Influence of the thin film precursor on the structural order of MoS_2 deposited by chemical vapor transport

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Two dimensional (2D) materials based on Transition Metal Dicalchogenide (TMD) recently attract a booming interest, due to their unique physical properties which potentially go beyond those of graphene [1].
In this context, studies on the controlled synthesis of atomically thin TMD have gained tremendous momentum since, up to few years ago, their investigation was limited to mechanically exfoliated flakes of geological TMDs.

MoS_2 is one of the most promising and studied TMDs. Several works report on the synthesis of few layers MoS_2 via Chemical Vapour Transport (CVT) deposition which involves MoO_3 and S powders heated in a quartz tube furnace. The main limitation of this approach is the lack of thickness control of the grown MoS_2; in fact mono-, bi- and tri-layers islands of MoS_2 are randomly distributed on the substrate surface at the end of such a process [2].
In the Thin Film Precursor CVT (TFP-CVT) approach, the MoO_3 powder is replaced by a Mo or MoO_x film with controlled thickness deposited on the substrate. In this way the growth of few MoS_2 layers on the cm^2 scale, with thickness uniformity, is possible.

Here we study the influence of the chemical-physical TFP properties (stoichiometry, morphology and thickness) on the quality of the grown MoS_2.
For this purpose, we report the results obtained starting from TFPs grown by means of different deposition techniques (e-beam evaporation from Mo foils and MoO_3 powder, atomic layer deposition) on several substrates. The TFPs have been characterized by means of XPS and AFM analysis before sulfurization in the tube furnace. In particular, we demonstrate that the chemical composition of the TFP has a limited impact on the MoS_2 quality. On the contrary, surface morphology and thickness of the TFP dramatically influence the structural in-plane and out-of-plane order of the grown MoS_2.
The structural order is evaluated by the analysis of the E^1_{2g} (in-plane) and A_{1g} (out-of-plane) Raman modes [3]. In particular, on MoS_2 grown on a SiO_2/Si substrate the number of curves employed in the fit of the Raman spectra suggests that the best in- and out of plane order is obtained at high temperatures (> 900°C) and 4 layers thickness. In the regime of low temperature and thickness (< 4 layers), the contribution of the additional components in the fitting of the Raman modes becomes more relevant, thus indicating a lower structural order of the TMD, in particular in the in-plane direction. AFM investigations suggest that the granular nature of the MoS_2 is the limiting factor, see Figure 1.
Small grains with lateral size in the 20-50 nm range are clearly visible in the bi-layers MoS_2 grown at an intermediate temperature (< 900°C). The observation of similar features on the TFP surface allows us to conclude that the sulfurization proceeds as a *heterogeneous* nucleation process at the grains of the TFP. Moreover, the analysis of the AFM topography suggests that, in this range of thicknesses, MoS_2 grains do not complete cover the surface. We attribute the grains disconnection to the high root-mean-squared (rms) roughness (0.3 nm) measured on the TFP topography, since it is comparable to a not negligible fraction of the bi-layer thickness, thus not allowing the formation of a compact film.

All these evidences can have a link to the extra components observed in the Raman modes. In fact, the limited size of the grains and their disconnection can produce a broadening of the Mo-S bond length distribution, thus affecting the phonon linewidth band.
Finally, the results obtained employing TFP grown on atomic-scale flat substrates (as sapphire) corroborate the picture that the Raman analysis provides a clear indication of the MoS_2 structural order at the inter- and intra-grain scale [4].

References

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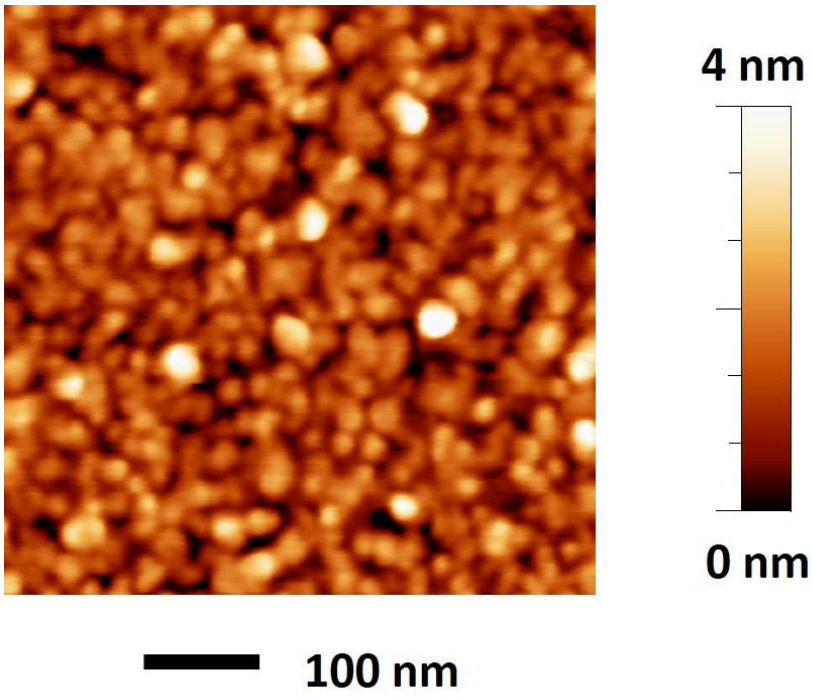

Figure 1 AFM topography of the MoS_2 bi-layers.