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Two Step Growth Phenomena of Molybdenum Disulfide – Tungsten Disulfide Heterostructures

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Here, we report the first demonstration of atomically thin vertically stacked MoS_2/WS_2 heterostructures, achieved via a two-step chemical vapour deposition (CVD) growth process. Highly ordered stacking of heterostructure domains and patterned defects have been observed. Computations based on first principles have been performed to understand observed enhanced photoluminescence of the heterostructure.

Transition metal dichalcogenides (TMDC) are a family of materials with two-third of its members assuming layered structures;¹ all with a range of electronic, optoelectronic, mechanical, thermal, and chemical properties.² Atomically thin films of TMDCs have gained considerable interest in the scientific community after the discovery of graphene, a two dimensional analogue of graphite.³ TMDCs of interest, which include MoS₂ and WS₂, have honeycomb structures where the transition metal atom (Mo, W) is sandwiched between two planes of sulphur (S) atoms as seen in Figure 2F.^{4,5,6,7,8,9,10,11} Monolayers of the TMDC's have been obtained via mechanical exfoliation, intercalation exfoliation, chemical vapour deposition (CVD), and physical vapour deposition (PVD), etc.^{12,13,14,15,16,17,18,19} However, relatively less is known about surface junctions formed in a heterostructure of two TMDC material. Investigations into graphene-TMDC heterostructure have demonstrated improved photon absorption in photovoltaic devices,²⁰ nonvolatile memory application,²¹ and evidence of band-gap tenability in MoS₂.²² In this study, we introduce a novel approach to growing a vertically stacked MoS₂/WS₂ heterostructure, via a two-step solution CVD process. The findings of this work may be applicable in understanding other TMDCs as well as future 2D materials synthesized using similar methods.

 MoS_2 films were first grown on 300 nm thick SiO_2 by using a drop cast of MoO_3 nanobelts synthesised according to previous works.^{9,23} An in-house thermal CVD system was used to sulfurize This journal is © The Royal Society of Chemistry 2012 the MoO_3 nanobelts in order to obtain MoS_2 domains.^{24,9,25,26} An aqueous suspension of MoO_3 nanobelts (5-10µL) was drop casted onto the SiO_2 substrate, as seen in Figure 1A, and placed in the middle section of the furnace. The sulphur was situated on the edge of the furnace where the temperature reached a maximum of 500°C. The sulphur amount can vary from a minimum of 300mg to up 600mg per square inch of sample, to account for possible minor oxygen leaks so that the excess sulfur will reduce any oxidation of the material.⁴ The furnace was ramped at a rate of 15°C/min to 750°C and kept at that particular temperature for 10-20 minutes, under argon flow and ambient pressure. Various triangular shaped MoS_2 islands or continuous sheets were observed across the substrate after the growth, as demonstrated in



Figure 1. Illustrated from A-D is the schematic of the heterostructure growth procedure.

Figure 1B. In the next step, an aqueous suspension of WO_3 nanobelts was applied to the MoS_2 grown samples (Figure 1C),

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and the aforementioned growth procedure was repeated in order to obtain WS_2 domains atop the MoS_2 domains. After the growth was completed, and the samples were cooled to room temperature, various MoS_2/WS_2 heterostructure species were noticed across the sample, as seen in the schematic in Figure 1D.



Figure 2. SEM images A-E) showing WS_2 domains growing on top of MoS_2 along with edge and surface defects. Molecular model is observed in image F. F. Atomistic representation of stacking pattern of MoS_2 on WS_2 .

The MoS₂/WS₂ heterostructure morphologies, along with various defects and stacking, were characterized using a scanning electron microscope (SEM) (Leo-supra, 1550). In Figure 2A, WS₂ domain is shown to grow in a manner where it stays contained within the MoS_2 grain. A similar phenomenon is observed in Figure 2C.²⁷ Defects affect the electronic and optical properties of pristine monolayer MoS₂. Since we start out with an oxide precursor as defects on the substrate in order to initiate growth, this greatly influences the how many defects we will have on our material.²⁶ After the growth, numerous popcorn-like features are observed along the edges of MoS₂ triangular domains, as seen in Figure 2B and Figure 2D. Similar features have also been observed in the CVD synthesis of graphene on Cu foils.²⁸ In this case, however, these features are due to the presence of oxysulfides in the form of (MoO_xS_{2-x}) .^{26,29,30} These popcorn features are spatially well oriented around the edge of the triangle, as seen in Figure 3A. The orientation of oxysulfides along the edges indicate an outwards growth, and with the presence of sulphur, these oxysulfides are expected to expand and form large coalescing features (Figure 4C).²⁶ Depending on the growth process we also observe these oxysulfides to be present on the surface of the domains as seen in Figure 2D. Due to an increase of the growth time, stacking of multi heterostructure features were observed across the sample forming pyramidal structures as seen in Figure 2E.

The height profiles and surface morphology of the heterostructures were studied using an AFM (Veeco) under tapping mode imaging, as illustrated in Fig. 3. It is known from exfoliated samples that monolayer AFM height is about 0.9 nm.³¹ The single layer heights of 1nm along with an inter-layer spacing of 0.6nm for the WS₂ and MoS₂ is previously reported.^{10,32} In our

height profile in Figure 3B and 3D we observe a progressive decrease in the layer thickness. Our height profile observations correspond very closely with the literature, whereas the number of layers increase the thickness becomes thinner.^{29,30}



Figure 3. AFM heterostructure stacking is observed in A-B along with its height profiles found in C-D.

In Figure 3A a very ordered pyramidal stacking is observed while showing an evolution of step heights from nearly 749pm to 518pm in Figure 3B. Similar results are seen in Figure 3C-3D with a different stacking orientation and many stacking agglomerations at the mid-point of the structure. These observations tells us that there might be some layer spacing between the substrate and first morphological layer due to lattice mismatch, but no pattern of the layer to layers bonding or spacing was observed.



Figure 4. In (a) we see the Raman spectra of heterostructure MoS_2/WS_2 and Photoluminescence data of heterostructure region and individual in (b). Optical images of before and after WS_2 growth found in C and D.

Raman and PL spectroscopy was used to characterize the vertical MoS_2/WS_2 heterostructures using a Renishaw DXR Raman spectroscopy system with a 532nm laser. As shown in Figure 4A, we observe Raman E^1_{2g} and A_{1g} modes at 379.4cm⁻¹, and 402.1cm⁻¹, respectively. These modes correspond to a monolayer MoS_2 which serves as a blanket substrate for the WS_2 domains, as depicted in Figure 4D.^{8,33} We also observe the E^1_{2g} mode at 351.9cm⁻¹ and A_{1g} mode at 414.1cm⁻¹ correspond to monolayer WS_2 .³⁴ There appears to be a discrepancy between the Raman intensity ratios of the E^1_{2g} and A_{1g} peaks for both single

layer MoS₂ and WS₂, when compared to previous literature, however these ratios can vary due to polarization effects, which can vary widely depending on the instrument setup.³⁵ Additionally, red shifting of the E_{2g}^1 mode and the blue shifting of the A_{1g} , resulting in a wider A_{1g} and E_{2g}^{1} difference, Δw , was also observed, $\Delta w=22.7 \text{ cm}^{-1}$ and $\Delta w=62.2 \text{ cm}^{-1}$ for MoS₂ and WS₂, respectively. This coincides with previous publications and predictions of stacked TMD heterojunctions.³⁵ The PL spectra, shown in figure 4B, shows two prominent peaks at 640 nm and 690 nm, corresponding to the excitonic transition energies of 1.93 eV and 1.79 eV, respectively.³⁶ These peaks at 640nm (1.93 eV) and 690nm (1.79 eV) can be attributed to the direct excitonic transition energies in the top WS₂ layer and bottom MoS₂ layer, respectively. The exhibition of two strong peaks confirms the formation of decoupled monolayer WS₂ on monolayer MoS₂. The suppression of the WS₂/MoS₂ peak is consistent with an earlier observation. WS₂ is seen to grow nicely on these MoS₂ blankets as evidenced by the transition images from Figure 4C-4D. This homogeneous growth is expected, because the lattice constant mismatch for these two materials is less than 0.5% and hence, the strain between the layers is negligible.³⁸

Raman mapping was conducted to confirm the presence of WS_2 and MoS_2 heterostructure. Figure 5A-5B shows Raman mapping of our sample, where E_{2g} and A_{1g} peaks correspond to the 379 cm⁻¹ and 402 cm⁻¹ vibrational modes respectively of MoS_2 layers. It is interesting to note that the MoS_2 coated in WS_2 appear to show a higher Raman intensity compared to free MoS_2 layers as noted by the red regions. This suggests that there is a coupling between the MoS_2 and WS_2 , thus altering their electrical and optical properties^{27.36}. In Figure 5C-5D the E_{2g} and A_{1g} vibrational modes correspond to the 352 cm⁻¹ and 414 cm⁻¹ respectively of WS_2 , which corresponds with the high intensity region of the MoS_2 mapped region.



Figure 5. In A and B we see the E_{2g}^{1} and A_{1g} corresponding to the MoS₂ Raman mapping and similarly in C and D WS₂ Raman mapping is shown.

To explain the observed photoluminescence, we calculate the electronic structure of a MoS_2 -WS₂ bilayer heterostructure. Our calculation is based on first-principles density functional theory (DFT) using the projector augmented wave method as implemented in the software package VASP.³⁹ The screened Heyd-Scuseria-Ernzerhof (HSE) hybrid functional,⁴⁰ with the screening parameter, μ = 0.26Å, has been employed.⁴¹ Spin-orbit coupling was included self-consistently within the band structure calculations. A Monkhorst-Pack scheme was adopted to integrate over the Brillouin zone with a k-mesh 9 x 9 x 1 for the monolayer and bilayer structures. A plane-wave basis kinetic energy cutoff of 300 eV is used. The lattice constant for the monolayer MoS₂ and WS₂ structures are obtained from bulk MoS₂ and WS₂ that have been optimized with van der Waals (vdW) interactions accounted for using a semi-empirical correction to the Kohn-Sham energies.⁴² The atomic coordinates for the monolayer structure are optimized at this fixed lattice constant. The atomic coordinates for the WS₂-MoS₂ heterostructure are optimized in all directions using the WS₂ lattice constant using the DFT-D2 dispersion corrections⁴³ until all of the interatomic forces are below 0.005 eV/Å. 15Å of vacuum spacing is added along the zaxis for the monolayer and bilayer structures. The HSE calculations of the monolayer structures result in bandgaps of 1.79 eV and 1.90 eV for MoS₂ and WS₂ respectively. This is in good agreement with the experimental bandgaps of 1.797 eV and 1.953 eV obtained in our PL data for monolayer MoS₂ and WS₂ respectively. The optimized van der Waals gap for the MoS₂-WS₂ bilayer structure is 3.11Å. At this separation distance the bandgap of the bilayer structure is indirect along Γ_v - K_c. The indirect gap is 1.513eV and the direct Kv-Kc gap is 1.563 eV.



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Figure 6. Bandstructure for MoS_2/WS_2 at the equilibrium vdW gap (blue) and 10% increase (light yellow) from its equilibrium value (a) and Direct gap (solid) and indirect gap (dotted) energy transitions for MoS_2/WS_2 for a range of increases in the vdW gap from the equilibrium vdW gap. The point of intersection indicates the indirect to direct transition vdW gap (b).

The valence band at Γv is composed of 28% p_z orbitals evenly contributed by the sulfur atoms at the vdW interface of the MoS2 and WS₂ layers and 67% dz² orbitals that are primarily from the W atoms. The valence and conduction band at K are localized on different layers of the heterostructure. The valence band, K_v, is composed of 40% dx² and 40% d_{xy} orbitals contributed entirely by the W atoms of the WS₂ layer. The conduction band, K_c, is composed of 90% dz² orbitals that are contributed entirely by the Mo atoms of the MoS₂ layer. To quantify the observed two distinct direct peaks in the PL measurement, we investigate the effect of changes in interlayer coupling on the electronic structure of the WS₂-MoS₂ bilayer. The change in the Γv -Kc indirect gap and the Kv-Kc direct gap is plotted in Figure 6B. An indirect to direct bandgap crossover in the MoS₂-WS₂ structure occurs when the vdW gap is increased by 0.1Å. Further increment in the interlayer separation above 0.1Å results in a direct bandgap. We also observed a similar indirect to direct transition when the vdW gap was increased by 25% of the equilibrium separation distances in bilayer, tri-layer and quad-layer MoS₂.⁴⁴

However, the direct band-gap and layer decoupling alone is insufficient to explain the PL spectra of our MoS_2/WS_2 heterostructure. Complexities induced by our growth process on the morphology and relative orientation between the two films are possible explanations for the PL spectra of our heterostructure.

In summary, we report the ability to obtain atomically thin 2D semiconducting vertical heterostructure with good crystalline qualities. We report edge and surface defects found in the growth process of exotic 2D materials. Highly ordered stacking of heterostructure domains is reported and confirmed via AFM characterization.

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