

Supplementary Information

Optical and grain boundary potential characteristics of sulfurized BiFeO₃ thin films for photovoltaic applications

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I. XRD patterns of sulfurized films in the 2θ range of 20° to 60°

The disappearance of perovskite BiFeO₃ peaks and the appearance of Bi₂S₃ phase are prominent with the progress of sulfurization at high temperatures. The close comparison of the 400 °C pattern with that of Bi₂S₃ phase suggests that any other phase did not form as a major phase. It is very interesting that the Fe-involved phase could not be found as crystalline phase.

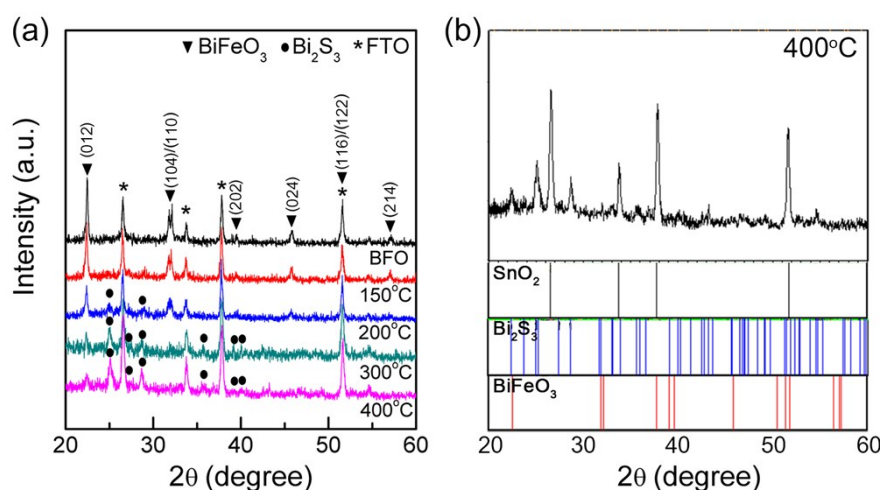


Fig. S1. (a) XRD patterns of BiFeO₃ and sulfurized BiFeO₃ thin films at different sulfurization temperatures, and (b) only the pattern of 400 °C sample with matched JCPDS peaks of each phase

II. XPS spectra of Fe 2p states

Detailed analysis results of the oxidation state of Fe are shown below. Note that Fe²⁺ state was observed in the unsulfurized BFO thin film. It is noticeable that the fitted area of Fe³⁺ state decreased with increasing sulfurization temperature. Based on the calculated fitted peak areas for Fe³⁺ and Fe²⁺, concentration ratios of Fe³⁺:Fe²⁺ in the BFO, 150 °C and 200 °C films were 89:11, 82:18 and 76:24, respectively, indicating that the presence of Fe²⁺ ions became significant with the progress of sulfurization. It is clear that the sulfurization produced the change of the oxidation state of iron, potentially supporting the existence of complex Bi-Fe(III)-Fe(II)-S-O compounds.

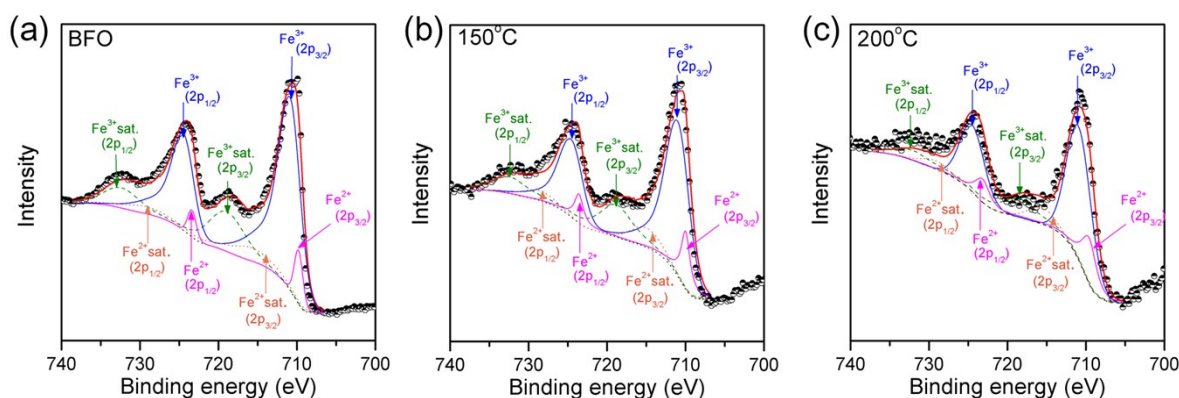


Fig. S2. XPS spectra of unsulfurized and 150 °C- and 200 °C- sulfurized BFO thin films in the Fe 2p binding energy region

III. Detailed XPS depth analyses

Additional XPS analyses were investigated by characterizing chemical states with film depth from the surface. Ar⁺-sputtering of the 200 °C-sulfurized sample was performed progressively from 0 second up to a few thousands seconds until all film part was eliminated. The resultant XPS spectra of the Fe 2p, Bi 4f and S 2s states with the sputter etching time are seen below. The Sn 3p peak observed in the Fe 2p XPS spectra (left) above 2,655 sec came from the F:SnO₂-coated glass substrate used here, indicating that all films were etched upon Ar⁺-sputtering. Thus we can calculate the etching rate using the known thickness of film. As a result, the etching rate is approximately 0.1 nm/s.

The Bi 4f peaks in the middle spectra below tend to shift toward higher binding energies with increasing etching time. It seems that the Bi-S bonds from the surface are gradually transformed to the Bi-O bonds. The shoulders at ~157 and ~163 eV (marked with *) are attributed to the metallic bismuth state since Ar ion sputtering changes considerably Bi³⁺ ions into Bi⁰ due to weak Bi-O bonds as reported in literature: Zhang et al., *Appl. Surf. Sci.* 257 (2011) 7461 and Jocalekic et al., *J. Alloy. Compd.* 469 (2009) 441. From the S 2s spectra (right), the existence of sulfur was also confirmed up to a certain etching time. Although the XPS depth profiles do not suggest actual compositions, the existence of sulfur from the film surface is again confirmed.

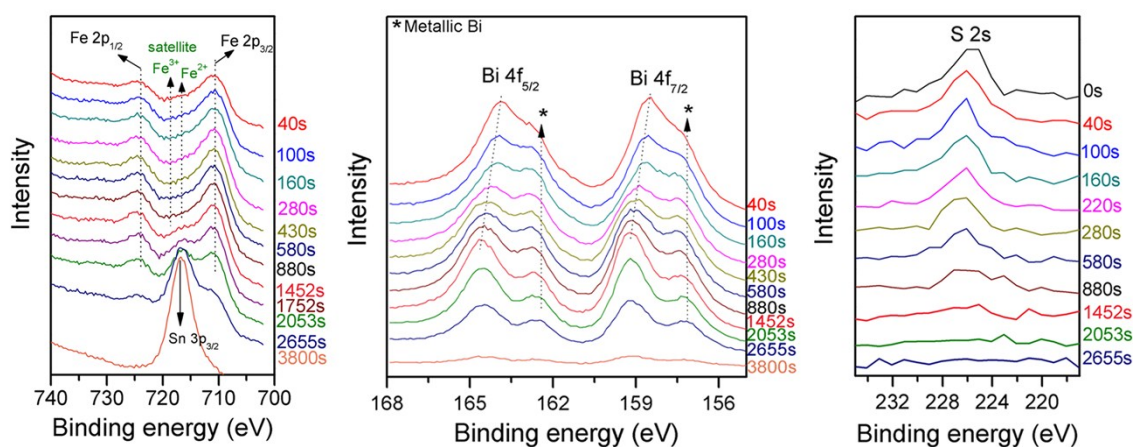


Fig. S3. Etching time-dependent XPS spectra of 200 °C-sulfurized BFO thin films in the binding energy regions corresponding to Fe 2p (left), Bi 4f (middle) and S 2s (right) peaks