In situ x-ray quantitative investigation of the grown of 2D TiS_2 transition metal dichalcogenide prepared by hybrid ALD/MLD

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Transition metal dichalcogenides (TMD) are receiving great interest in the past few years due to their future applications in super-capacitors, batteries, electronics and optoelectronics etc [1]. Lamellar titanium disulfide TiS_2, which consists of S-Ti-S layers separated by van der Walls gaps, is also considered to be integrated into emerging energy devices such as rechargeable batteries [2]. Ultra-thin films of TiS_2 are equally technologically challenging to prepare in large-scale production for device application. Among the various growth methods, atomic layer deposition (ALD) is the technique that could produce a high-quality ultra-thin film of TiS_2 in a controlled manner [3]. Recently, our group has demonstrated the controlled growth of TiS_2 ultra-thin films by a two-step process composed of (i) ALD/MLD step using inorganic and organic precursors (tetrakis-dimethylamido titanium and 1,2-ethanedithiol); (ii) annealing under Ar/H_2 atmosphere [4]. This work aims to understand both steps, i.e. the reaction of precursors with the substrate and subsequent growth cycles using *in situ* monitoring by X-ray. The growth of ultra-thin films has been carried out on thermal SiO_2 on Si substrate in a custom-built portable reactor designed to be installed on the 6-axis diffractometer of beamline SIRIUS at SOLEIL Synchrotron for in situ characterization [4]. X-ray fluorescence (XRF), X-ray reflectivity (XRR) and X-ray absorption spectroscopy (XAS) have been performed *in situ* during the sample growth and the subsequent annealing, to understand and control the growth mechanism. The XAS measurements have been performed at both the Ti and S K-edges.

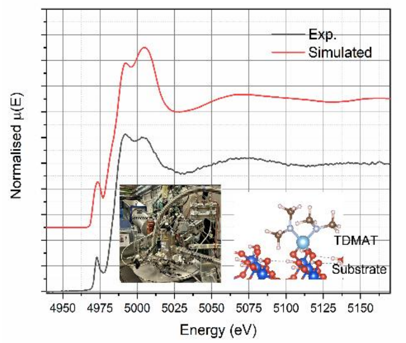

Figure: Experimental and simulated XANES spectra at Ti K-edge for the first half cycle. Insets show experimental setup and possible bonding with surface.

To understand the initial growth process, Density Functional Theory (DFT) calculations have been performed to obtain the best suitable model structure. The DFT-optimized structures are used to simulate the XANES spectra, and the initial model is revised until the best matching. The analysis gives an atomistic view of the mechanism underlying the initial growth cycles with a quantitative approach (*in situ* XAS and DFT). The quantitative analysis of S K-edge data gives stronger evidence of the formation of TiS_2 ultrathin layers at the final stage.

References

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