The (Mostly) Unwelcome Guest in 2D Chalcogenides: Native oxidation and the effects of oxygen during processing MoS_2, TiS_2, and $Zr(S,Se)_2$

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Being a very hard anion, oxygen bonds very differently to transition metals than do the chalcogens. Trace oxygen in a transition metal dichalcogenide (TMD) has a substantial impact on material processing and properties, much more so than for instance trace selenium in a sulfide. Since oxygen is all around us, it is essential to understand and control the effects of oxygen on processing 2D materials. We report studies of the effect of oxygen on processing TMDs. We find that lowering trace oxygen concentration in the reactor makes it possible to lower the processing temperature for large-area TiS_2 films, made by reacting Ti thin films with H_2S gas. We quantify how lowering oxygen concentration enables faster metal sulfurization at lower temperatures (down to 500 °C), leading to thin films that are smooth and homogeneous. In contrast, we find the opposite trend for MoS_2: *adding* trace oxygen enables lower processing temperatures (down to 375 °C) for large-area MoS_2 films, made by sulfurizing Mo thin films. We understand these contrasting effects in the light of particulars of Ti-O and Mo-O bonds, including molecular dynamics (MD) simulations that suggest that oxygen is a catalyst for Mo-S bond formation. We also report studies of the native oxidation of MoS_2, and $Zr(S,Se)_2$. The native oxides of these semiconductors may ruin or enable future devices, depending on the oxide processing and properties. We use spectroscopic ellipsometry (SE) and scanning transmission electron microscopy (STEM) to characterize native oxidation processes, and reactive molecular dynamics (RMD) to understand key atomistic mechanisms. MoS_2 surfaces remain pristine for over a year in laboratory ambient conditions, without a trace of oxide formation. Under dry thermal conditions, MoS_2 native oxide growth proceeds via a process of oxidation, sublimation, re-deposition, and crystallization, resulting in epitaxial growth of standalone MoO_3 crystals. Non-thermal processing is needed to oxidize-in-place, to make a conformal and amorphous coating. In contrast, $Zr(S,Se)_2$ alloys oxidize rapidly in ambient conditions, with the native oxide growing at a rate up to 0.5 Å/min. RMD reveals the kinetic mechanisms that limit native oxide growth for MoS_2 and promote it for $Zr(S,Se)_2$, despite oxide formation in ambient conditions being thermodynamically-favorable in all cases. Our results provide quantitative guidance for accounting for oxygen in the design and processing of TMD devices.