Direct growth of WS_2 on graphene and other substrates towards functional hetero-stacks

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Both profound research into two-dimensional (2D) materials and their use in applications is by no means limited to graphene. Instead, graphene, with its striking properties such as electron mobility and mechanical flexibility, marked the beginning of a new era in material science.[1]Novel emerging 2D materials might overcome some of the shortcomings of graphene for selected applications. By displaying a measurable direct band-gap,semiconducting transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) offer exciting prospects for the development of novel electronic and optoelectronic devices. Indeed, opportunely designed 2D-heterostacks hold the potential to outperform conventional materials for a wide variety of applications[2] - including flexible and transparent electronics with low power consumption - and might potentially push applications like the hydrogen evolution reactor over the barrier of sufficient effectivity for industrial fabrication[3].

Up to recently, WS_2 has attracted the second most attention within the TMD family, after MoS_2, but is now considered superior over MoS_2 regarding several key properties such as a higher carrier mobility, a larger valence band splitting allowing for easier observation of the valley hall effect and a much higher photo luminesce emission.[4]Unlike Graphene, single sheets of WS_2 do not exhibit the thickness of one atom but rather of one molecule, since a single atomic layer of W is sandwiched between two atomic layers of S. Strong covalent W-S bonds provide for a high intra-layer stability, while inter-layer cohesion is produced by much weaker van der Waals forces only, therefore classifying WS_2 as a 2D material.

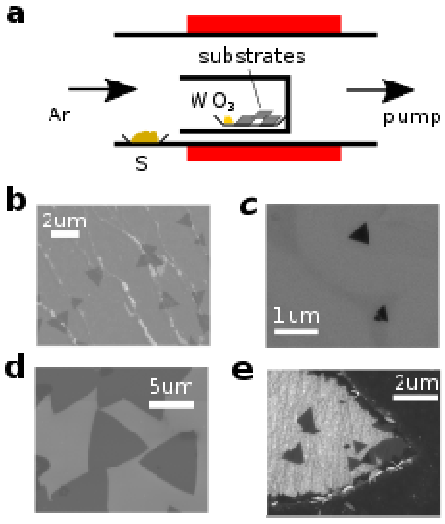

Fig. 1 | Simultaneous CVD growth of WS_2 on various substrates.
a, Schematic experimental setup for CVD growth. The red marked zone corresponds to the hot (900°)zone within the furnace. **b-e**, Typical SEM images of the as-grown WS_2 crystals on graphene (**b**), SiC (**c**), SiO2 (**d**) and an hBN-flake (**e**).

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9. We acknowledge our colleagues V. Miseikis, D. Convertino and N. Mishra for providing the graphene on exfoliated hBN, graphene on SiC and transfered graphene substrates.

To date, the synthesis of WS_2 still lags behind the ongoing technological progress of graphene regarding the fast and relatively cheap fabrication of large and high quality mono-crystalline layers[5]. WS_2 flakes are typically obtained by mechanical exfoliation of 3D crystals and WS_2-containing heterostacksare realized by a cumbersome process of mechanical assembly.The limited lateral dimension of the resulting samples restricts the access to conventional surface-science techniques for fundamental studies and is a serious hurdle towards the implementation of a scalable technology. Clearly, significant advances in the scalable synthesis of highly crystalline WS_2 on a variety of substrates are called for.

In this work we present a cost-effective vapor-phase reaction approach which allows for the simultaneous deposition of WS_2on a variety of substrates ranging from classical 3D dielectrics to novel 2D materials. The quality, crystallinity and thickness of the deposited layers is thoroughly characterized via Raman spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

In Fig. 1(a), we illustrate schematically our typical growth setup. A large diameter quartz tube is placed within a LENTON furnace. Inside the tube, we position a second semi-sealed tube of smaller diameter whose purpose is to create a semi-confined volume of reactants for an increased reaction cross section. In the hot zone, the tungsten trioxide (WO_3) precursor is placed next to the receiving substrate(s) within a quartz crucible. The sulfur (S) precursor is placed just in front of the open end of the small diameter tube outside of the furnace. Argon gas (Ar) is flown with a rate of 80-200 sccm as a carrier gas from one end, while a roughing pump on the other side caters for a pressure of a few mbar. After 10 min of pumping and purging with Ar flow, the temperature is first raised at a rate of 10°C per minute to 400°C and then at a rate of 45°C per minute until the growth temperature of 900°C is reached.The growth time isfixed at 90 minutes followed by a natural cool down.

Panels (b-e) in Figure 1 report SEM micrographs of single crystals of WS_2 obtained

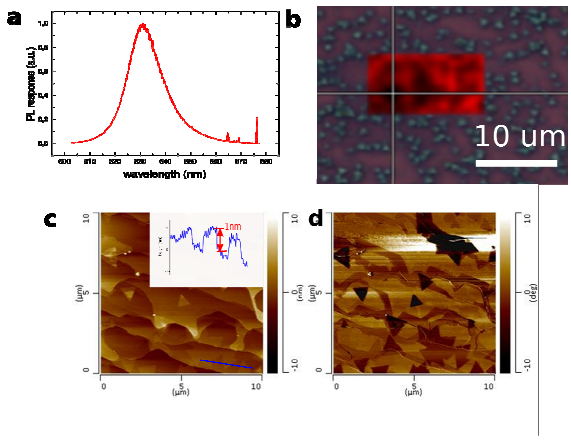

Fig. 2 | Verification of monolayer WS_2 depositions. **a,** Strong photoluminescence response of WS_2 on SiO_2 to a 1200nm excitation. **b**, Map showing the intensity of the 340-360 nm Raman signal (characteristic for WS_2) overlaid over an optical image. **c**, AFM images of signal amplitude (profile along blue line shown in inset) and **d**, signal phase.

on silicon carbide (SiC), silicon dioxide (SiO_2),graphene, and hexagonal boron nitride (h-BN), respectively. On all substrates we obtain triangular grains of □m size, with the largest crystals (>5□m) on SiO_2.

In all cases we confirmed the thickness of the vast majority of the deposited TMD to be a single layer via AFM analysis.The AFM topography image and line profile reported in Fig. 2(c) highlight the monolayer thickness (~1nm) of the triangular WS_2 mono-crystals obtained on epitaxial graphene on SiC[6]. The phase AFM image in panel (d)clearly evidences the chemical and physical differentness from the underlying graphene terraces. Thestrong photoluminescence measured for WS_2 on SiO_2(due to its direct band gap[7]) is reported in Fig. 2(a).In Fig. 2b,we present an optical micrograph of WS_2 grown on CVD graphene[5] transferred to $SiO_2$with a superimposed map showing the intensity of the Raman response between 340 and 360nm, which has been identified as a fingerprint for WS_2[8].

In summary, in this work we report a robust growth process for the simultaneous synthesis of single-crystal □m-sized monolayer WS_2 on various substrates[9]andthoroughly characterize the synthetized TMD by using different spectroscopic and microscopic techniques.