Comparative analysis of group IV bulk TMDs' surface stability under ambient conditions

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Group IV Transition Metal Dichalcogenides (TMDs) possess attractive electronic properties, such as a tunable band gap in the 1–2 eV range and predicted charge carrier mobilities in the thousands of $cm^2 \cdot V^{-1} \cdot s^{-1}$ [1]. Unlike most TMDs, they are not chemically inert under ambient conditions. Oxidation can alter their surface properties and morphology, making it essential to study the changes as they impact technological processing of group IV TMDs and their performance in electronic devices.

In our earlier work, we demonstrated that $HfSe_2$ undergoes rapid oxidation, resulting in Se-rich blister formation, oxygen diffusion into the bulk of the crystal, and HfO_2 growth on the surface [2]. In this study, we extend our investigation to HfS_2 and ZrS_2, comparing the impact of ambient air exposure on their surfaces with that observed for $HfSe_2$. Scanning electron microscopy (SEM) reveals morphological differences: while $HfSe_2$ shows bright blister-like features, sulfides develop areas with different charge carrier concentration that gradually rise in number with increasing exposure time to ambient air. Raman spectroscopy (RS) indicates that the vibrational modes of HfS_2 and ZrS_2 remain mostly unaffected, suggesting higher chemical stability compared to $HfSe_2$, whose RS modes change drastically as the surface oxidation progresses. Complementary X-ray photoemission spectroscopy (XPS) data describes the influence of the ambient air exposure on the investigated materials' surface chemical composition.

These results provide a comprehensive picture of the morphological and chemical differences in group IV TMD oxidation, highlighting the role of chemical composition in determining their surface stability, which affects their integration potential with silicon-based electronics.

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[2] K. Kwiecien, et. al, *Appl. Surf. Sci.*, 2025, **690**, 162546.