Study of oxidation and degradation mechanisms of $ZrSe_2$ in ambient conditions

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Recently, there has been increased interest in Zr-based transition metal dichalcogenides (TMDs) as potential silicon substitutes in electronics. Similar to silicon, $ZrSe_2$ is a semiconductor with a bandgap of roughly 1 eV in bulk that rises to 1.5 when reduced to monolayer. ZrO_2, the native oxide of $ZrSe_2$, has a bandgap of 5.3 eV and is a member of the so-called "high-k" insulators, which have been replacing SiO_2 recently due to their higher dielectric constant. This suggests that $ZrSe_2/ZrO_2$ may create a semiconductor/insulator couple similar to Si/SiO_2, with the advantage that it can be reduced to few layers [1]. Moreover, because $ZrSe_2$ has a native oxide, compatibility issues with the deposited oxides are reduced because it does not require a distinct metal dielectric. This makes it even more favorable than MoS_2 and Black Phosophorus [2].To fully benefit from all these features and achieve a smooth TMD/oxide interaction, it is crucial to first fully understand how the oxidation process appears.

In this study we present a systematic examination of $ZrSe_2$ surfaces in air using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) on specific flakes during a 30-day period. It's interesting to note that SEM significantly alters the $ZrSe_2$ surface's texture, preventing the development of hemispherically shaped protrusions on it, which were observed, instead, on aged flakes that were not previously scanned. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) offered a deeper understanding of the nature of the surface protrusions that result to be Se-rich, as observed for other selenium-based 2D materials [3]. Raman spectroscopy also provided valuable insights into the evolution of the degradation process, that appears to be not self-limiting. In the end, our density functional theory simulations revealed how $ZrSe_2$ interacts with air molecules and which features are the most effective nucleation sites for molecules' adsorption.

To prevent the $ZrSe_2$ degradation, we suggested an encapsulating strategy. Raman spectroscopy verified that, under various circumstances, our encapsulation approach has been successful in preventing the $ZrSe_2$ reaction with the environment. Therefore, field effect transistors have been fabricated with both Ni/Au and Cr/Au metal contacts on encapsulated flakes. Preliminary current -voltage measurements results are here reported and can be considered a first valuable stage towards the improvement of $ZrSe_2$-based devices.

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