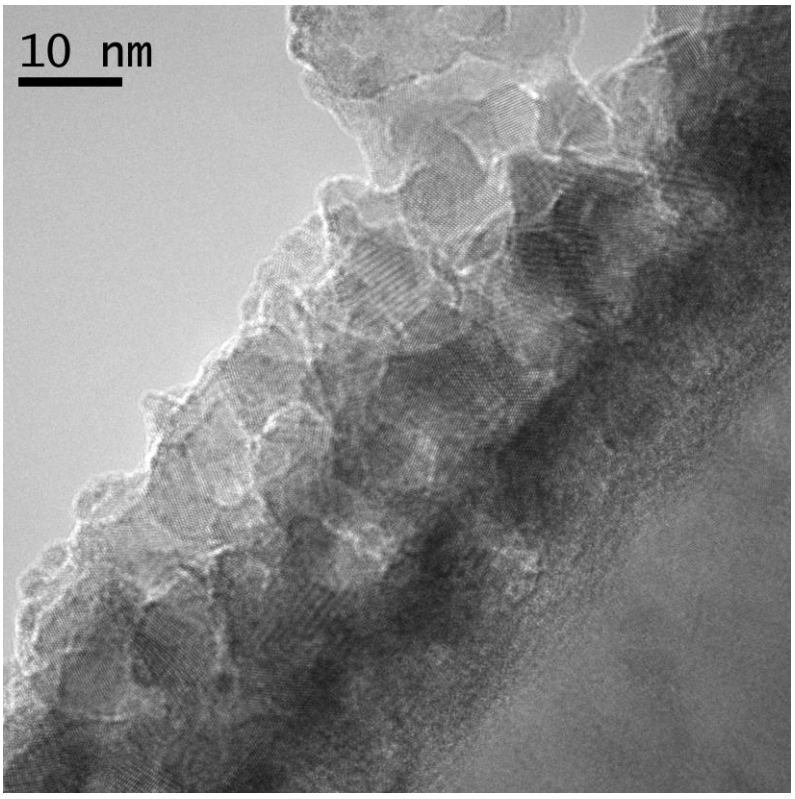

Figure 4. Cross-sectional TEM image of a UV-Ozone treated ZnO thin film, 75.8 HFW.

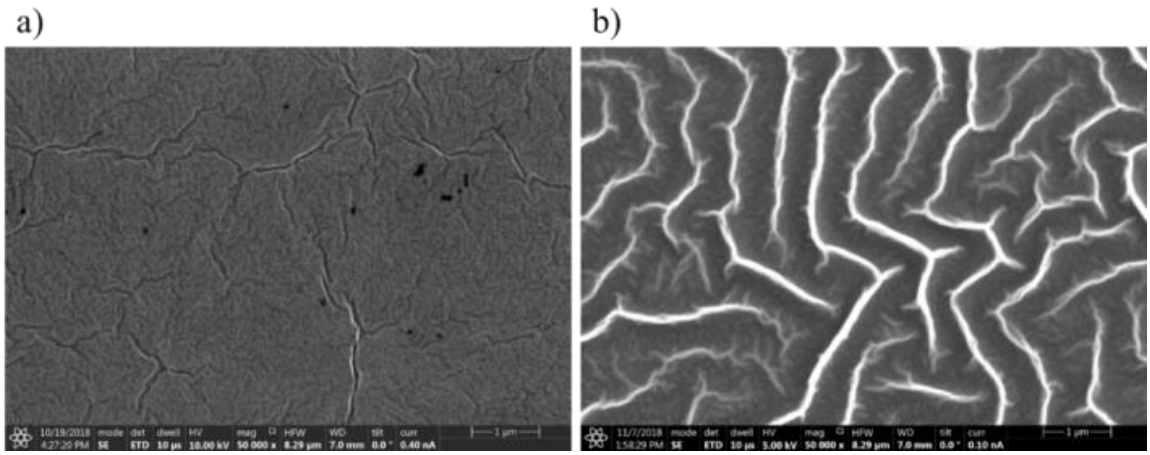

Figure 5. SEM images from ZnO thin films used in FETs. Through altered annealing conditions, ZnO films can be made a) in a planar or b) patterned fashion. Patterning of ZnO does not yield differences in FET characteristics, but can play a large role in photodiode performance.

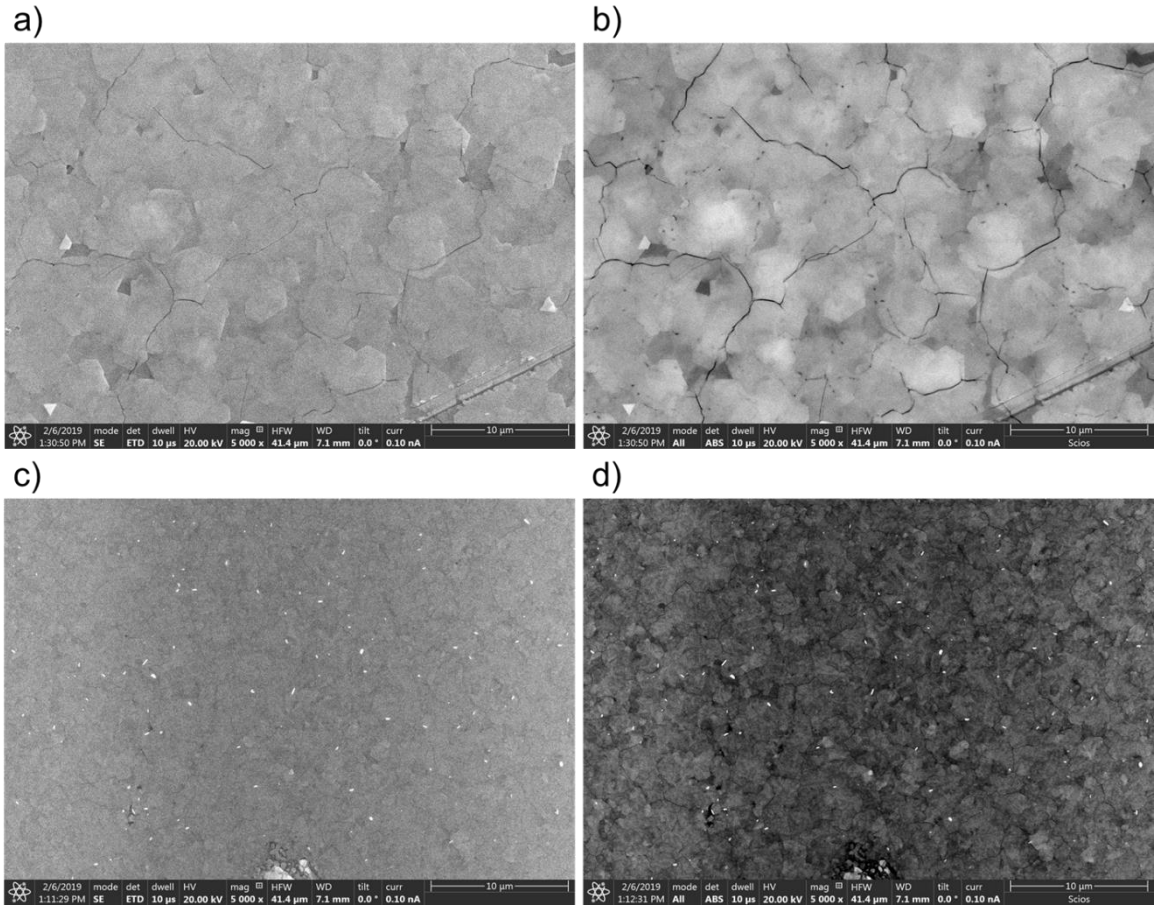

Figure 6. SEM images of PbI_2 films grown at different locations. a) and b) are SE and BSE of a film grown in the center of the furnace. c) and d) are SE and BSE of a film grown 3 inches further from the center, resulting in smaller grain sizes.

References

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[2] A. Laudari, A. Pickett, F. Shahedipour-Sandvik, K. Hogan, J.E. Anthony, X. He, S. Guha, Textured Poling of the Ferroelectric Dielectric Layer for Improved Organic Field-Effect Transistors, Advanced Materials Interfaces, 6 (2019) 1801787.
[3] A. Pickett, A. Mohapatra, A. Laudari, S. Khanra, T. Ram, S. Patil, S. Guha, Hybrid ZnO-organic semiconductor interfaces in photodetectors: A comparison of two near-infrared donor-acceptor copolymers, Org. Electron., 45 (2017) 115-123.
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Publications As a Result of EM Excellence Award

A. Laudari, A. Pickett, F. Shahedipour-Sandvik, K. Hogan, J.E. Anthony, X. He, S. Guha, Textured Poling of the Ferroelectric Dielectric Layer for Improved Organic Field-Effect Transistors, Advanced Materials Interfaces, 6 (2019) 1801787.

A. Pickett, A.A. Mohapatra, S. Ray, C. Robledo, K. Ghosh, S. Patil, S. Guha, Interfacial Effects of UV-Ozone Treated Sol-Gel Processable ZnO for Hybrid Photodetectors and Thin Film Transistors, MRS Advances, (2019) 1-8.