Controlled Growth of 2D Heterostructures and Prevention of TMD Oxidation

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ABSTRACT

This paper presents a review of the controlled growth of transition metal dichalcogenide (TMD) heterostructures, and the elucidation of the role of underlying two dimensional (2D) materials on temporal degradation of transition metal dichalcogenides (TMDs). Chemical vapor deposition (CVD)-growth is carried out to achieve localized, patterned, single crystalline or polycrystalline monolayers of TMDs, including MoS₂, WS₂, WSe₂ and MoSe₂, as well as their heterostructures. The localized growth of TMDs has an important implication for nonlinear optics applications. Extensive material characterization is performed to illuminate the role of dissimilar 2D substrates in the prevention of interior defects in TMDs. This characterization provides a detailed observation of the oxidation rates and behaviors of TMDs, which corroborate the role of underlying 2D layers in the prevention of in-air oxidation in TMDs. The epitaxial growth is demonstrated to create TMDs on hBN and graphene, as well as vertical/lateral heterostructures of TMDs, uniquely forming in-phase 2D heterostructures.

1. INTRODUCTION

Recent advances in atomically thin 2D materials have led to a variety of promising future technologies in the areas of electronics, energy, photonics and optoelectronics. 2D materials exhibit strong in-plane bonding along with weak out-of-plane bonding, enabling the exfoliation of the materials into single crystal, two-dimensional flakes with atomic level thickness. 2D materials are comprised of layered van der Waals solids such as atomically flat graphene, h-BN, phosphorene, SiC, Si₂BN, and transition metal dichalcogenides (TMDs) (MX₂ (X-M-X layer) where M=Ti, Zr, Hf, V, Nb, Ta, Mo, W, and X = S, Se, Te). Graphene has superior properties, including high carrier mobility, ultrahigh surface area, excellent thermal conductivity, and quantum confinement effect. Graphene is poised to compete with or replace current transparent conductive coatings widely used in electronic products, such as touch screen displays, e-paper (electronic paper) and organic light-emitting diodes (OLEDs). Massive government and industry investments are currently underway in graphene research, such as in Europe ($100 Million Euros per year for 10 years) and Asia (Samsung in Korea) for fundamental research, as well as developmental work. However, the lack of band gap is a serious limitation for the use of graphene in electronic devices. For this reason, the general class of 2D materials, especially TMD monolayers, has generated enormous interest in the research community, in large part owing to their novel properties complementing graphene.

A variety of methods have been developed to fabricate TMDs, which include mechanical exfoliation, chemical exfoliation, sulfurization of Mo thin films, and chemical vapor deposition (CVD). Large-scale growth of TMDs using metal organic chemical vapor deposition (MOCVD) on fused silica and SiO₂ substrates, as well as chip-scale monolayer WS₂ growth on Au substrates using low-pressure chemical vapor deposition (LPCVD), have been reported. In spite of recent advances, the degradation of TMDs by oxidation under ambient conditions is a potential roadblock for practical TMD applications. CVD-grown TMDs on SiO₂ or sapphire substrates with small grain sizes (few microns) have numerous internal grain boundaries which are prone to rapid oxidation in air, accelerated by humidity, UV irradiation and heat. The oxidation of TMDs on SiO₂ is visible under an optical microscope within several weeks after growth, when stored in an ambient environment as also discovered/witnessed by our research group. To avoid in-air oxidation, most researchers would fabricate devices right after TMDs are grown, or keep the materials in a vacuum chamber. Though hBN or polymer encapsulation can reduce oxidation, applications including gas sensors, DNA sensors and other bio-applications require direct exposure of TMDs to the
environment. Therefore, there is no long-term solution for practicality of these materials unless the issue of in-air oxidation is fully addressed.

This paper gives an overview of our CVD-growth and characterization of TMD heterostructures, and our effort to find conditions of 2D heterostructures resistant to TMD oxidation. We show controlled growth monolayers of TMDs, including MoS$_2$, WS$_2$, WSe$_2$, and MoSe$_2$, as well as their heterostructures. We extensively characterize TMD heterostructures to observe the oxidation rates and behaviors of TMDs on different underlying 2D layers. Our van der Waals epitaxial growth creates TMDs on hBN and graphene, as well as vertical/lateral heterostructures of TMDs. We show that the grown heterostructures are perfectly in-phase aligned.

2. CONTROLLED GROWTH OF 2D HETEROSTRUCTURES

We have performed an LPCVD-growth of MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$ monolayers. The patented ‘contact-growth’ enables the growth of TMDs on ‘contacted’ areas only, due to the controlled distribution of gas phase transition metal on these contacted areas. Figure 1a depicts the photograph images of the growth setup. This novel growth strategy facilitates the control of diffusion length from the source materials before being incorporated into TMD crystals. In this process, the thin-film transition metal oxide (TMO) is deposited on a substrate as a TMO source (“source substrate”) and ‘contact’ a bare substrate (i.e., SiO$_2$ or sapphire) face-to-face (Figure 1b). In this growth configuration, the flow rate of carrier gas through the gap between two substrates is dramatically suppressed (and controlled). This suppression of the gas flow enables optimized reaction of the gas phase of TMO with the gas phase of chalcogenide, which can diffuse between the two substrates at the growth temperature. Figure 2 shows the PL spectra (top) and optical images (bottom) of four representative TMDs grown on SiO$_2$ using this growth strategy. The results show large single crystalline growth (>150 μm) of WS$_2$ and WSe$_2$ as well as fully covered polycrystalline growth of MoS$_2$ and MoSe$_2$ up to a chip scale. We utilized Raman/photoluminescence (PL) spectroscopy, optical
microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and high resolution transmission electron microscope (HRTEM) to characterize growth formation, crystallinity, substrate orientation and the thickness of grown materials. The full-width half maximum (FWHM) of the PL spectrum from one of our CVD-grown WS$_2$ was ~50 meV, even sharper than the FWHM of typical exfoliated WS$_2$ (~75 meV) at room temperature, confirming the high quality growth of WS$_2$ monolayers. Their HRTEM images show the hexagonal lattice of WS$_2$ with a hexagon side length of 1.85+/-0.03 Å, in agreement with the literature and with the expected value of 1.836 Å from published crystal structures. SAED patterns from these samples show sharp points in a six-fold pattern confirm the monolayer nature of the growth and the high crystallinity. For WS$_2$, the lattice spacing was measured to be 2.74 +/- 0.02 Å, in agreement with other reported values $^{34}$.

Figure 3a shows optical and SEM images of the patterned WS$_2$ monolayers $^8$. With the pre-growth treatment of the target substrate, WS$_2$ monolayer growth filled the surface of the target substrate, whereas the lines were devoid of WS$_2$, as evidenced by a lack of Raman signals in those regions (Figure 3b (red color)), which shows the patterned growth (without post-lithography). The PL spectrum appears at 623 nm (1.99 eV). Amongst different samples we have observed PL peak energies ranging from 621 nm to 641 nm (2.00 eV – 1.94 eV) which agrees with the range observed by other research groups $^{35-37}$. Figure 4 shows the controlled localized growth of an array of MoS$_2$ monolayer islands directly from MoO$_3$ dot patterns $^{31}$. We increased the amount of MoO$_3$ on the source substrate to optimize the monolayer growth on the growth substrate. This result shows clear feasibility of ‘selective’ growth of TMD monolayers without post-lithography, which would potentially facilitate the device fabrication without polymer residues.

![Figure 2: PL spectra and optical images of large single crystalline WS$_2$ and WSe$_2$ as well as fully covered polycrystalline MoS$_2$ and MoSe$_2$.](image)

![Figure 3: (a) Optical images of WS$_2$ monolayers grown via the patterned growth process. Polycrystalline monolayer WS$_2$ (darker) fills the area between the lines (lighter). (b) Raman spectra, showing absence of WS$_2$ in the trenches.](image)

Transfer of arrays of TMD monolayers is an important task. Here, arrays of CVD-grown MoS$_2$ monolayers were successfully transferred on a silicon dioxide substrate (i.e., 1 cm x 1 cm). Figure 5a shows image of the transferred array of MoS$_2$ monolayers on an oxidized silicon substrate, maintaining the originally grown formation. Figure 5b shows an enlarged SEM imaged of transferred MoS$_2$ flake, which shows sharp and clear edges without wrinkles. Raman and PL spectra of the same point before and after transfer are shown in Figure 5c, where we observed a clear
blue shift around 30 meV with PL quenching after transfer, which can be explained by the effects of strain relaxation and the desorption/adsorption of molecules during the transfer.\textsuperscript{38–41}

Figure 4: Optical images of the MoS\textsubscript{2} arrays grown directly MoO\textsubscript{3} dot patterns.

Transferring 2D materials into multi-stacked structures (i.e., heterostructures) often introduces unwanted doping and reduced carrier mobility.\textsuperscript{42–45} The nature and effects of contaminants were investigated through cross sectional HRTEM using contaminant-inducing polymer based transfer methods, showing that the polymer is typically not fully removed.\textsuperscript{13,46,47} To this end, we have epitaxially grown (via van der Waals epitaxy) several 2D heterostructures with different combinations, including MoS\textsubscript{2} on hBN (Figure 6). The quality of the growth was found very positive. The PL maximum of MoS\textsubscript{2} monolayers grown on hBN was at 1.88 eV, comparable to that of typical free-standing MoS\textsubscript{2}.

Figure 5: Transferred MoS\textsubscript{2} at the chip-scale. (a) Optical image of MoS\textsubscript{2} islands before and after transfer. (b) Magnified SEM image. (c) Raman and PL spectra of the same point before and after transfer.

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Figure 6: Epitaxial growth of TMD heterostructures on different 2D materials. (a) PL spectrum and optical image of MoS\textsubscript{2} monolayers grown on a CVD-grown hBN monolayer. (b) PL spectra and optical image of the lateral WSe\textsubscript{2}/MoSe\textsubscript{2}/WS\textsubscript{2} heterostructure. (inset) Optical image of the vertical MoSe\textsubscript{2}/MoS\textsubscript{2} heterostructure. (c) SAED pattern of the vertical WSe\textsubscript{2}/WSe\textsubscript{2} heterostructure.
(1.90 eV). Its FWHM was 48 meV at room temperature, comparable to those of free-standing exfoliated MoS2 (50-60 meV), indicating that this MoS2 on hBN exhibits low charge impurity and clean interface.

3. GRAPHENE-ASSISTED ANTI-OXIDATION OF WS2

We have worked on the growth of WS2 monolayers on graphene to form a WS2/graphene heterostructure as well as other CVD-grown TMDs. Graphene was synthesized and transferred from the copper foil to a SiO2/Si substrate using a conventional transfer method. The copper was etched with copper etchant and the film was then rinsed and dried. The graphene on a SiO2 substrate was annealed at 400 °C for 2 hours, and was then immediately covered by a tungsten source carrier. The recipe of WS2 growth on graphene was similar to that of exclusive WS2 growth, with the exception of the hydrogen flow rate. After growth, WS2 monolayers covered the basal plane of graphene, and multilayered WS2 appeared to cover graphene boundaries and defects. SAED characterization confirms that the grown WS2 is monolayer (Figure 7a). In Figure 7b, the hexagonal pattern of graphene (red) in SAED encloses that of WS2 (blue), since the lattice constant of WS2 (3.15 Å) is larger than that of graphene (2.46 Å). Figure 7c shows PL spectra of WS2 monolayers on graphene and WS2 monolayers on SiO2 substrate. PL from WS2 monolayers on graphene (blue) was significantly quenched due to interlayer relaxation of photo-generated excitons before recombination, caused by the strong interlayer interaction between WS2 and graphene. The WS2 Raman modes E12g and A1g show a red shift by

![Figure 7](image_url)

Figure 7: Epitaxial growth of WS2 on a graphene substrate: (a) False colored SEM image of WS2 epitaxially grown on a graphene/SiO2 substrate. The dark purple, light purple, green and gray colors represent WS2 monolayers on graphene, graphene, few-layer WS2 on graphene and multilayers of WS2 originating at the edges of graphene, respectively. (b) SAED pattern of WS2 on graphene. (c) PL spectra of a WS2 monolayer on a SiO2 substrate and WS2/graphene on a SiO2 substrate.

![Figure 8](image_url)

Figure 8: Substrate-dependent oxidation of WS2. (a) Raman mapping of a WS2 monolayer on a SiO2 substrate (inset) Optical image of as-grown WS2 monolayers on a SiO2 substrate after 1 month expose in air. (b) False-colored SEM image of an epitaxially grown WS2 monolayer on a SiO2 substrate after 4 months of exposure in air. The dark purple, light purple and green colors represent WS2 monolayers on graphene, oxidized WS2 (along the WS2 grain boundary) and few-layer WS2 on graphene, respectively. (c) Raman mapping of a WS2 monolayer on graphene and its optical image (inset). The oxidized areas exhibit a complete Raman quenching. (d) Raman mapping of the WS2/graphene on the TEM grid, which confirms the material is not oxidized.
3 cm⁻¹ and 2 cm⁻¹ in the WS₂ monolayers on graphene (blue) as compared to WS₂ monolayers (black) on a SiO₂ substrate, which show a strong interlayer coupling between WS₂ and graphene.

Here we found the role of the underlying graphene on the oxidation rates of WS₂. As confirmed by optical imaging (Figure 8a), an as-grown WS₂ single crystal appeared to be clean in optical, SEM and AFM images was completely oxidized after 4 months in air. On the other hand, the oxidation rates and areas of WS₂ on a SiO₂ substrate and WS₂ on a graphene/SiO₂ substrate were very different. Figure 8b is a false colored SEM image of WS₂ on a graphene/SiO₂ substrate left in an ambient environment for 4 months. The light purple lines (appearing like cracks) in the SEM image represent WO₃ (i.e., oxidized WS₂) along the WS₂ grain Raman quenching. Raman mapping is more reliable than PL to characterize WS₂ oxidation, since graphene suppresses PL due to unidirectional charge transfer but does not modify the Raman intensity. Figure 8c shows Raman mapping of the same 4-month old WS₂ on a graphene/SiO₂ substrate, confirming that oxidation occurred only at the WS₂ grain boundaries (i.e., no interior oxidation). The oxidation characteristics of other TMD monolayers is expected to be very similar to that of WS₂, since they have similar crystal structures. Surprisingly, Figure 8d shows Raman mapping of the WS₂/graphene on the TEM grid, which confirms the material is not oxidized.

We have furthermore corroborated the anti-oxidation phenomenon by performing XPS measurements of a 200 µm sample area at several locations of as-grown WS₂ on a SiO₂ substrate, in-air oxidized WS₂ on a SiO₂ substrate and WS₂/graphene on a TEM grid after 10 months of exposure in ambient conditions (Figure 9). The W4f electron is known to be a sensitive probe with up to 4 eV shifts from the W(IV) to the W(VI) oxidation state, clearly distinguishing WS₂ from WO₃, with smaller yet measurable peak shifts for W suboxides (WOₓ). The XPS result of WS₂/graphene on a TEM grid left in air for 10 months showed a complete lack of W oxide signal. These results indicate that graphene plays a significant role in suppressing the oxidation of WS₂.

Figure 9: XPS measurement results: XPS spectra of an as-grown WS₂ monolayers showing W4f5/2 and W4f7/2 doublet with peak energies of 32 and 34 eV (left). XPS spectra of oxidized WS₂, a new doublet appears at 35.44±0.20 eV from W(VI) oxide (WO₃) (center). XPS spectra of 10-month old WS₂/graphene transferred on a TEM grid, of which the data shows a similar pattern as the as-grown WS₂ (right).

4. CONCLUSIONS

This paper presents an overview of the research progress concerning the epitaxial growth of 2D materials and the role of 2D substrates on the prevention of TMD degradation. A direct growth process was explored to enable localized, patterned, single crystalline or large-scale polycrystalline monolayers of MoS₂, WS₂, WSe₂ and MoSe₂ along with their heterostructures. We showed that the contact-growth method permits the growth of TMDs on the ‘contacted’ areas only, enabling fabrication of in-phase 2D heterostructures. To address the issue of TMD oxidation in air, CVD-growth and extensive material characterization were performed to illuminate the role of dissimilar 2D substrates in the prevention of interior oxidation in TMDs, thus uncovering the conditions of 2D heterostructures resistant to TMD oxidation. The epitaxial growth of TMDs on hBN and graphene, as well as vertical/lateral heterostructures of TMDs, was performed, uniquely forming in-phase 2D heterostructures. If these fabrication and applications could be developed to be highly reliable and high fidelity, it could have a large impact on the future research and commercializability of TMD-based devices.

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REFERENCES


