

Nanofabrication Limits in Layered Ferroelectric Semiconductors via He-ion Beam

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Advances in nanofabrication are the driving force behind the technological breakthroughs in device performance and miniaturization. Functional layered materials with dielectric properties, such as insulators, semiconductors, and correlated electron materials will be necessary for fabrication and delivery of new age devices.¹ Helium (and Neon) ion beam nanofabrication has the benefits of clean, resist-free processing; smaller penetration depth into the material, and reduced active ion implantation, common in standard Focused Ion Beam (FIB) lithography applications.²

We demonstrate the use of HIM to create a variety of micro-sized structures with varying chemical properties atop several transition metal thiophosphates³ (TPS) compositions; a broad class of van-der-Waals layered solids. TPS compounds exhibit large band-gaps and a pronounced flexibility to ionic substitution in the metal sites with over 260 combinations known for the sulfides alone.

To investigate the effects of the stoichiometric ratio of Cu/In on the growth of nanostructures, we irradiated the surface of the different Cu compositions with varying He doses. Figure 1 illustrates Band Excitation Piezoresponse Force Microscopy (BE-PFM) results for same levels of irradiation in $\text{Cu}_{0.05}\text{In}_{1.32}\text{P}_2\text{S}_6$ and $\text{Cu}_{0.7}\text{In}_{1.1}\text{P}_2\text{S}_6$. Irradiated areas with ferrielectrically active Cu phase grow at a higher rate vertically and horizontally as opposed to the paraelectric $\text{In}_{4/3}\text{P}_2\text{S}_6$. The nanostructures have shown an overall increase of area, volume. Our Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) results, shown in Figure 2, show a significant increase in the amount of oxygen penetration into the sample as a function of dose.

In summary, we have explored the effect of helium ion impact on the surface of a library of TPS compounds using AFM and ToF-SIMS. After the helium exposure, we have used the AFM to observe surface nano- and micro- structures that scale, in area and volume, to the total dose of the helium ion beam, as well as the overall copper concentration in the sample. Furthermore, our ToF-SIMS results show that after ion irradiation, the oxygen concentration in the irradiated areas is significantly increased.

References:

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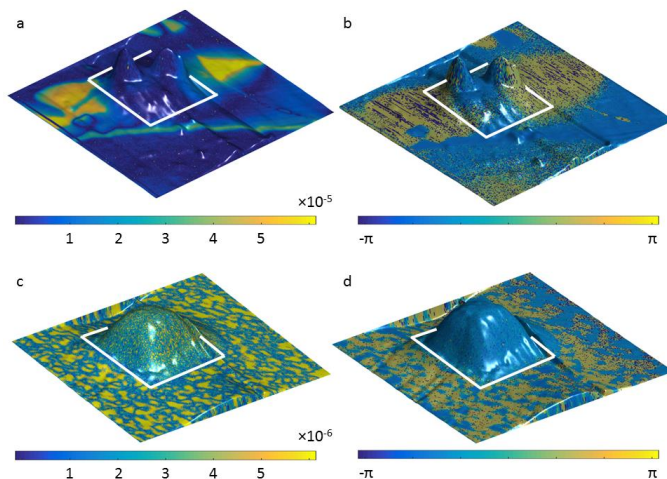


Figure 1: Band Excitation Piezoresponse Force Microscopy (BE-PFM) results. The BE-PFM amplitude (a, b) and phase (c, d) of $\text{Cu}_{0.19}$ samples (a, c) and $\text{Cu}_{0.70}$ (b, d). The BE-PFM signal colormap for both samples is overlaid on the topography as captured by AFM. Black boxes in all images indicate the HIM irradiated areas.

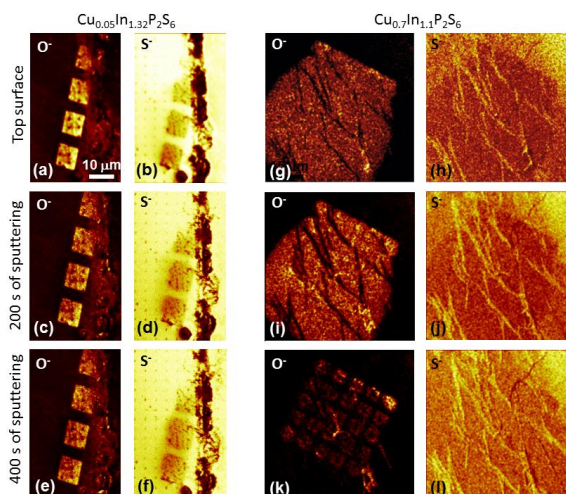


Figure 2: Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) results on irradiated regions. Secondary ion mass spectrometry of oxygen of irradiated boxes in a (a-f) low Cu concentration sample ($\text{Cu}_{0.05}$) and a (g-l) high Cu concentration sample ($\text{Cu}_{0.70}$) at different sputtering times (depth) for both oxygen (a, c, e, g, i, k) and sulfur (b, d, f, h, j, l).