Facilitating Uniform Large-scale MoS$_2$, WS$_2$ Monolayers and Their Heterostructures Through Van der Waals Epitaxy

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ABSTRACT: The fabrication process for the uniform large-scale MoS$_2$, WS$_2$ transition metal dichalcogenides (TMDCs) monolayers and their heterostructures has been developed by Van der Waals epitaxy (VdWE) through the reaction of MoCl$_5$ or WCl$_6$ precursors and the reactive gas H$_2$S to form MoS$_2$ or WS$_2$ monolayers, respectively. The heterostructures of MoS$_2$/WS$_2$ or WS$_2$/MoS$_2$ can be easily achieved by changing the precursor from WCl$_6$ to MoCl$_5$ once the WS$_2$ monolayer has been fabricated or switching the precursor from MoCl$_5$ to WCl$_6$ after the MoS$_2$ monolayer has been deposited on the substrate.

These VdWE-grown MoS$_2$, WS$_2$ monolayers and their heterostructures have been successfully deposited on Si wafer with 300 nm SiO$_2$ coating (300 nm SiO$_2$/Si), quartz glass, fused silica and sapphire substrates using the protocol we have developed. We have characterized these TMDCs materials with a range of tools/techniques including scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), micro-Raman, photoluminescence (PL), atomic force microscopy (AFM), transmission electron microscope (TEM), energy-dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED). The band alignment and large-scale uniformity of MoS$_2$/WS$_2$ heterostructures have also been evaluated with PL spectroscopy. This process and resulting large-scale MoS$_2$, WS$_2$ monolayers and their heterostructures have demonstrated promising solutions for the applications in next generation nanoelectronics, nanophotonics and quantum technology.
1. Introduction

Transition metal di-chalcogenides (TMDCs) such as MoS\(_2\), MoSe\(_2\), WS\(_2\) and WSe\(_2\) are two-dimensional (2D) Van der Waals (VdW) layered materials. Unlike graphene, TMDCs are semiconductors that could offer, in particular, bandgap engineering properties through both their chemical compositions and number of layers.\(^1,2\) The applications of the use of TMDCs are very promising in the area of transistors,\(^1\) light emitting diodes,\(^3,4\) photodetectors,\(^5\) sensing\(^6,7\) and memory devices,\(^8\) as well as the potential substitution for Si in conventional electronics\(^9\) and of organic semiconductors in wearable and flexible systems.\(^10\)

The current fabrication processes for these emerging TMDCs include exfoliation,\(^1,11\) hydrothermal process,\(^12\) physical vapour deposition,\(^13\) transition metal oxides sulfurization,\(^14\) electrochemical deposition,\(^15\) thermolysis of transition metal chalcogenide compounds\(^16,17\) and chemical vapour deposition (CVD).\(^18-20\) The majority of TMDCs fabricated by these techniques are in the form of flakes with the sizes in the range of a few hundred square micrometers in area. However, the challenge for large-scale fabrication of TMDCs is to provide a reliable complementary metal-oxide-semiconductor (CMOS)-compatible process for the integration of 2D TMDCs on a desired wafer-scale substrate.\(^2,21\)

We have been working on the synthesis of chalcogenide materials using vapour phase deposition processes\(^22-27\) such as CVD, atomic layer deposition (ALD) and VdWE. Apart from offering conformal coating and stoichiometric control of thin film compositions, these processes are scalable and compatible with a range of substrates. In particular, VdWE has been demonstrated to carry out the epitaxy of layered TMDCs on the substrates even with lattice constants mismatch.\(^28-30\) In this paper, we have developed the fabrication process for the uniform large-scale MoS\(_2\), WS\(_2\)
TMDCs monolayers and their heterostructures by VdWE through the reaction of MoCl$_5$ or WCl$_6$ precursors and the reactive gas H$_2$S to form MoS$_2$ or WS$_2$ monolayers, respectively. The heterostructures can easily be achieved by changing the precursor from WCl$_6$ to MoCl$_5$ once the initial WS$_2$ monolayer is fabricated or switching the precursor from MoCl$_5$ to WCl$_6$ after MoS$_2$ monolayer has been deposited on the substrate.

2. Experimental Setup

The VdWE apparatus we developed is shown schematically in Figure 1. The precursors, MoCl$_5$ (99.6 % pure from Alfa Aesar) and WCl$_6$ (99.9 % pure from Sigma-Aldrich) were kept in the bubblers inside the dry N$_2$ purged glovebox. The MoCl$_5$/WCl$_6$ vapours were delivered by high purity argon gases through the mass flow controllers (MFCs) to the VdWE apparatus with the flow rate of 300 standard cubic centimeters per minute (sccm). The system equipped with a bespoke furnace with three heating zones, individually controlled by proportional integral derivative (PID) controllers, with maximum temperature of 1200 °C and temperature uniformity of ±3 °C can be achieved over 450mm length to facilitate the uniform large-scale deposition of TMDC monolayers. The reactive gases were H$_2$S mixed with another argon gas through individual MFCs with the flow rates of 50 sccm and 300 sccm respectively. All the gases were purified by passing through the individual point of use purifiers (SAES MicroTorr) and the moisture level of all gases were monitored by the dewpoint sensors (Michell Instrument Pura pure gas trace moisture transmitters) before entering the VdWE reactor. The typical moisture readings of the Ar and H$_2$S/Ar mixture were -99.6 °Cdp (~7 ppb) and -90.2 °Cdp (~42 ppb) respectively. The process was set at 30 mBar using a pump (Vacuubrand MV 10C NT Vario) with a pressure controller for the entire deposition. With this VdWE apparatus, uniform large-scale TMDCs monolayers have been successfully
deposited on various substrates, including 300 nm SiO₂/Si, quartz glass, fused silica or c-plane sapphire. The sizes of the substrates were typically 25 mm × 25 mm, however up to a 40 mm × 100 mm substrate can be loaded into the VdWE apparatus, which consists of a 50 mm O.D. × 1000 mm long quartz reaction tube. The substrates were cleaned with acetone using an ultrasonic bath at 50 °C for 10 minutes, then rinsed with isopropanol, deionized water and subsequently blow dried with N₂ gas. The temperatures for the growth of MoS₂ and WS₂ monolayers were set at 850 °C and 900 °C respectively. The reactive H₂S gas and MoCl₅/WCl₆ precursors were introduced to VdWE system once the furnace reached the set temperature. MoS₂/WS₂ were formed after the MoCl₅/WCl₆ precursors met with H₂S gas after the injection tube inside the quartz reaction tube. With sufficient amount of MoCl₅/WCl₆ precursors flux, MoS₂/WS₂ monolayers can be uniformly deposited on the substrates and the resulting MoS₂/WS₂ monolayers tend to be polycrystalline due to the high flux of precursors. Although the substrates might affect the deposition of TMDCs, we didn’t see significant differences in quality of the MoS₂, WS₂ monolayers and their heterostructures on the substrates we used. This is probably due to the VdWE process can overcome the mismatch of substrate lattice constants. To achieve uniform MoS₂ and WS₂ monolayers, a deposition time of 4 minutes and 5 minutes was required for the MoS₂ and WS₂ monolayers respectively.
3. Results and Discussion

We have achieved large area MoS$_2$ and WS$_2$ monolayers as shown in Figure 2(a) on quartz glass and in Figure 2(b) on 300 nm SiO$_2$/Si substrates respectively. These results have demonstrated that wafer scale deposition of MoS$_2$ and WS$_2$ monolayers is feasible through a modification of the VdWE system with a larger reaction chamber.

Raman spectroscopy was carried out for the initial study of the quality of the VdWE-grown MoS$_2$ and WS$_2$ monolayers on quartz glass and 300 nm SiO$_2$/Si substrates using a Renishaw Ramascope. 532 nm and 473 nm excitation lasers were used to excite the MoS$_2$ monolayer and
WS$_2$ monolayer samples and the Raman shift spectra were shown in Figure 2(c) and 2(d) for MoS$_2$ and WS$_2$ respectively. As shown in Figure 2(c), two MoS$_2$ Raman peaks, $E^{12g}$ in-plane phonon mode and $A_{1g}$ out-of-plane phonon mode were revealed at 384.0 cm$^{-1}$ and 403.7 cm$^{-1}$ respectively. The number of MoS$_2$ layers can be evaluated by the energy difference between these two Raman peaks ($\Delta$).$^{31}$ From Figure 2(c), the $\Delta$ value is 19.7 cm$^{-1}$ for the VdWE-grown MoS$_2$ monolayer, which is similar to the reported literature.$^{31}$ On the other hand, in order to reduce the second order 2LA phonon mode in the WS$_2$ Raman measurement,$^{32}$ a 473 nm laser was used to reveal two WS$_2$ Raman peaks, $E^{12g}$ and $A_{1g}$ at 359.2 cm$^{-1}$ and 419.4 cm$^{-1}$ respectively. Again, the $\Delta$ value can be also used to evaluate the number of WS$_2$ layers.$^{32}$ From Figure 2(d), the $\Delta$ value is 60.2 cm$^{-1}$ for the VdWE-grown WS$_2$ monolayer, which is also matching with the literature.$^{32}$

The photoluminescence (PL) spectroscopy from the VdWE-grown MoS$_2$ monolayer on quartz glass and WS$_2$ monolayer on 300 nm SiO$_2$/Si substrates were studied using the same Raman microscope. Two excitonic peak A and peak B at 666.3 nm (1.86 eV) and 614.3 nm (2.02 eV) respectively were found in the PL spectrum of VdWE-grown MoS$_2$ monolayer on quartz glass substrate as shown in Figure 2(e). These results are similar to the reported literature.$^{33}$ On the other hand, the PL spectrum of VdWE-grown WS$_2$ monolayer on 300 nm SiO$_2$/Si substrate confirmed the direct band emission at 616.1 nm (2.01 eV) as shown in Figure 2(f). Again, this result agrees with the literature reports.$^{34}$
**Figure 2.** (a) photo of VdWE-grown MoS$_2$ monolayer on quartz glass substrate, (b) photo of WS$_2$ monolayer on 300 nm SiO$_2$/Si substrate, (c) Raman spectrum of VdWE-grown MoS$_2$ monolayer on quartz glass (with 532 nm excitation laser), (d) Raman spectrum of VdWE-grown WS$_2$ monolayer on 300 nm SiO$_2$/Si substrate (with 473 nm excitation laser), (e) Photoluminescence spectrum of VdWE-grown MoS$_2$ monolayer on quartz glass (with 532 nm excitation laser), and (f) Photoluminescence spectrum VdWE-grown WS$_2$ monolayer on 300 nm SiO$_2$/Si substrate (with 532 nm excitation laser).

Furthermore, the PL spectra mapping was carried out to study the uniformity of large-scale VdWE-grown WS$_2$ monolayer on a 300 nm SiO$_2$/Si substrate. The map of the PL emission at 2.01 eV shown in Figure 3 reveals a very good uniformity of the WS$_2$ monolayer over an area of 35 mm × 50 mm. This has been achieved by our in-house built apparatus and this process could be scalable for even large wafer-scale process if a larger reactor is available.
X-ray photoelectron spectroscopy (XPS) was carried out to study the compositions of these VdWE-grown MoS$_2$ and WS$_2$ monolayers using a Thermo Scientific Theta Probe XPS System. For MoS$_2$ monolayer, two core levels, Mo 3d and the S 2p, have been investigated. As shown in Figure 4 (a), two MoS$_2$ peaks, Mo (IV) 3d$_{3/2}$ and Mo (IV) 3d$_{5/2}$, were found at 233.0 eV and 229.9 eV respectively. In the same spectrum, S 2s peak was observed at 227.2 eV and a peak at 236.0 eV was assigned to the Mo (VI) 3d$_{3/2}$ indicating a small amount of oxidation which resulted from the sample being exposed to the ambient environment. It should be noted that a Mo (VI) 3d$_{5/2}$ peak
overlaps with Mo (IV) 3d\textsubscript{3/2} at 233.0 eV. For the MoS\textsubscript{2} S 2p core level, two peaks labelled in Figure 4(b) as S 2p\textsubscript{1/2} and S 2p\textsubscript{3/2} corresponding to MoS\textsubscript{2} were found at 163.9 eV and 162.7 eV respectively. In addition, with semi-quantitative method to investigate the ratio of elements, the atomic ratio of S/Mo was found to be approximately 1.93 with slight S deficiency. These results are in line with literature.\textsuperscript{35} On the other hand, for the WS\textsubscript{2} monolayer, two core levels, W 4f and S 2p, have been studied. As shown in Figure 4(c), two WS\textsubscript{2} peaks, W(IV) 4f\textsubscript{5/2} and W(IV) 4f\textsubscript{7/2} were found at 35.2 eV and 33.0 eV respectively and in the same spectrum, two peaks at 38.5 eV and 36.3 eV were assigned to W(VI) 4f\textsubscript{5/2} and W(VI) 4f\textsubscript{7/2} which again indicate a small amount of oxidation. It should also be noted that W(VI) 4f\textsubscript{5/2} peak overlaps with W(VI) 5p\textsubscript{3/2} at 38.5 eV. For the WS\textsubscript{2} S 2p core level, two peaks labelled in Figure 4(d) as S 2p\textsubscript{1/2} and S 2p\textsubscript{3/2} corresponding to WS\textsubscript{2} were found at 164.0 eV and 162.8 eV respectively. In addition, the atomic ratio of S/W was found to be approximately 1.96 with slight S deficiency. These results also agree with literature very well.\textsuperscript{36}
Figure 4. XPS measurements of VdWE-grown MoS$_2$ and WS$_2$ monolayers (a) Mo 3d scan of MoS$_2$ monolayer (b) S 2p scan of MoS$_2$ monolayer (c) W 4f scan of WS$_2$ monolayer (d) S 2p scan of WS$_2$ monolayer on 300 nm SiO$_2$/Si substrate.

In order to evaluate the crystalline structures of these VdWE-grown MoS$_2$ or WS$_2$ monolayers, commercially available 40 nm SiO$_2$ membranes TEM grids with 200 nm thick Si$_3$N$_4$ supporting frames (PELCO® Silicon Dioxide Support Films for TEM) were used to directly deposit these MoS$_2$ and WS$_2$ monolayers on this type of TEM grids. The optical image of as-deposited MoS$_2$ monolayer on TEM grid is shown in Figure 5(a) with a 532 nm laser spot on the center of the MoS$_2$/40 nm SiO$_2$ membrane. The Raman spectrum of the MoS$_2$ monolayer/40 nm SiO$_2$ sample is
shown in Figure 5(b). Again, two characteristic MoS₂ Raman peaks, E₁²g and A₁g modes were found at 385.8 cm⁻¹ and 402.9 cm⁻¹ respectively with the Δ value of 17.1 cm⁻¹ for the VdWE-grown MoS₂ monolayer on 40 nm SiO₂ membrane TEM grid. It should be noted that the Δ value appears less than that typically reported for the MoS₂ monolayer due to the weak Raman signal from the sample which increased the experimental uncertainty. In addition, the smaller Δ value could be also due to softening of the A₁g mode. The E₁²g mode is insensitive to substrates but the A₁g mode is sensitive to charge density.⁷ Despite these issues however, the monolayer nature has been revealed. In the PL spectrum, shown in Figure 5(c), only the excitonic peak A at 661.1 nm (~1.88 eV) was found for this sample on 40 nm SiO₂ TEM membrane whereas the B exciton could be only weakly detected. The sample was inspected by scanning TEM with a high-angle-annular-dark-field (HAADF-STEM), using FEI Talos F200x, USA, operating at 200 kV and equipped with an energy-dispersive X-ray spectrometer (EDX) system. The TEM image shown in Figure 5(d) has revealed the polycrystalline nature of VdWE-grown MoS₂ monolayer on 40 nm SiO₂ TEM membrane and the grain sizes are around 10 nm. The selected area electron diffraction (SAED) patterns shown in Figure 5(e) also confirmed the polycrystalline structures of this MoS₂ monolayer. The elemental mapping was carried out in the STEM-EDX mode. As shown in Figure 5(f) and 5(g), the Mo and S respectively were quite uniform over the measured area.
Figure 5. TEM measurements of VdWE-grown MoS$_2$ monolayer on 40 nm SiO$_2$ membrane/Si$_3$N$_4$/Si TEM grid (a) photo of sample with a 532 nm laser spot (b) Raman spectrum of VdWE-grown MoS$_2$ monolayer sample (c) PL spectrum of VdWE-grown MoS$_2$ monolayer sample (d) TEM image of VdWE-grown MoS$_2$ monolayer sample (e) Selected area electron diffraction (SAED) patterns of VdWE-grown MoS$_2$ monolayer sample (f) Energy-dispersive X-ray spectroscopy (EDX) mapping of Mo atom on the selected area of MoS$_2$ monolayer sample (g) EDX mapping of S atom on the selected area of MoS$_2$ monolayer sample.

The optical image of as-deposited WS$_2$ monolayer on TEM grid is shown in Figure 6(a) with a 532 nm laser spot on the center of the WS$_2$/40 nm SiO$_2$ membrane. The Raman spectrum of WS$_2$ monolayer/40 nm SiO$_2$ sample is shown in Figure 6(b). Two WS$_2$ Raman peaks, 2LA phonon
mode and A$_{1g}$ mode were found at 352.9 cm$^{-1}$ and 416.0 cm$^{-1}$ respectively. In addition, as shown in Figure 6(c), the direct band emission at 620.0 nm (2.00 eV) was revealed from the PL spectrum. Again, these results agree with the literature reports.$^{26,34}$ The TEM image shown in Figure 6(d) has revealed the polycrystalline nature of VdWE-grown WS$_2$ monolayer on 40 nm SiO$_2$ TEM membrane and the grain sizes are around 10 nm. The selected area electron diffraction (SAED) patterns shown in Figure 6(e) also confirmed the polycrystalline structures of this WS$_2$ monolayer. The elemental mapping was carried out in the STEM-EDX mode. As shown in Figure 6(f) and 6(g), the W and S respectively were quite uniform over the measured area.

**Figure 6.** TEM measurements of VdWE-grown WS$_2$ monolayer on 40 nm SiO$_2$ membrane/Si$_3$N$_4$/Si TEM grid (a) photo of sample with a 532 nm laser spot (b) Raman spectrum of VdWE-grown WS$_2$ monolayer sample (c) PL spectrum of VdWE-grown WS$_2$ monolayer sample (d) TEM image of VdWE-grown MoS$_2$ monolayer sample (e) Selected area electron
diffraction (SAED) patterns of VdWE-grown WS\textsubscript{2} monolayer sample (f) Energy-dispersive X-ray spectroscopy (EDX) mapping of Mo atom on the selected area of WS\textsubscript{2} monolayer sample (g) EDX mapping of S atom on the selected area of WS\textsubscript{2} monolayer sample.

A MoS\textsubscript{2}/WS\textsubscript{2} monolayer heterostructure on the fused silica substrate was prepared for further investigation with the abovementioned VdWE process. WS\textsubscript{2} monolayer was firstly grown on 25 mm x 25 mm fused silica substrate, followed by the second MoS\textsubscript{2} monolayer grown on the top of WS\textsubscript{2} monolayer/fused silica sample. As the Raman spectrum shown in Figure 7(a), two typical MoS\textsubscript{2} E\textsubscript{1g} and A\textsubscript{1g} peaks are revealed along with the WS\textsubscript{2} peaks labeled as WS\textsubscript{2}(2LA-2E\textsubscript{2g}), WS\textsubscript{2}(2LA-E\textsubscript{2g}), WS\textsubscript{2}(2LA+E\textsubscript{2g}) and WS\textsubscript{2}(A\textsubscript{1g}). The band alignment of MoS\textsubscript{2}/WS\textsubscript{2} monolayer heterostructures has also been evaluated with the PL spectrum shown in Figure 7(b) which revealed that the VdWE-grown MoS\textsubscript{2}/WS\textsubscript{2} on fused silica sample forms a type-II heterojunction with more detailed discussion in the supporting information.
Figure 7. (a) Raman spectrum of MoS$_2$/WS$_2$ heterostructure on fused silica (b) PL spectrum of MoS$_2$/WS$_2$ heterostructure on fused silica.

It is very difficult to see the contrast between MoS$_2$ and WS$_2$ monolayers in the VdWE-grown MoS$_2$/WS$_2$ heterostructures since the VdWE provide the uniform and continuous atomically thin TMDCs. To visualize the MoS$_2$/WS$_2$ heterostructures, MoS$_2$ monolayer flakes were prepared on a 300 nm SiO$_2$/Si substrate with the conventional CVD process,$^{38}$ followed by the coating with a uniform WS$_2$ monolayer with the VdWE process. The structure of these VdWE-grown WS$_2$ continuous film / CVD-grown MoS$_2$ flakes heterostructures illustrated in Figure S1(a) with the optical image in Figure S1(b). The detailed characterizations of AFM, Raman, XPS and PL are discussed in the supporting information (Fig. S1).

The spatial uniformity in the VdWE WS$_2$/MoS$_2$ heterostructures are investigated by PL mapping. A recent report$^{39}$ has shown that the PL uniformity in exfoliated 2D materials is strongly correlated to the uniformity in the spectral properties, such as the emission energy and spectral weighting. A similar analysis is applied here to investigate the uniformity of the heterostructures in terms of the emission energies of each of the corresponding layers in the heterostructure and offer a baseline for comparisons with future studies. Since there is an abundance of heterostructures flakes, the uniformity analysis extends naturally from intra-flake (within one heterostructure flake) to inter-flake (between multiple flakes), that could provide additional insight for future growth optimizations. The monolayer MoS$_2$ flakes on this sample are mostly equilateral triangles, hexagrams and partial hexagrams of various sizes and orientations. To sample this geometric distribution, an area is selected using optical microscopy, shown in Figure 8 (l) that
contains five numerically labelled flakes, with flakes F1, F2 and F5 being triangles, F4 being a hexagram and F3 being a partial hexagram, the regions outside of these flakes corresponds to the VdWE WS$_2$ monolayer film. A PL map of the whole region was acquired, using a Horiba LabRAM spectrometer, with 532 nm Laser (637 kW/cm$^2$, 5 seconds integration time), focused through a 100x 0.95 NA objective lens, and the emission dispersed with a 600 lines/mm grating. The mapped region is 40 µm by 40 µm in size and the raster scan step size is 0.5 µm. Maps of individual heterostructure flakes were then isolated from the recorded PL map by a MATLAB program. From Figure 8 (m) the WS$_2$ region has a single peak at ≈ 2.00 eV (WS$_2$ exciton), while two peaks appear in the heterostructure spectrum at ≈ 1.84 eV (MoS$_2$ exciton) and ≈ 1.98 eV (WS$_2$ exciton).
Figure 8. Intra-flake and inter-flake PL spatial and spectral uniformity analysis for five different flakes, as indicated by the optical image (l) with a white scale bar representing 10 µm, on the sample with VdWE-grown WS$_2$ monolayer on CVD-grown MoS$_2$ monolayer flakes heterostructure on 300 nm SiO$_2$/Si. (a, c, e, g, i) Maps of fitted MoS$_2$ peak energies for flakes F1-F5, with red scale bars representing 5 µm. (b, d, f, h, j) Maps of fitted WS$_2$ peak energies for flakes F1-F5, with red scale bars representing 5 µm. (k) MoS$_2$ and (n) WS$_2$ peak energy histograms for
F1-F5 plotted on top of each other, all histograms have energy bins 1 meV wide. Typical PL spectrum measured from the heterostructure and the surrounding WS$_2$ are also plotted in (m).

Spatial variations in emission energy are apparent for both MoS$_2$ and WS$_2$, as revealed from the peak energy maps in Figure 8 (a-j). Across all flakes, the peak energy from both materials exhibits similar spatial patterns, where a local area that indicate blueshifts (or redshift) in one material corresponds to blueshifts (or redshift) in the other at the same spatial location. Though for the MoS$_2$ peak, its intra-flake energy range, taken as the 95% confidence region in the histograms shown in Figure 8 (k) is up to $\approx$ 10 meV, compared to $\approx$ 4 meV for that of WS$_2$, from Figure 8 (n). There is a pronounced edge-effect for WS$_2$, less so for MoS$_2$, where the peak appears to exhibit significant blueshift at the edge of all heterostructures measured. This also explains the differences which are apparent from the histograms plotted in Figure 8(k) and Figure 8(n), showing largely monomodal distribution for MoS$_2$ and bimodal for WS$_2$. The two modes in Figure 8(n) corresponds to the interior and edge peak energy distributions for WS$_2$ and the means of these two modes are separated by $\approx$ 17 meV. The fact that all measured flakes exhibit similar behavior, independent of the flake size, geometry and orientation suggests that strain is the likely mechanism to explain this, as its magnitude could be changed at the edge WS$_2$ layer as its substrate changes from MoS$_2$ to silicon dioxide. For MoS$_2$ the peak shift at the flake-edge is much less pronounced, up to 5 meV on average, which is smaller than the inhomogeneity in the MoS$_2$ peak energy of $\approx$ 10 meV, so that only in the smallest flake measured (F5) this modal separation is apparent. Overall, the inter-flake uniformity is well-behaved, i.e., does not fluctuate significantly from flake to flake regardless of size geometry and orientation, which suggests that the growth-process has good reproducibility between heterostructures. The intra-flake uniformity is also well-behaved if the edge-effects can
be ignored, which could be valid for large area heterostructure flakes. However, charge transport phenomena at the edge that change this behaviour, which could be an interesting avenue to explore in a future study with a device, as PL-uniformity analysis alludes to the optical transport phenomena only.

4. Conclusion

In conclusion, we have demonstrated a scalable fabrication process for TMDC monolayers and their heterostructures by Van der Waals epitaxy. These VdWE-grown MoS₂, WS₂ monolayers and their heterostructures have been successfully deposited on CMOS-compatible substrates, such as 300 nm SiO₂/Si wafer, quartz glass, fused silica and sapphire. Detailed characterizations of these TMDCs materials have been carried out with SEM, AFM, XPS, micro-Raman, micro-PL, TEM, EDX and SAED techniques and the band alignment and large-scale uniformity of MoS₂/WS₂ heterostructures has also been evaluated with spatially-resolved PL spectroscopy. These results have demonstrated not only the excellent characteristics of MoS₂ and WS₂ monolayers with large-scale uniformity but also the feasibility of large-scale TMDCs heterostructures can be achieved by the VdWE in this work. We believe this process and resulting large-scale MoS₂, WS₂ monolayers and their heterostructures have demonstrated promising solutions for the applications in next generation nanoelectronics, nanophotonics and quantum technology.

Acknowledgements

The authors would like to acknowledge Dr. Yohann Franz for Raman measurement with 473nm laser at Diamond Light Source and the technical assistance of Mr Chris Craig. The 2D materials
work is funded by the Engineering Physical Sciences Research Council through the Chalcogenide Photonic Technologies (EPSRC EP/M008487/1) and the Future Photonics Manufacturing Hub (EPSRC EP/N00762X/1) at the University of Southampton, United Kingdom. This work received funding from the UK Government’s Department for Business, Energy and Industrial Strategy (BEIS) through the UK’s National Measurement System programmes at the National Physical Laboratory, United Kingdom.

Author Contributions

C.-C.H. conceived the VdWE apparatus designs and carried out initial fabrication, testing and characterizations. H.W. prepared CVD-grown single crystals and 2D heterostructures and characterized these materials. Y.C., F.R and S.W. preformed the characterizations of WS₂/MoS₂ heterostructures. E.W. assisted in the construction of VdWE apparatus. S.J., D.W., Y.D., X.L. and P.W. assisted in the TEM measurements. T.P., D.W., P.W., Y.C. and C.-C.H coordinated the research collaboration. Y.C. and C.-C.H wrote manuscript and all authors contributed to technical discussions and paper writing.

Supporting Information Available

Additional band structure calculations of VdWE-grown MoS₂/WS₂ on fused silica sample and detailed characterization of VdWE-grown WS₂/CVD-grown MoS₂ heterostructures on 300nm SiO₂/Si substrate.
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