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Analytical Electron Microscopy of Thin Film / Ionic Liquid Interfaces Prepared using a Focused Ion Beam

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Materials that exhibit metal-insulator transitions find widespread use in technological applications. Field effect transistors use an applied bias to induce a metal-insulator transition, but there are limitations on how much voltage can be applied. Ionic liquids are becoming a widespread means of forcing charge accumulation at an interface. The high capacitance of the electric double layer (EDL) can result in a sheet carrier density on the order of $10^{14}/cm^2$, [1] which is greater than can be typically obtained by applying a bias.

Ionic liquids have been used to gate a variety of materials; however, their use is controversial because electrochemical reactions can occur between the film and the ionic liquid under certain biasing conditions. Cyclic voltammetry can be used to assess reactivity,[2] but spatially resolved observations of the interface have not been made. The direct observation of an ionic liquid/thin film interface in the transmission electron microscope provides an assessment of the system on the nanoscale. The purported effects of charge accumulation at the interface are investigated using electron energy loss spectroscopy in the scanning transmission electron microscope (STEM-EELS). This methodology is the only technique that can provide sub-nanometer spatial characterization of the electronic environment for thin films gated by an ionic liquid.

Lanthanum strontium ferrite, $La_xSr_{1-x}FeO_3$, (LSFO) thin films were deposited on STO (001) substrates using molecular beam epitaxy (MBE). An ionic liquid with melting temperature of 70°C was placed on specimens that were heated above 70°C as a bias was applied; the bias was maintained for one hour and as the specimens were cooled to room temperature. Samples were prepared for TEM and STEM analysis using a FEI Strata DB235. Gallium implantation was minimized by using the electron beam to deposit platinum prior to any ion beam exposure, as shown in Figure 1A. Figure 1B shows a cross section that has been thinned nearly to electron transparency in the FIB. The integrity of the ionic liquid and quality of the ionic liquid / LSFO interface is shown in Figure 1C.

The ability of an ionic liquid to maintain charge accumulation is evaluated using STEM-EELS. Figure 2A shows a high angle annular dark field (HAADF) image, and Figures 2B-D show the EELS fine structure for a specimen that has been biased to -1V using ionic liquid. As shown in Figure 2B, the relative intensity of the pre-peak of the O K edge increases after the first few nanometers from the interface, and the fine structure changes notably in the 533-537 eV range. As shown in Figure 2C, the Fe L_3 edge is shifted to a lower energy closer to the interface. Observed changes in both the Fe L and O K edge are consistent with a decrease in the Fe valence near the interface.[3] The effectiveness of the ionic liquid at inducing electronic changes, which could be used to control metal-insulator transitions, is evaluated by comparing EELS spectra from specimens biased under different conditions.

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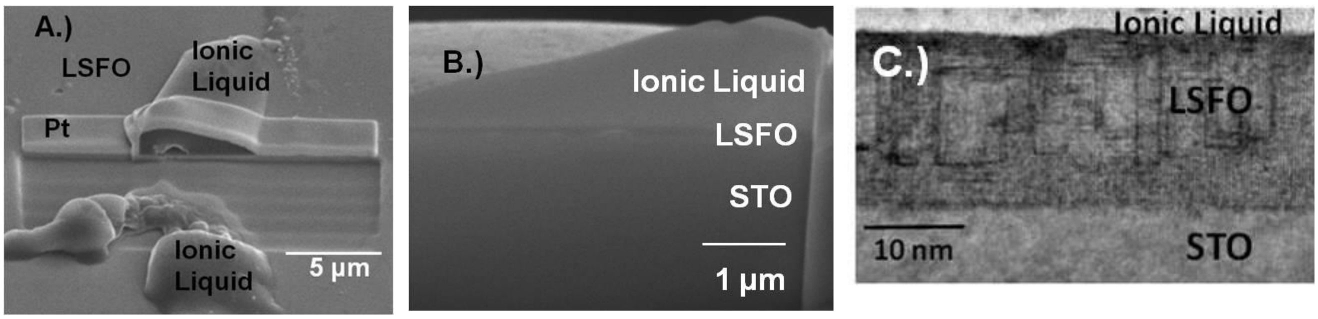

Figure 1: A.) SEM image showing ionic liquid that has been protected with electron beam deposited platinum and milled from one side. **B.)** Cross sectional SEM image of an ionic liquid / LSFO / STO specimen thinned by FIB. **C.)** HR-TEM image showing the ionic liquid / LSFO interface.

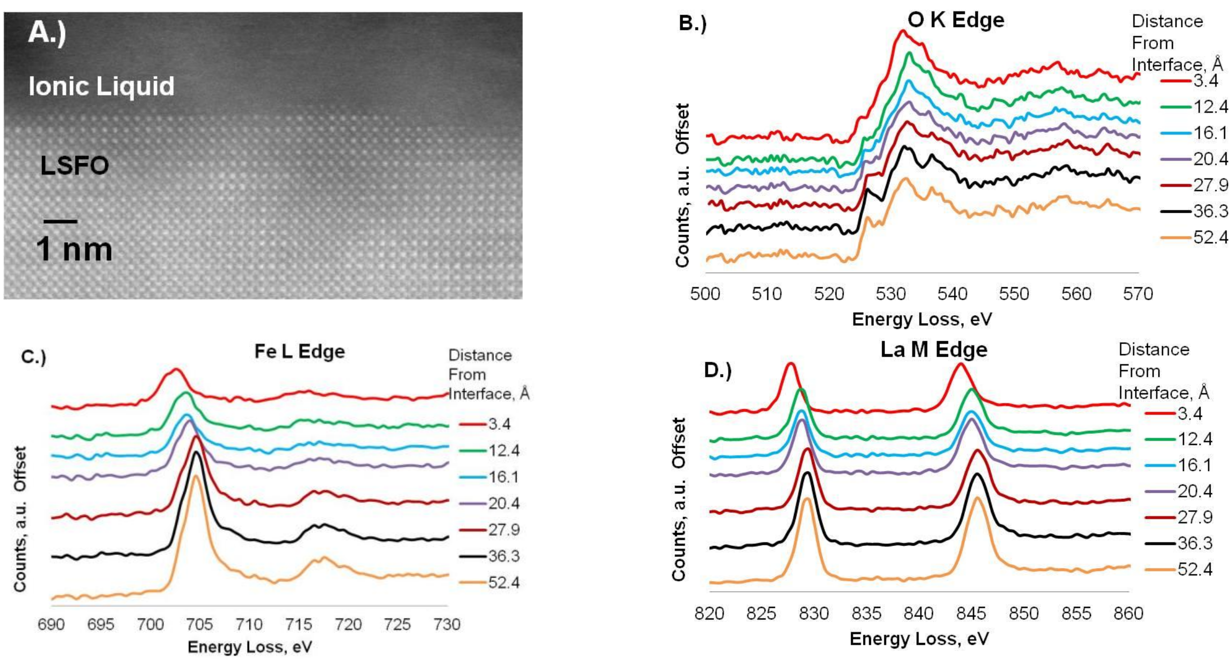

Figure 2: A.) STEM-HAADF image of the ionic liquid / LSFO interface. **B.-D.)** EELS showing the fine structure at varying distances from the ionic liquid / LSFO interface for the **B.)** O K edge, **C.)** Fe $L_{2,3}$, edge, and **D.)** La $M_{4,5}$ edge.

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