Controllable, eco-friendly, synthesis of highly crystalline 2D-MoS$_2$ and clarification of the role of growth-induced strain

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Abstract

A controlled and eco-friendly, scalable CVD method for the production of single and few layer MoS$_2$ crystals is proposed. The MoS$_2$ crystals are fabricated at atmospheric pressure through the reaction of pre-deposited sodium molybdate (Na$_2$MoO$_4$) in solution and elemental sulfur at 800 °C, offering the flexibility to achieve two growth regimes - either homogeneously distributed single layer MoS$_2$ crystals or continuous MoS$_2$ films - by varying the Na$_2$MoO$_4$ solution concentration. In particular, for low precursor concentrations, isolated single layer MoS$_2$ crystals with controllable mean lateral size were produced. Higher concentrations resulted in continuous single layer films grown in tandem with highly oriented few layer epitaxial domains. The area of the monolayer relative to the few-layer domains can be adjusted. The significant impact on the optical properties of single layer MoS$_2$ crystals due to the growth induced strain is also examined. The grown monolayer crystals are found to experience ~0.3% biaxial tensile strain relative to the exfoliated ones, while a strain relief of 0.6% is measured when these CVD crystals are transferred to another plastic substrate. Moreover, in their photoluminescence (PL) spectra, the neutral exciton and negative trion peaks are shifted linearly with biaxial strain. By correlating PL and Raman spectroscopies the deformation potential of the direct optical transition in single layer MoS$_2$ can be determined.

Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) possess a unique combination of fundamental solid-state physical phenomena including strong Coulomb exchange, many-body interactions [1, 2], rich excitonic effects [3, 4], large spin–orbit [5, 6] and spin-valley coupling [3, 7] and thus provide a benchmark to test the physics of 2D systems. Moreover, TMDCs have shown a great potential for diverse applications such as gas sensing [8], actuation [9–11], nanophotonics [12, 13], renewable energy devices (photovoltaics and hydrogen production) [14, 15], electronics [16, 17], quantum manipulation, spintronics and valleytronics [18].

In order to successfully extend the usage of these materials from laboratory to real-life applications, large scale and cost-effective production methods are required. During the past years, several bottom-up [14, 19–28] and top-down [29–35] strategies for the fabrication of atomically thin films have been developed. As has already been proven in the case of graphene, chemical vapour deposition (CVD) method is compatible with industry providing large area high quality material suitable for optoelectronic applications [36]. Extensive attempts to grow atomically thin molybdenum disulphide (MoS$_2$) through CVD methods have also taken place. In general, the methods developed so far can be divided in one- and two-step processes [37]. In the former method the Mo precursor is introduced in the reactor to act as source for gaseous Mo containing species, while in the latter the Mo precursor is pre-deposited on the substrate prior to thermal treatment [38].

The first and most common single step CVD synthetic route for the fabrication of 2D MoS$_2$ is the
vapour phase reaction between a molybdenum oxide, typically MoO₃ or MoO₂, and elemental sulfur in relatively high temperatures (650 °C–900 °C) [19, 25, 26, 39–41]. By this approach, triangular single-layer (SL) MoS₂ crystals can be effectively fabricated on the target substrate. Through a continuous refinement of this technique, the quality and the size of the 2D crystals has increased from a few microns [19] to single crystals with lateral dimensions of hundreds of μm [42, 43]. In some cases, even continuous polycrystalline monolayer films in the nm regime have been obtained, for example, by a space-confined set-up [37, 44]. Continuous films have also been fabricated using MoCl₅ instead of MoO₃, and was shown that the thickness of the MoS₂ film depends on the partial pressure of the MoCl₅ species, and thus on the amount of the introduced solid MoCl₅ in the reactor [45].

Although, one step methods yield relatively large and high-quality crystals, it has been proven difficult to control. More specifically, the nucleation density of MoS₂ crystals on the substrate is inhomogeneous [42] depending strongly on the geometry of the CVD system and, most importantly, on the proximity of the substrate to the MoO₃ source, where sharp spatial concentration gradients occur [43, 46, 47]. Such gradients affect the local Mo:S atomic ratio, which in turn has considerable impact on the growth kinetics of the 2D crystals [46]. Therefore, qualities of the resulting crystals (size, thickness etc) depend strongly on the geometrical characteristics of the reactor and the utilized substrate, hindering an easy scaling-up of this method [37]. A series of efforts to attain better control of the reaction kinetics in one-step methods, yielding promising results, are the so-called space-confined approaches which have been summarized in a recent review [37].

Two-step methods try to overcome the inhomogeneous nucleation problem by pre-depositing the Mo precursor directly onto the substrate before the reaction with sulfur vapors. Typically, the Mo precursor is a film of elemental Mo, MoO₂, MoO₃ or even a thiomolybdate salt such as (NH₄)₂ MoS₄ [48–50]. In most cases the produced MoS₂ films are predominantly few-layered [48] and may require a low pressure CVD setup in tandem with more complex substrate preparation and treatment which would increase the fabrication costs. It was found that the thickness of the produced MoS₂ film depends on the thickness of the pre-deposited precursor film [50], but so far, obtaining a continuous single-layer (SL) film of MoS₂ has proven to be a non-trivial task.

In this work, a two-step atmospheric pressure CVD method is presented, exhibiting controlled and large area growth of 2D-MoS₂ single and few-layered (FL) crystals through the reaction between sulfur vapours and pre-deposited sodium molybdate (Na₂MoO₄) on a Si/SiO₂ substrate. Sodium molybdate, in contrast to MoO₃ [51], is a non-toxic and environmental friendly water-soluble precursor commonly used as a fertilizer. It is worth noting here that in the past, a hydrothermal reaction between Na₂MoO₄ and KSCN has been utilized to synthesize bulk MoS₂ [52].

It is shown that for low precursor concentrations (<1.67 mg ml⁻¹) the shapes of the fabricated crystals are predominantly SL triangles or three-point stars containing a nucleation point located at their centers. For higher concentrations (>1.67 mg ml⁻¹) the crystals tend to merge, forming progressively a continuous SL film with highly oriented and randomly distributed epilayers. Further increase of the precursor concentration results in the coalescence of the epilayers and the production of a bulk crystal. Most importantly, the lateral size and the thickness of the crystals as well as the substrate coverage (monolayer and epilayer domain areas) can be controlled by varying the Na₂MoO₄ precursor concentration providing a more efficient production route. The advantage of the proposed method lies on its flexibility to achieve two different growth regimes depending on the Na₂MoO₄ solution concentration. For low concentrations, isolated and homogeneously distributed monolayer MoS₂ triangles or three-point stars are produced with controllable mean lateral size, while for high concentrations continuous SL films with FL domains are epitaxially formed as was verified from electron diffraction images.

X-ray photoelectron spectroscopy (XPS), optical, electron and atomic force microscopies were employed to verify the stoichiometry, crystal quality and morphology of the produced crystals. A variety of crystals were spatially investigated by means of Raman and photoluminescence (PL) mapping. Based on our previous Raman & PL analysis for SL MoS₂ crystals [53], the level of doping and mechanical strain is quantified and compared with exfoliated samples. A release of the mechanical strain was observed after the deposition of the fabricated CVD crystals onto a polymer substrate. Also, the determination of the mechanical strain imparted to fabricated or transferred SL crystals, enabled the extraction of the direct optical band gap deformation potential for SL-MoS₂ which is in accordance with recent theoretical and experimental studies. The work highlights the importance of the mechanical strain in MoS₂ growth and transfer, while the level of induced strain is adequately high to reliably extract important physical parameters such as deformation potentials and Grüneissen parameters.

**Methods**

2D MoS₂ crystals were synthesized by the reaction of sodium molybdate (Na₂MoO₄) and sulfur vapors in atmospheric pressure and high temperature under inert N₂ atmosphere. In particular, an aqueous solution of Na₂MoO₄·2H₂O (Aldrich no. 331058) was spin coated (2000 rpm for 2 min) onto a Si/SiO₂ wafer which was then placed at the centre of the high temperature zone of a quartz tube (1-inch diameter) furnace. A series of samples with different precursor
concentrations, namely 0.1 mg ml\(^{-1}\), 0.2 mg ml\(^{-1}\), 1 mg ml\(^{-1}\), 2 mg ml\(^{-1}\), 5 mg m\(^{-1}\) and 10 mg m\(^{-1}\) were prepared. A quartz crucible filled with sulfur powder (Aldrich no. 84683) was placed in the independently controlled low temperature zone, located near the tube end. The tube was purged with nitrogen with a flow of 50 sccm and kept constant during the whole production process. The temperature increased up to 800 °C with a fixed ramp rate of 13 °C min\(^{-1}\) and held constant at that temperature for 15 min. When the main zone’s temperature reached 800 °C, the temperature of the sulfur powder increased at a ramp rate of 60 °C min\(^{-1}\) up to 300 °C, well above the sulfur’s melting point. Then, the sulfur vapours were carried by the inert nitrogen gas flow towards the reaction zone. After 15 min the reactor was immediately removed from the furnace to cool down to room temperature. It should be noted that the mass of 2 g of elemental sulfur was identical for all runs.

Transmission electron microscopy (TEM) observations were performed using a FEI Tecnai F20 ST microscope operated at 120 KeV to reduce the radiation damage on the MoS\(_2\) flakes during the observation. The images were captured with a Gatan MSC794 camera. To prepare the samples for TEM observations, the MoS\(_2\) crystals were transferred onto Quantifoil grids using a standard wet transfer procedure (see figure S1 in the supplementary information (stacks.iop.org/TDM/5/035035/mmedia)) [54]. First, a protective layer of PMMA was spin-coated onto the Si/SiO\(_2\) wafer with MoS\(_2\) crystals, then the wafer was detached by etching the SiO\(_2\) in 1 mol l\(^{-1}\) KOH for several hours. The MoS\(_2\)-PMMA film was transferred onto a clean wafer and Quantifoil grids were inserted between the film and the wafer. The sample was allowed to dry overnight, then the grids were removed and heated to 200 °C to relax the PMMA, which was then removed in vapours of acetone.

The x-ray photoemission experiments were carried out in an ultra-high vacuum system equipped with a SPECS LHS-10 hemispherical electron analyzer. In all XPS measurements the monochromatized Al K\(\alpha\) line at 1486.6 eV and an analyzer pass energy of 36 eV, giving a full width at half maximum (FWHM) of 0.9 eV for the Au 4f\(_{7/2}\) peak, were used. The XPS core level spectra were deconvoluted by means of mixed Gaussian-Lorentzian peaks after a Shirley background subtraction. Errors are found to be less than 10% (peak areas), while the accuracy of the recording binding energies is ±0.1 eV.

AFM images were taken using a Dimension Icon (Bruker Nano) AFM with ScanAsyst Air or ATESP probes having force constants of 0.4 N m\(^{-1}\) and 40 N m\(^{-1}\), respectively.

Raman and photoluminescence spectra were collected in the backscattering geometry using a Renishaw InVia 2000 spectrometer equipped with a 2400 grooves mm\(^{-1}\) and 1200 grooves mm\(^{-1}\) gratings, providing a spectral resolution of nearly 2.5 cm\(^{-1}\) and 7 cm\(^{-1}\), respectively. The spectral accuracy was better than 0.1 cm\(^{-1}\) for both gratings (figure S2). For excitation, the 514.5 nm line of an Ar\(^+\) laser was focused on the sample by means of an ×100 objective lens (NA = 0.85) yielding a beam waist of 470 nm (see supplementary material and figure S3). In order to avoid unintentional heating of the sample the excitation power was kept below 100 µW in all measurements.
Results and discussion

XPS spectra were collected before and after the reaction of elemental sulfur on top of a Na$_2$MoO$_4$ coated substrate and are presented in figure 1. The XPS survey scan (figure 1(a)) revealed that Mo, Si, C and O were present while sulfur was detected only after the treatment. Besides, sodium was detected before treatment and, interestingly, only traces (<0.5 atom%) were found after the reaction. Before treatment, the existence of a peak doublet (figure 1(b)) located at 232.6 eV and 235.8 eV corresponding to Mo$_{3d5/2}$ and Mo$_{3d3/2}$, respectively, can be assigned to Mo$^{6+}$ chemical state [55]. After treatment, the Mo$^{3d}$ doublet shifted to lower energies at 229.0 eV (Mo$_{3d5/2}$) and 232.1 eV (Mo$_{3d3/2}$), and a new peak appeared at 226.3 eV corresponds to the S$_{2s}$. Moreover, the S$_{2p}$ peak doublet (figure 1(d)) located at 162.9 eV (S$_{2p1/2}$) and 161.8 eV (S$_{2p3/2}$) is assigned to S$_{2p1/2}$ and S$_{2p3/2}$. The recorded binding energies of Mo$_{3d}$, S$_{2s}$ and S$_{2p}$ core levels indicate the fabrication of MoS$_2$ phase on the SiO$_2$ substrate [56]. Using the peak areas of Mo$_{3d}$, S$_{2p}$ and the appropriate sensitivity factors (based on Wagner’s collection and adjusted to the transmission characteristics of the electron analyzer) the atomic ratio S:Mo is calculated as 1.8 ± 0.2.

Figures 2(a)–(d) correspond to optical microscopy images of the grown flakes at low levels of Na$_2$MoO$_4$ concentration (≤2 mg ml$^{-1}$) while figure S4 shows the grown continuous films at higher levels of Mo precursor concentration up to 10 mg ml$^{-1}$. For concentrations of Na$_2$MoO$_4$ lower than 5 mg ml$^{-1}$, the total area (∼1.5 × 1.5 cm$^2$) of the substrate was uniformly covered by three-point star MoS$_2$ flakes which is a signature of sulfur-rich conditions in the growth region [46, 57]. It has been found that this type of shape is usually developed when the growth rate of the Mo edge is at least three times faster than that of the S edge in the initial hexagonal nuclei [57, 58]. As can be seen in figures 2(a)–(d) and in the insets, the average crystal size and the nucleation density increase with the Mo precursor solution concentration. At 5 mg ml$^{-1}$ the flakes merged and the substrate was almost completely covered, mainly by single- and few-layered MoS$_2$ as was further verified by Raman and PL spectroscopies (figure S5). It should be noted that at specific locations on the monolayer, MoS$_2$ epilayers with three-point star or dendritic shapes formed (figure S4(a)). These features are associated with instabilities of the growth process connected with surface diffusion and self-accelerated localized growth that happens when the corners of the regular shape have access to a higher concentration of Mo precursor [59, 60]. Finally, at 10 mg ml$^{-1}$ the substrate was fully covered by bulk crystals of MoS$_2$ (figure S4(b)).

The morphometric analysis (see supplemental material and figure S6) unveiled a correlation between the Mo precursor concentration and the coverage of the substrate with MoS$_2$ crystals (monolayers and epilayers). In particular, for concentrations in the range of 0.1 mg ml$^{-1}$ to 2 mg ml$^{-1}$ the percent coverage of the substrate (Cov(%)) increases from 10% to 30%, respectively. While for concentrations higher than 5 mg ml$^{-1}$, Cov(%) reaches almost 100% due to the formation of a continuous MoS$_2$ film (figure S4). The dependence between Cov(%) and the Mo precursor solution concentration, C, is illustrated in figure 2(e) where the experimental data are fitted by the linear relation: Cov(%) = (9.5 ml mg$^{-1}$) C + 10%. In the supporting information table S1 summarizes the substrate’s coverage and the ratio of single-layer MoS$_2$ (or epilayer) domain area to the total MoS$_2$ area for the precursor concentrations used in this work. As can be verified from table S1 and the insets in figure S4, the ratio of the monolayer domain area to that of the epilayer MoS$_2$ area decreases for concentrations higher than 1.67 mg ml$^{-1}$. 
In a large number of three-point star crystals (figures 2(a)–(d)), and at their exact centre, a nucleation point can be clearly identified (blue or white features). As has been proved recently [61], this nucleation centre possesses a core/shell-like structure consisting of an oxysulfide core wrapped in a FL-MoS2 shell. This fullerene-like structure represents the early stages of the flake growth when the surface is under sulfur deficient atmosphere [61]. It is interesting to note that by increasing the precursor concentration the diameter of the nucleation centre increases and becomes more pronounced and visible denoting the addition of more MoS2 layers on the shell structure.

At low levels of precursor concentration (<2 mg ml$^{-1}$), the flakes are isolated and randomly oriented on the SiO$_2$ substrate as shown in figure 3(a). In figure 3(b) an AFM topography image is presented for a monolayer crystal fabricated with a precursor concentration of 1.67 mg ml$^{-1}$. The darker region in the top left corner of the image is the SiO$_2$ substrate. Epilayer seed crystals have grown on the surface of the monolayer (scale bar 10 µm). (c) Polar directional histogram that shows the dominant directions of the epilayers on MoS2 monolayer (black squares) and the lack of any preferred orientation of the MoS2 monolayers on amorphous SiO$_2$ (red circles).

Figures 4(a)–(c) shows high-resolution TEM images of the folded edges from regions of the film with different thicknesses, reflecting the growth of additional layers for 6 mg ml$^{-1}$ precursor concentration. The investigation of the (0 0 2) lattice fringes at the folds (highlighted by the white arrows) reveals that the local film thickness varies from 1 to 4 layers, and the additional layers grow epitaxially. Electron diffraction analysis of spectra obtained from different regions of the crystals confirmed the epitaxial growth. Figure 4(d) shows an electron diffraction pattern from the internal (not folded) region of the flake shown in figure 4(a). The pattern reveals an individual set of reflections, arranged in a hexagonal system with specific distances compatible with an individual MoS2 crystal, with layers stacked without rotational defects.
The produced crystals were further investigated by optical spectroscopic techniques such as PL and Raman which have been successfully employed to extract information concerning, among others, the number of layers [63], defects [64], mechanical or thermal strain [65–69], thermal conductivity [70] doping effects [71], stacking order [72] and structural stability [73]. In figure 5(a) an optical microscope image of a supported CVD MoS2 crystal (Mo precursor concentration of 1.67 mg ml$^{-1}$) is shown, exhibiting two well-defined regions of different optical contrast, assigned as I and II. The PL intensity map of the direct exciton (see below) near 1.80 eV for this crystal is presented in figure 5(b). Two regions, exhibiting high and low PL intensities can be clearly distinguished, corresponding to regions-I and II of figure 5(a). High PL emission in the visible range is a characteristic feature of the direct bandgap present in monolayer MoS2, while low PL intensity is indicative of an indirect bandgap few-layered (2 to 6 layers) or even bulk MoS2 crystal [74]. For freestanding monolayer MoS2, an enhancement in luminescence efficiency by a factor of $10^2$ and $10^4$ compared to bilayer and bulk counterparts has been observed [75]. Representative spectra from these regions are depicted in figure 5(c). The individual PL spectra from both regions contain a pronounced peak near 1.80 eV associated with the direct excitonic transitions at the K and K’ points of the Brillouin zone [74]. The valence band of MoS2 is split in two bands at K/K’ due to the notable spin–orbit coupling arising from the metal d-orbitals [76]. Therefore, two distinct optical transitions assigned as A and B excitons occur in MoS2 with the former one located -in freestanding samples- at 1.88 eV and the latter located at 2.05 eV [74, 77]. The PL spectrum from region-II contains another spectral feature near 1.40 eV, absent from the spectrum of region-I (see inset in figure 5(b)). This peak, assigned as the I-exciton, is associated with the indirect gap of few-layered or bulk MoS2 coming from optical transitions located at the middle point between the high symmetry points K/K’ and Γ in the Brillouin zone [74, 78]. Therefore, these observations verify that region-I corresponds to monolayer MoS2. Moreover, the exploration of the morphology by means of AFM, of a similar crystal located at the same substrate showed that region-II corresponds essentially to an MoS2 bilayer (see figure S9). Note that the epilayer coverage of the crystal in figure 5 is significantly higher than the average epilayer coverage of crystals fabricated with 1.67 mg ml$^{-1}$ precursor concentration (about 11%) as shown in table S1. However, it was chosen for reasons of clarity.

A histogram of the PL peak positions (~1000 spectra) for region I (monolayer) is presented in figure 5(d). The mean value of the PL peak position is 1.78 eV. We found that the PL peak position for many monolayer samples fabricated by the CVD method presented here, is about 1.80 eV, regardless of the Mo precursor concentration (see table S2). This value is about 40 meV redshifted relative to the one reported for exfoliated monolayer MoS2 on SiO2 [53, 77]. It is well documented that freestanding MoS2 is undoped and as a result the A$^0$ neutral exciton (~1.88 eV) dominates the PL emission spectrum. On the other hand, MoS2 monolayers supported on SiO2 are n-doped and the PL emission is dominated by the recombination of negative trions (A$^-$) (~1.84 eV) [53, 75, 77]. In figure 6(a), a map of the $\Delta \omega$ value—i.e. the frequency difference between the A$^i$ and E’ Raman modes of SL-MoS2—of the above-mentioned MoS2 crystal is presented (see supporting information). The single layer and bilayer MoS2 regions exhibit an average $\Delta \omega$ value of 21.8 cm$^{-1}$ and 23.9 cm$^{-1}$, respectively. The reported $\Delta \omega$ values for exfoliated SL-
MoS\textsubscript{2} range between 18.4 cm\textsuperscript{−1}–19.5 cm\textsuperscript{−1} while, for bilayer and trilayer MoS\textsubscript{2} the $\Delta\omega$ values concentrate close to 21.5 cm\textsuperscript{−1} and 23.5 cm\textsuperscript{−1}, respectively [53, 63]. Comparing the $\Delta\omega$ values of exfoliated MoS\textsubscript{2} with those obtained in the present study for CVD MoS\textsubscript{2} crystals, a significant deviation is noted and will be explained later. Another characteristic example of a CVD MoS\textsubscript{2} crystal exhibiting similar spectral features is presented in figure S11. Note that in that case, the epilayer seeds did not merge and as a result no continuous epilayer formed, yet the spectral response is similar in both cases.

Additional evidence supporting the assignment of regions I and II as a single- and bi-layer MoS\textsubscript{2}, respectively, can be given by correlating the Raman scattering intensity of the underlying silicon substrate, $I$(Si), to the number of MoS\textsubscript{2} layers ($N$). Due to optical interference effects, the dependence of $I$(Si) versus $N$ is non-trivial (see supporting information). Our calculations show that for $N \leq 3$ and a SiO\textsubscript{2} layer thickness of 90 (300) nm, the $I$(Si) is found to decrease roughly by 15% (17%) per MoS\textsubscript{2} layer, while, for 20 nm SiO\textsubscript{2} thickness $I$(Si) is practically constant (figure S12(b)). These results are consistent with the experimental data presented in figures S13 and S14, were a decrease of $I$(Si) by (20 ± 4)% and (20 ± 2)% was observed for CVD MoS\textsubscript{2} on 90 nm SiO\textsubscript{2} and for exfoliated MoS\textsubscript{2} on 300 nm SiO\textsubscript{2}, respectively. Besides, for CVD MoS\textsubscript{2} crystals grown on 20 nm SiO\textsubscript{2} layer no measurable change in $I$(Si) was detected (figure S15).

The spectral differences between CVD and exfoliated MoS\textsubscript{2} monolayers reflect the effect of growth conditions and the interaction between the CVD grown crystal and the substrate. This interaction is capable of straining or doping the 2D-crystals with excess charges [79–82]. Moreover, the thermal expansion coefficient (TEC) mismatch between MoS\textsubscript{2} and the Si/SiO\textsubscript{2} substrate can also strain the overlying crystal during the cooling stage [67]. The strain transfer can be influenced due to oxygen dangling bonds present on the SiO\textsubscript{2} surface, which act as anchoring centers for the MoS\textsubscript{2} crystals [83]. It is well documented that mechanical strain can have a measurable impact on both the phonon frequencies [68, 84] as well as the electronic band structure of MoS\textsubscript{2} [66, 85]. This makes Raman and PL spectroscopies suitable non-destructive probes of strain that may be present in 2D-MoS\textsubscript{2} crystals. Additionally, changes in carrier concentration affect both the Raman modes of MoS\textsubscript{2} [71] and its PL response [75]. Recently, we have undertaken a systematic study to quantify strain and unintentional doping effects in MoS\textsubscript{2} samples grown or transferred on Si/SiO\textsubscript{2} substrate, assuming reasonably that both effects are decoupled from each other at
relatively low strain and doping levels [53]. More specifically, we have shown that it is feasible to quantify local mechanical strain (ε) and doping (n) levels in a SL-MoS2 crystal, by correlating the Pos(A′) − Pos(E′) values obtained in a detailed Raman mapping.

In figure 7(a) the Pos(A′) versus Pos(E′) plot for a series of representative SL-MoS2 samples fabricated by CVD or micromechanically exfoliated on different substrates (SiO2 and PMMA), is presented. Additionally, in the same figure, the strain − charge density (ε − n) axes are drawn. Each point in the plot corresponds to the average values for the E′ and A′ phonon mode frequencies, extracted from intensive Raman maps collecting hundreds up to a few thousand spectra. The error bars represent the standard deviation of the corresponding dataset. The data presented graphically in figure 7 are summarized in table S2 in the supplementary materials.

The data lie roughly on a line with a slope of about 0.01% and 0.14 eV/% for the A′ and A′− trion, respectively. This is very close to the calculated value of the deformation potential of SL-MoS2 for biaxial strain as well as a very recent experimental measurement. Representative PL spectra for each sample type used in this work are presented in figure S16. It must be noted that since exfoliated SL-MoS2 crystals on SiO2 are known to be n-doped, no measurable neutral exciton peak was found in the PL signal of our corresponding sample. However, both the A− as well as the A′ components were detected in the PL response of the SL-MoS2 crystal which was exfoliated onto PMMA. For the two exfoliated samples the negative trion is found to be roughly at 1.83 eV, supporting the conclusion that these particular samples experience similar amounts of strain. The strain and doping levels of the CVD samples are concentrated around 0.3% and −0.8 × 10^13 electrons cm^−2, respectively. We found that transferring the CVD samples (blue points) to about 19.0 cm^−1 in as fabricated samples to about 19.0 cm^−1 in transferred CVD samples. These strain and doping differences are also responsible for the aforementioned increased ∆ω values of the CVD MoS2 crystals relative to the exfoliated crystals, namely, 18.4 cm^−1 and 19.7 cm^−1 for the SL-MoS2 exfoliated on SiO2 and PMMA, respectively. It must be noted that the transferring of a 2D crystal is a sample sensitive, multiple step procedure. As a result, the PL peak position for the A′′ exciton (solid shapes) and A′ trion (open shapes) for the samples (see table S2) presented in figure 7(a) are plotted against the average relative strain that was calculated from the Raman mappings. The strain and doping differences are meaningful [53].

At first glance, it is evident that all samples experience similar doping levels −0.5 to −1.0 × 10^13 electrons cm^−2, except for the SL-MoS2 crystal exfoliated on SiO2 substrate which was found to be more n-doped. The exfoliated samples, regardless of substrate, experience similar amounts of strain roughly between ±0.05%. The strain and doping levels of the CVD samples are concentrated around 0.3% and −0.8 × 10^13 electrons cm^−2, respectively. We found that transferring the CVD samples (blue points) releases the accumulated strain values in the range of 0.0% to −0.2%. As a consequence, the ∆ω value is decreased from 21.7 cm^−1 in as fabricated samples to about 19.0 cm^−1 in transferred CVD samples. These strain and doping differences are also responsible for the aforementioned increased ∆ω values of the CVD MoS2 crystals relative to the exfoliated crystals, namely, 18.4 cm^−1 and 19.7 cm^−1 for the SL-MoS2 exfoliated on SiO2 and PMMA, respectively.

Figure 6. (a) Raman image and (b) histogram of the Δω values (i.e. the frequency difference between the A′ and E′ Raman modes of MoS2) of the crystal presented in figure 5(a). The scale bar in (a) is 20 μm.

Conclusions

A novel, controlled and eco-friendly, scalable CVD method for the production of 2D-MoS2 is developed. 2D MoS2 crystals are fabricated on Si/SiO2 substrates through the reaction of Na3MoO4 and elemental
sulfur at high temperature (800 °C) and atmospheric pressure. Two different growth regimes were observed depending on precursor concentration. Isolated single layer MoS₂ crystals were produced with controllable mean lateral size for concentrations lower than 1.67 mg ml⁻¹, while continuous single layer films with few layer domains are epitaxially fabricated for higher concentrations. The method provides homogeneously distributed crystals on the substrate at large scales and control of the monolayer and epilayer areas by varying the Na₂MoO₄ solution concentration. The epilayers were found to be highly oriented, a phenomenon that was attributed to the high crystallinity of the underlying single layer MoS₂.

The CVD crystals exhibit optical spectral differences with respect to their exfoliated counterparts, including higher Δω values and redshifted PL peak positions. It was made possible to interpret these peculiarities via a strain – doping (ε – n) correlation plot. The CVD crystals were found to experience tensile strain (~0.3%) relative to the exfoliated ones, while a release of 0.6% strain was observed when these CVD crystals were transferred to another plastic substrate. Moreover, the neutral exciton and negative trion peak positions of the fabricated crystals varied linearly with biaxial strain in excellent agreement with previous theoretical and experimental studies. Therefore, the correlation of PL and Raman spectroscopies and the relative high level of mechanical stain induced by growth and transfer enabled an indirect measurement of the deformation potential of the direct optical transition of MoS₂ under biaxial strain. The measured deformation potentials were found equal to ~0.16 eV/% and ~0.14 eV/% for A₀ and A⁻ transitions, respectively, indicating a significant impact of the fabrication method on the optical properties of SL-MoS₂.

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