#195 - Synthesis of MoS2 nanosheets from Molybdenum oxide film precursors

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The impact of Molybdenum disulphide (MoS_2) is rapidly increasing because of its unique physical and chemical properties at the ultrathin thickness scale, down to a two-dimensional monolayer. Such properties are exploited to integrate MoS_2 as active material in prototypical devices, such as field-effect transistors and photodetectors, for low-power, ultra-scaled nano-, opto- and spin-electronics.

MoS_2 with lateral size in the micrometer range and thickness down to the monolayer can be easily obtained in the form of flakes by mechanical/chemical exfoliation from geological crystals, taking advantage of its bulk structure at ultrathin thickness characterized by weakly interacting layers, as in other transition metal dichalcogenides. However, this approach has severe limitations in terms of technology transfer, where wafer-size synthesis of MoS_2 in the form of a thin film with atomic control of thickness is required. How to overcome this limitation is still an open issue.

In this frame, we synthesized MoS_2 nanosheets by using S powder and sub-stoichiometric oxidized Molybdenum thin films in a heterogeneous vapor–solid reaction at high-temperature. In this chemical vapor deposition approach, the morphology of the precursor film plays a crucial role in dictating MoS_2 structural properties, as observed considering the granular nature and grain size in MoS_2 layers obtained from the sulfurization of electron-beam deposited precursor films [1]. To gain a deeper insight into this aspect, we also carried out sulfurization starting from thin solid precursor Molybdenum oxide films grown by atomic layer deposition (ALD), where extremely high conformality and thickness control are achievable in the film growth [2].

We found that the thickness dependence of the MoS_2 structural properties is directly connected with the observed granularity of the MoS_2, which derives from the precursor film morphology. The basic mechanism governing MoS_2 crystalline order relies on the connection–disconnection between adjacent grains. Further, ALD based synthesis of MoS_2 has a quality comparable to the natural crystals at thicknesses down to four layers, while at very low thicknesses the interface energetics between the ALD precursor film and SiO_2 substrate dramatically affects the evolution of the sulfurization process leading to MoS_2 nanoclustering. Such limitation is overcome by exploiting monocrystalline sapphire substrate as support for the precursor.

Our results evidence the potential of a heterogeneous vapor–solid reaction process to synthesize MoS_2 nanosheets with high conformality, uniformity and thickness control on the cm^2 scale. Further, precursor/substrate interface engineering represents a promising way to control the physical/chemical properties of the MoS_2 nanosheet.

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#196 - Dephasing in strongly anisotropic black phosphorus

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Black phosphorus (bP) is a direct gap semiconductor which, thanks to its layered structure, can be exfoliated down to the monolayer, called phosphorene. This material recently attracted great interest thanks to the band gap tunable with the number of layers, which can provide an opportunity to fill the gap among graphene and transition metal dichalcogenides [1]. Moreover, anisotropic transport, optical, and thermoelectric properties have been recently observed and related to the puckered structure of bP layers [2].

Here, we will report measurements of weak localization on a 65 nm thick black phosphorus field effect transistor [3]. Weak localization is a quantum effect, related to coherent scattering at low temperatures. Using the Hikami-Larkin-Nagaoka model [4],

the dephasing length L_ϕ (or inelastic scattering length) can be inferred from weak localization. Our study is performed for various gate voltages, in the hole-doped regime, in a closed cycle ^{3}He cryostat, at temperatures down to 250mK.

The dephasing length is found to increase with increasing hole density, attaining a maximum value of 55 nm at a hole density of approximately 10^{13}cm^{-2}, obtained from the Hall effect.

The temperature dependence of L_ϕ was also investigated. Above 1K it decreases, with a weaker temperature dependence than $T^{-1/2}$, the one expected for electron-electron interaction in two dimensions. Rather, the observed power law was found to be close to that observed previously in quasi-one-dimensional systems such as metallic nanowires and carbon nanotubes. We attribute our result to the crystal structure of bP which host a `puckered' honeycomb lattice forming a strongly anisotropic medium for localization. Therefore, we found a further effect where the anisotropic structure of black phosphorus plays a crucial role.

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#197 - Large scale production of 2D crystals by wet jet milling

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Efficient and scalable two-dimensional (2D) crystals production methods are urgently required for a rapid clearing of technological hurdles towards the development of a 2D crystals-based industry, satisfying the specific requirements of different application areas.[1] The outstanding properties of the 2D crystals is boosting the research activity in several application areas, ranging from polymer composites for aircraft to quantum computers, and applications in biology, electronics, and medicine.[1] However, the practical realisation of any commercial application requires efficient production methods.[2] Although many production techniques have been developed,[2] the most promising approach for large-scale production of 2D crystals relies on liquid phase exfoliation (LPE) of their bulk counterparts. However, the main limitation of this method is the time-consuming process, i.e. in the exfoliation using sonic waves, the sonication time ranges from 6 to 90 hours,[3,4] achieving concentrations in order of grams per litre; or the shear mixing process[5], which can produce graphene dispersions with a concentration of 0.1 gL^{-1} after more than 60 hours.[5]

Here, we show a novel approach we recently developed for the exfoliation of layered crystals. The process is based on high-pressure wet jet milling (WJM). This technique allows us to produce large quantities of single and few layer 2D flakes in dispersion. The WJM has been successfully applied to graphite, *h*-BN, transition metal dichalcogenides, and black phosphorus. By using WJM we can produce more than 2 litres per hour of 2D crystals in dispersion with a concentration exceeding 10 gL^{-1}. In the case of graphene, the exfoliated crystals show low defectiveness (Raman peak intensity ratio ID/IG = ~0.5). A further purification by centrifugation allows us to prepare dispersions discriminating the thick or un-exfoliated flakes, keeping a concentration as high as 1 gL^{-1}. Finally, we will present the results obtained with the integration of the as-produced dispersions in different applications. We have indeed used them as active material in lithium ion battery anodes, as reinforcement in Nylon-graphene composite, and as flame-retardant additive in fibre glass.

References

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