# The Solid State Conversion Reaction of Epitaxial $FeF_2(110)$ Thin Films with Lithium Studied by Angle-Resolved X-Ray Photoelectron Spectroscopy: Supporting Information

Ryan Thorpe,<sup>\*</sup> Sylvie Rangan, and Robert A. Bartynski<sup>†</sup> Department of Physics and Astronomy and Laboratory for Surface Modification, Rutgers University, 136 Frelinghuysen Road, Piscataway, New Jersey 08854, United States

Ryan Whitcomb

Department of Applied Physics, University of Michigan, 450 Church Street, Ann Arbor, MI 48109, United States

Ali C. Basaran, Thomas Saerbeck,<sup>‡</sup> and Ivan K. Schuller Department of Physics and Center for Advanced Nanoscience, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093, United States

### SI. HELIUM ION MICROSCOPY OF THE IRON FLUORIDE FILM



FIG. S1: Helium Ion Microscope image of the as-grown  $\text{FeF}_2(110)$  thin film showing 10-15 nm lateral domain size and a film thickness of ~ 50 nm.

Figure S1 shows an image of the as-grown FeF<sub>2</sub>(110) film as taken by a Zeiss ORION Helium-Ion Microscope (HIM) operating at an accelerating voltage of 35 kV, a beam current of 1 pA, and a 1  $\mu$ s dwell time. During imaging, the sample surface was oriented at a 45° angle with respect to the ion beam in order to simultaneously image the surface and cross section of the film. Three distinct regions are visible in this image: a textured region at the top of the image, a narrow band in the center, and a uniform layer at the bottom. These features are attributed to the FeF<sub>2</sub>(110) surface (with < 1 nm corrugations), the bulk FeF<sub>2</sub> layer, and the MgF<sub>2</sub> substrate respectively. This image confirms that the FeF<sub>2</sub> film is about 50 nm in thickness and suggests that the film is composed of 10-15 nm domains.

## SII. IDENTIFICATION OF IRON CHEMICAL SPECIES



FIG. S2: Fe 2p XPS spectrum of the FeF<sub>2</sub>(110) sample after 160 minutes of total Li exposure. The satellite features of the Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> component are clearly visible, and are not fit by any combination of iron fluoride or oxide reference spectra.

Figure S2 shows a Fe 2p core level spectrum obtained from the FeF<sub>2</sub> surface after exposure to atomic Li for 160 minutes. The Fe 2p spectral components arising from FeF<sub>2</sub> and Fe<sup>0</sup> were both taken from reference spectra, and were not sufficient to fit the data. In particular, the presence of the satellite features at binding energies of -716 eV and -730 eV, labeled in Figure S2 was not consistent with any known iron fluoride or oxide species.<sup>1-4</sup> An additional component was then constructed, and subsequently identified as Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub>, using the Fe 2p spectrum taken after the final Li exposure (160 min), as shown in Figure S2. This was chosen as the spectrum with the highest ratio of Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub>:FeF<sub>2</sub>.

Identification of the  $Fe_x Li_{2-2x}F_2$  component was accomplished via comparisons with previous studies. Ko and coworkers have previously observed an expansion in the LiF rock salt lattice upon delibilitation of an

 $FeF_2$  cathode.<sup>5</sup> This was attributed to the formation of  $Fe_x Li_{2-2x}F_2$ .



FIG. S3: Fe 2p XPS spectrum from a cycled FeF<sub>2</sub> cathode showing the same spectral components as the thin film sample.<sup>6</sup>

The formation of  $Fe_x Li_{2-2x} F_2$  was also observed in recent *ex situ* XPS measurements of electrochemically cycled FeF<sub>2</sub> electrodes.<sup>6</sup> Figure S3 shows the peak fitting scheme used for a delithiated electrode in this previous work. These measurements showed that the  $Fe_x Li_{2-2x} F_2$  did not fully dissociate upon the delithiation of the electrode, and hence this ternary compound might be partially responsible for the capacity losses observed in FeF<sub>2</sub> cells.

#### SIII. EVOLUTION OF IRON PEAKS

The reduction of the FeF<sub>2</sub> film upon exposure to lithium was quantified by fitting the Fe 2p peak with a sum of Fe<sup>0</sup>, FeF<sub>2</sub>, and Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> components. Figure S4 shows the evolution of the normal emission Fe 2p spectra for several different lithium exposures. The spectra have been normalized by their maximum intensities in order to highlight their visual differences. From these spectra, it can be seen that the relative intensities of the Fe<sup>0</sup> and Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> components increase monotonically as a function of lithium exposure, while the FeF<sub>2</sub> intensity simultaneously decreases. The Fe:Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> ratio increases slightly as a function of exposure, from 0.85 after 5 minutes of exposure to 1.10 after 160 minutes.

#### SIV. ARXPS DETAILS

The model used to fit the  $R(\theta, d)$  curves consisted of an infinitely thick film of FeF<sub>2</sub> with an inhomogeneously thick overlayer of Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> and Fe metal, as shown in Figure S5. In order to model the attenuation of the FeF<sub>2</sub> photoelectrons, the overlayer was divided vertically into four different types of regions: (1) thick Fe<sup>0</sup>, (2) thick



FIG. S4: Fe 2p spectra of the  $FeF_2$  film taken at normal emission after each lithium exposure.

Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub>, (3) thin Fe<sup>0</sup>, and (4) thin Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub>. The relative coverages of Fe<sup>0</sup> and Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> were determined by the ratio of the specific volume of each species, such that 85% of the surface was covered by Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> and 15% by Fe<sup>0</sup>. This columnar geometry of overlayer compounds is consistent with the Fe<sup>0</sup> and Fe<sub>x</sub>Li<sub>2-2x</sub>F<sub>2</sub> spectral intensities being equal for all angles and overlayer thicknesses.

The  $FeF_2$  signal was then calculated from the following



FIG. S5: Model of the Li-FeF<sub>2</sub> conversion reaction used to generate  $R(\theta, d)$  curves. The FeF<sub>2</sub> substrate is divided into four distinct regions of overlayer thicknesses and compositions.

equation:<sup>7</sup>

$$I_{\rm FeF_2}(d,\theta) = I_{\rm FeF_2}^{\infty} \sum_{i=1}^{4} \Theta_i \left[ \exp\left(-\frac{d_i}{\lambda_i(d,\theta)\cos\theta}\right) \right]$$
(S1)

where  $\Theta_i$  is the fractional coverage of each region and  $\lambda_i(d,\theta)$  was calculated for each species, thickness, and emission angle using a procedure described below. Similarly, the  $Fe^0$  and  $Fe_x Li_{2-2x} F_2$  signals were then calculated by:

$$I_{\rm Fe}(d,\theta) = I_{\rm Fe}^{\infty} \sum_{i=1}^{4} \Theta_i \left[ 1 - \exp\left(-\frac{d_i}{\lambda_i(d,\theta)\cos\theta}\right) \right].$$
(S2)

The ratio R was then calculated as

$$R(\theta, d) = \frac{I_{\rm Fe}(d, \theta)}{I_{\rm FeF_2}(d, \theta)}.$$
 (S3)

The effective attenuation lengths were calculated using the NIST EAL Calculator.<sup>8–11</sup> Table SI shows the EALS calculated at normal emission for each species. Similar tables were calculated at each  $5^{\circ}$  increment from  $0-50^{\circ}$ .

#### SV. STRUCTURAL PARAMETERS

 $FeF_2$  has a  $P4_2$ /mnm rutile (tetragonal) structure with lattice constants a = b = 4.697 Å and c = 3.309 Å at

d (nm)	$\lambda_{\rm FeF_2}$ (nm)	$\lambda_{\rm Fe} (\rm nm)$	$\lambda_{\mathrm{Fe}_{x}\mathrm{Li}_{2-2x}\mathrm{F}_{2}}$ (nm)
0.2	1.44	1.04	2.35
0.4	1.42	1.03	2.33
0.6	1.41	1.01	2.32
0.8	1.40	1.01	2.30
1.0	1.40	1.00	2.29
2.0	1.38	0.98	2.26
3.0	1.36	0.96	2.24
4.0	1.35	0.95	2.23
5.0	1.35	0.96	2.22

TABLE SI: Effective attenuation lengths of each iron	com-
pound calculated at normal emission using the NIST	EAL
Database.	

room temperature. Each  $Fe^{2+}$  ion in the bulk is bound to six F<sup>-</sup> ions in a distorted octahedral configuration with metal-ion distances of 2.03 Å and 2.10 Å.<sup>12</sup> The FeF<sub>2</sub> [110] channels have nearly square cross sections and are located between the octahedra in the lattice. This square cross section measures  $2.10 \times 2.10$  Å, from the centers of the fluorine ions at the boundaries. Including the radii of the  $F^-$  ions, the cross section of the [110] channel is approximately 0.6 Å, which is smaller than the diameter of either Li<sup>0</sup> or Li<sup>+</sup>. This geometrical argument supports the assertion that lithium cannot diffuse into the  $FeF_2(110)$  surface. In comparison, the  $FeF_2$  [001] channels are  $3.43 \times 3.43$  Å from the centers of the bounding ions and  $2.18 \times 2.18$  Å including the ionic radii, which is large enough to accomodate either Li<sup>0</sup> or Li<sup>+</sup> diffusion.

Element	Charge	Radius (pm)
Li	0	145
Li	1+	76
F	2-	133
Mg	2+	72
Fe	0	126
Fe	2+	78
Fe	3+	64

TABLE SII: Summary of relevant atomic and ionic radii from Shannon<sup>13</sup> and Slater.<sup>14</sup>

- \* Fellow, Nanotechnology for Clean Energy IGERT
- <sup>†</sup> Electronic address: bart@physics.rutgers.edu
- $^\ddagger$  Current address: Institut Laue-Langevin, 71 avenue des Martyrs, 38000 Grenoble, France
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