

Supporting Information

Oxidation Effect in Octahedral Hafnium Disulfide Thin Film

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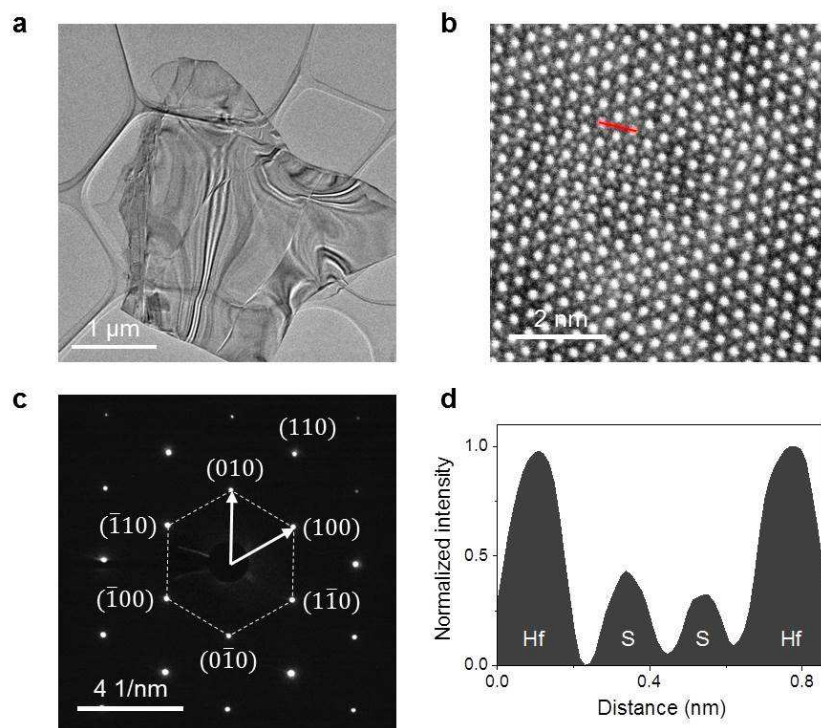


Figure S1. Transmission electron microscopy (TEM) measurement of HfS₂. (a) TEM image of exfoliated HfS₂. Exfoliated HfS₂ was deposited onto carbon grids inside a Cu TEM grid. (b) Unfiltered scanning transmission electron microscopy (STEM) image of HfS₂ showing that Hf and S atoms contrast clearly. Blurred parts are due to differences in thickness; however, there is no aggregation. (c) Selective-area electron diffraction (SAED) image of HfS₂ showing a hexagonal lattice structure with labeled symmetric points in the reciprocal lattice. Interplane distances are slightly different from the data extracted from the STEM image in the main text: 0.35 (100) and 0.20 (110) nm. (d) Normalized intensity profile from the STEM image (red line). Each atom is identified through intensity difference.

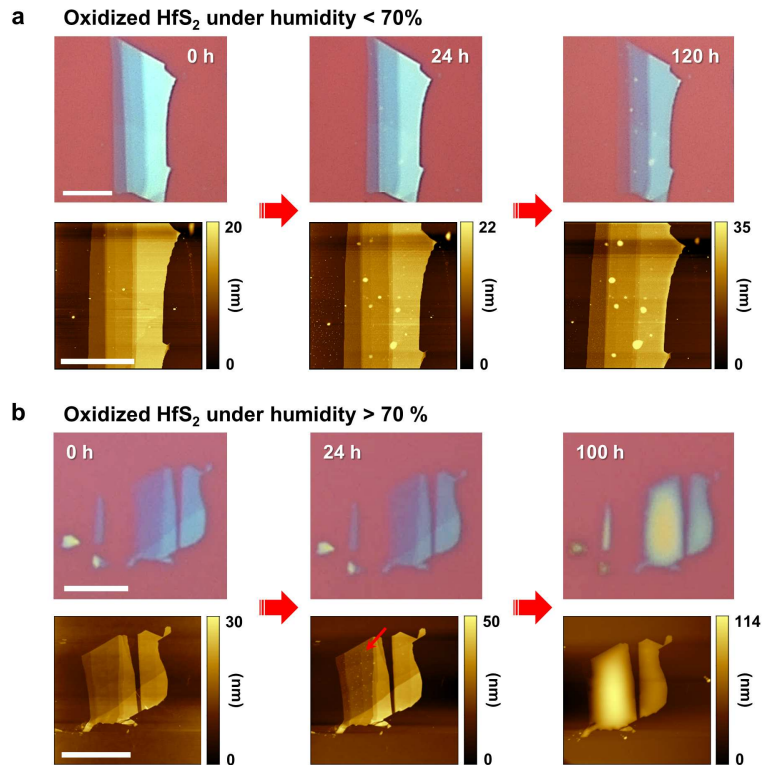


Figure S2. Time-dependent morphological degradation of HfS₂. (a, b) Optical (top) and topological (bottom) images of exfoliated HfS₂ show degradation of each samples due to oxidation effect. HfS₂ flakes were prepared by mechanical exfoliation onto SiO₂ (300 nm)/Si substrates. Oxidation seems to start from defect sites of the sample with faster oxidation process, so that partly more oxidized parts (protrusions) have larger thickness as shown in both images with bubble-like shape.¹ Finally, whole thickness increases uniformly proportional to the time. Oxidation process was conducted in the limited environment with (a) high and (b) low humidity to control the oxidation speed. Oxidation process involves oxygen and water molecules, and humidity is an important factor in oxidation of HfS₂ as compared between (a) and (b). The scale bar is 10 μm .

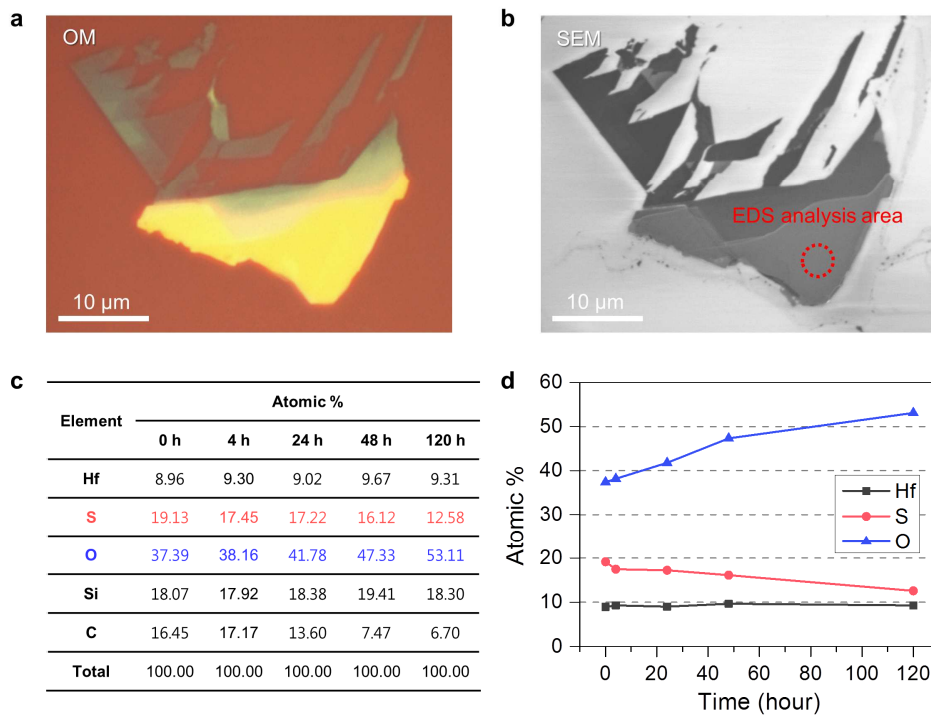


Figure S3. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) analysis for oxidized HfS₂. (a) Optical and (b) SEM images of exfoliated HfS₂ flake. The scale bar is 10 μm. (c) EDS result with time variation (0, 4, 24, 48, and 120 h) for the HfS₂ flake being exposed in air. (d) The atomic percentage of S keeps reducing under air exposure. In contrast, the atomic percentage of O keeps increasing.

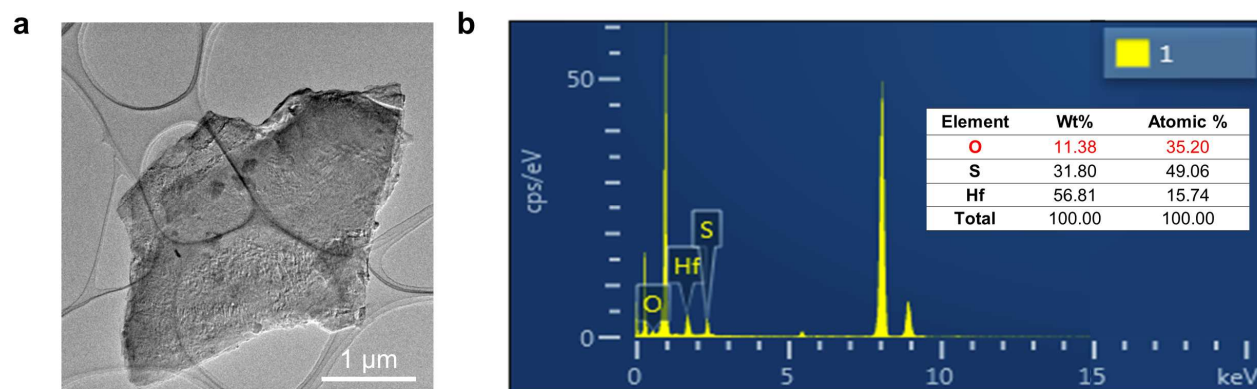


Figure S4. TEM measurement of oxidized HfS_2 (HfO_x). (a) TEM image of oxidized HfS_2 . HfS_2 was exposed to air in order to measure its oxidized parts (HfO_x). TEM image of this part seems to show a rough and aggregated surface. (b) Energy-dispersive X-ray spectroscopy (EDS) data of an oxidized part showing evidence of oxidation of HfS_2 with a high-intensity oxygen component.

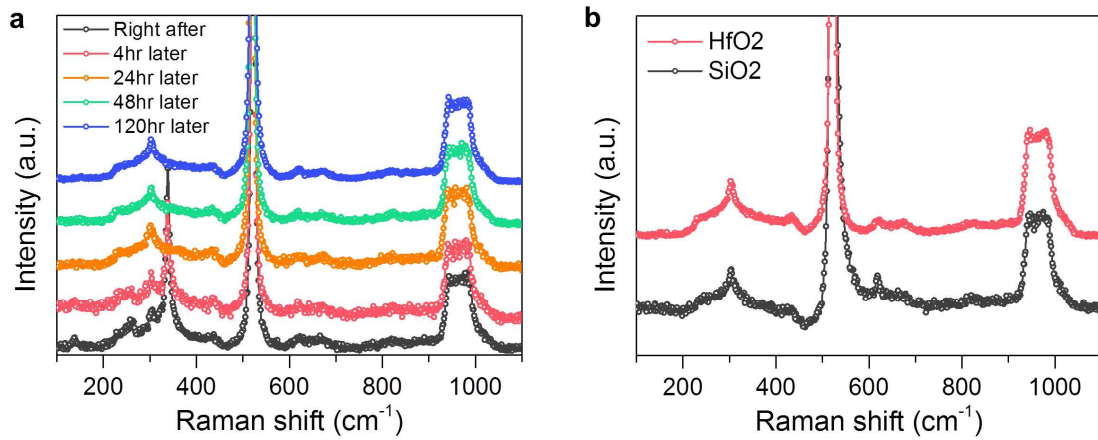


Figure S5. Raman spectra analysis for HfS₂. (a) Raman spectra of HfS₂ with time variation from 100 to 1100 cm⁻¹. HfS₂ was mechanically exfoliated onto a SiO₂ (300 nm)/Si substrate. Raman spectra show HfS₂ Raman modes with several oxidation modes. (b) Raman spectra of SiO₂ and HfO₂. HfO₂ was deposited onto a SiO₂ (300 nm)/Si substrate by atomic layer deposition. Raman spectra of HfO₂/SiO₂/Si are in great accordance with those of SiO₂/Si, therefore, it is difficult to distinguish HfO₂ Raman modes and its intensity change from those of HfS₂ with time variation. The intrinsic peak of HfO_x are buried into SiO₂ peak due to the poor crystallinity of HfO_x.^{2,3}

References

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3. Borowicz, P.; Taube, A.; Rzodkiewicz, W.; Latek, M.; Gieraltowska, S. Raman Spectra of High- κ Dielectric Layers Investigated with Micro-Raman Spectroscopy Comparison with Silicon Dioxide. *Sci. World J.* **2013**, 2013, 208081-208087.