

Príloha č. 3 k záverečnej monitorovacej správe projektu 09I03-03-V04-00709

D5. Report on PtSe₂, MoSe₂, and MoS₂ layers on the steel substrates.

Initial tests of the deposition of TMDCs were performed by direct synthesis on the 16MnCr5 steel substrates. Specifically, MoS₂ and PtSe₂ layers were synthesized via thermally assisted conversion (TAC) at 400 °C, whereas MoSe₂ was grown via chemical vapor deposition (CVD) at 800 °C. These temperatures were chosen based on previous optimization experiments on Si and sapphire substrates that were reported in Technical Report 1. In particular, this approach involved selenization of a 10 nm Pt layer for PtSe₂ and a 10 nm Mo layer for MoS₂ for 30 minutes, while MoSe₂ synthesis was performed using MoO₃ and Se powder placed together with substrates in the CVD chamber for 1 hour. To characterize the samples, we performed optical microscopy and Raman analysis. These analyses demonstrate that direct deposition attempts resulted in only partial coverage of the substrates, as shown in Figure 1a for TAC deposition, indicating poor film adhesion. Furthermore, Raman spectra confirmed the formation of only MoS₂ and PtSe₂ layers, while no peaks related to MoSe₂ were detected in the CVD-grown samples, which can be attributed to their low crystallinity (Figure 1 d-f). Contact profilometry measurements after deposition revealed large variations in film thickness, with values reaching up to 11 µm compared to the initial 0.1 µm (Figure 2) on the uncoated substrate. These changes can be attributed to inhomogeneous film growth across the surface and partial delamination caused by high-temperature processing. In contrast, similar processes parameters on reference Si and sapphire substrates resulted in a controlled film thickness of approximately 40 nm.

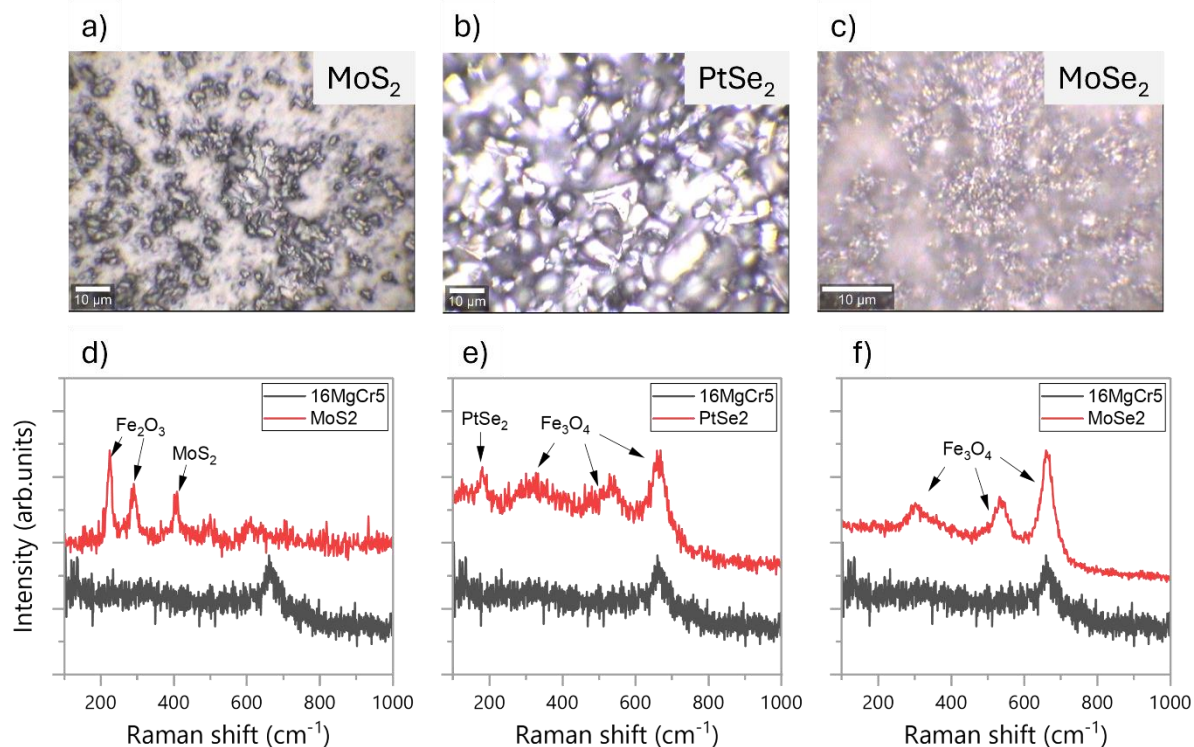


Figure 1. Microscope images (a-c) and Raman spectra (d-f) of direct TAC and CVD deposited TMDS on 16MnCr5 steel substrates. (a,d) – MoS₂, (b,e) – PtSe₂, (c,f) – MoSe₂

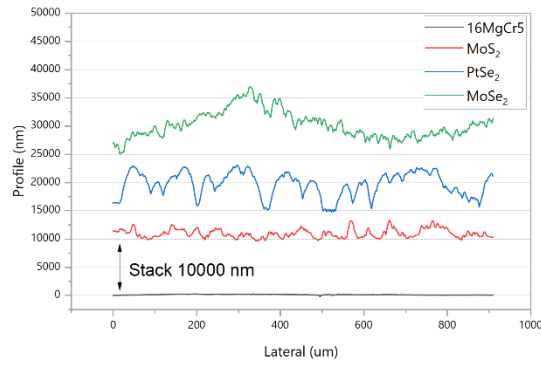


Figure 2. Contact profilometry profiles of the bare 16MnCr5 steel substrate compared with MoS₂, PtSe₂, and MoSe₂ layers after deposition

These initial comparative experiments demonstrated that the direct application of PtSe₂ and MoSe₂ layers to steel substrates is limited by poor adhesion. Furthermore, while PtSe₂ layers exhibit excellent stability in both air and vacuum, ideally oriented MoSe₂ layers undergo rapid tribo-oxidation under friction in ambient air [Attachment 12]. Consequently, to overcome these limitations and focus on the more stable material, subsequent research concentrated on enhancing PtSe₂ film adhesion. To address this adhesion failure, an alternative deposition strategy was employed, in which the Pt layer was deposited onto steel substrates with pre-coated sublayer.

Sublayers are widely used to improve film adhesion for electronic and mechanical devices. These sublayers can be deposited via various low-temperature methods, such as physical vapor deposition (PVD), CVD, or atomic layer deposition (ALD), that preserve the integrity of the underlying substrate. Among these techniques, ALD offers uniquely uniform coverage and exceptional conformality, making it a preferred method for surface protection and advanced electronics. In surface engineering, ALD buffer layers prevent substrate interdiffusion, passivate surface defects and dangling bonds, and enable precise tailoring of the morphology and structure of subsequent coatings. During this high-temperature selenization step, these ALD layers also served as a protective barrier, preventing corrosive selenium vapor from reaching the substrate.

To evaluate the effectiveness of the protective sublayer, the steel substrates were first mechanically polished to improve adhesion. This involved sequential grinding with grit sizes ranging from 400 up to 1200 grit, followed by final polishing with an oxide polishing suspension, which reduced the surface roughness (R_q) to ~ 1.5 nm as measured over a 3×3 μm area (Figure 3a). Subsequently, thin ALD oxide sublayers (specifically HfO₂, Al₂O₃, or TiO₂) were pre-coated onto the polished steel substrates using a Beneq TFS-200 ALD system at a growth temperature of 250 °C. Trimethylaluminum, tetrakis(ethylmethyamido)hafnium, and titanium tetraisopropoxide served as the metal precursors for Al₂O₃, HfO₂, and TiO₂, respectively, with water utilized as the oxygen reactant. AFM image of the sample after ALD deposition of HfO₂ sublayer is presented in Figure 3b. To target a nominal film thickness of ~ 30 nm for each buffer layer, the number of ALD cycles was set to 300 for Al₂O₃, 390 for HfO₂, and 820 for TiO₂. This approach utilizing TiO₂ as an ALD sublayer was initially proposed for Ti₃C₂T_x MXene samples, with related data presented at the 8th International Conference on Multifunctional, Hybrid and Nanomaterials as a poster report (**Attachment 6**).

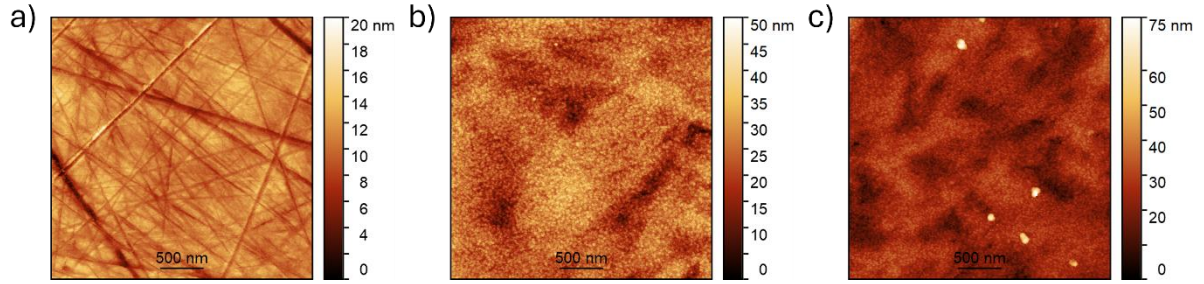


Figure 3. AFM topography image of steel substrate after polishing with oxide polishing suspension (a), after HfO₂ deposition on the polished steel (b) and after PtSe₂ deposition on HfO₂/Steel substrates (c)

Following oxide deposition, PtSe₂ films were fabricated on the buffer layers via the TAC method. First, a 3 nm-thick platinum film was deposited onto the oxide-buffered substrates using DC magnetron sputtering. These pre-deposited Pt films were subsequently selenized at 400 °C in an N₂ atmosphere at ambient pressure. These TAC processing conditions successfully yielded PtSe₂ films with an average thickness of ~14 nm, and Rq roughness 5.12 nm (AFM image Figure 3c). Unfortunately, the TiO₂ sublayer proved ineffective and delaminated during selenization, leaving HfO₂ and Al₂O₃ as the successful buffer layers (Figure 4).

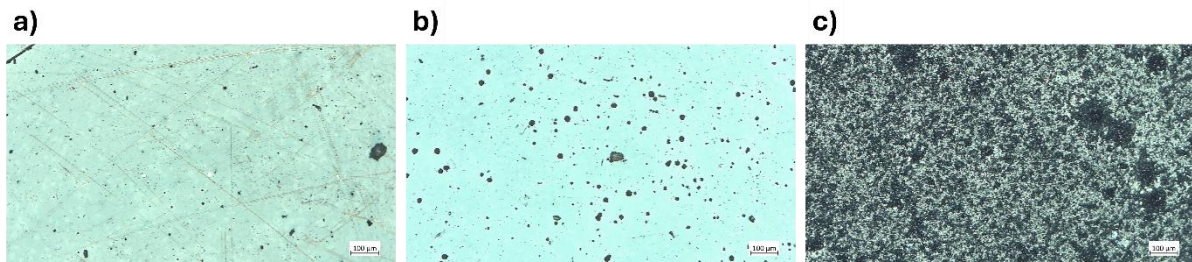


Figure 4. Microscope images of PtSe₂ on 16MnCr5 steel substrates with Al₂O₃ (a), HfO₂ (b), and TiO₂ (c) sublayers.

The successful deposition of these films on the remaining HfO₂ and Al₂O₃ sublayers was confirmed by XPS, Raman spectroscopy, and AFM (Figures 3-5), which assessed their surface topography, structural properties, and chemical composition.

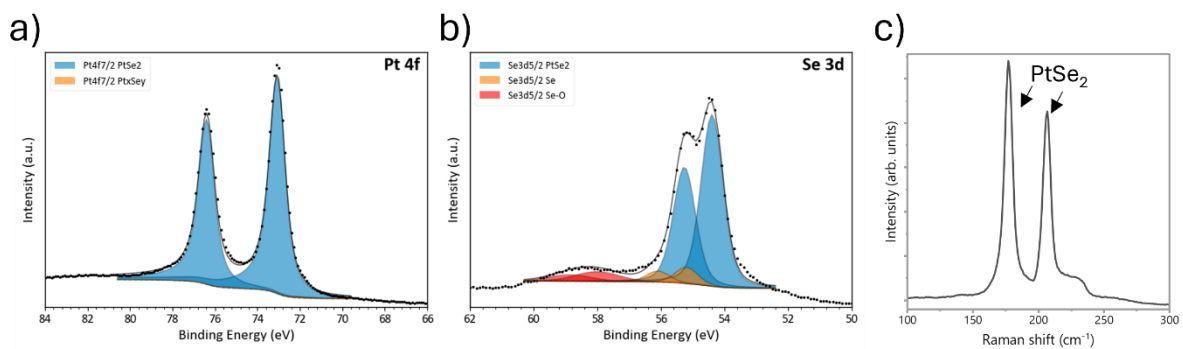


Figure 5. XPS and Raman spectra of PtSe₂ on HfO₂ sublayer on 16MnCr5 steel substrate

These findings were compiled and presented at the “NordTrib 2026” conference (**Attachment 16**). Building upon this conference presentation, the complete study was compiled into a manuscript and submitted for publication (**Attachment 17**).