Epitaxial growth of wafer-scale transition metal dichalcogenide monolayers by metalorganic chemical vapor deposition

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Abstract

The epitaxial growth of wafer-scale semiconducting TMDs monolayers (MoS_2, WS_2, WSe_2) on c-plane sapphire by metalorganic chemical vapor deposition (MOCVD) is demonstrated and the resulting structural and optical properties of the films are compared to elucidate trends based on metal and chalcogen species. The sulfur based TMDs exhibit improved epitaxy, fewer defects and increased photoluminescence intensity on sapphire compared to WSe_2 which is attributed to a smaller effective lattice mismatch and improved stability.

Introduction

Transition metal dichalcogenides (TMDs) form a compelling class of 2D materials with potential applications in optoelectronics, flexible electronics, chemical sensing and quantum technologies. At the monolayer limit, the semiconducting TMDs (*e.g.*, MX_2 where M = Mo/W and X = S/Se) exhibit direct band gaps within the visible range, large exciton binding energies and spin-valley polarization. The lack of out-of-plane bonding on the van der Waals surface of these materials enables heterostructure formation without the constraints of lattice matching.

Epitaxial growth of single crystal TMD monolayers at the wafer-scale is of significant interest for device applications. Metalorganic chemical vapor deposition (MOCVD) is a promising approach for TMD growth as it enables the use of high substrate temperatures (700-1000°C) and chalcogen/metal ratios (10^3-10^5) [1] which are beneficial for epitaxy. In addition, the flow rate of precursors can be modulated during growth to enhance the surface diffusion of metal-containing species and control the lateral growth rate of TMD domains [1]. C-plane sapphire has emerged as the substrate of choice for TMD epitaxy due to its crystallographic compatibility and good chemical stability in the CVD environment. In addition, steps on the sapphire surface can be used to induce a preferred alignment of TMD domains resulting in a significant reduction in inversion domains in the films [2,3]. The availability of large area MOCVD-grown monolayers films has enabled benchmarking studies of field-effect device performance [4] and photodetectors for sensing platforms [5].

In this study, the growth and properties of wafer scale MoS_2, WS_2 and WSe_2 monolayers grown by MOCVD on 2" diameter c-plane sapphire are compared and contrasted. The results provide insights into the role of the metal and chalcogen species on film growth and properties of large area TMD monolayers.

Experimental

MOCVD growth was carried out in a horizontal cold-wall reactor that includes an induction-heated rotating SiC-coated graphite susceptor and separate gas inlets for the metal and chalcogen precursors (Figure 1). Metal hexacarbonyls ($Mo(CO)_6$ and $W(CO)_6$) and hydrides (H_2S and H_2Se) were used as precursors in a H_2 carrier gas. Typical growth conditions include growth temperatures ranging from 850-1000°C, reactor pressures from 50-200 Torr and high chalcogen/metal ratios (~10^4) resulting in growth rates on the order of 1-3 monolayers/hour. The films were characterized post-growth using atomic force microscopy and room temperature confocal Raman/photoluminescence spectroscopy.

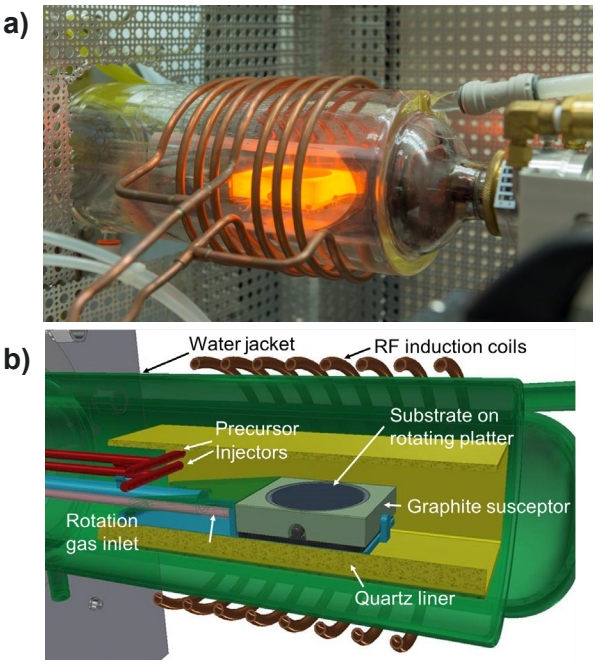

Fig. 1: Photo (a) and schematic (b) of horizontal cold wall MOCVD reactor used for TMD growth.

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Results and Discussion

MoS_2 monolayers were grown by MOCVD on 2" c-plane sapphire using $Mo(CO)_6$ and H_2S in a single step process at 1000°C and 50 Torr reactor pressure. The growth time was varied from 10-15 mins to achieve a fully coalesced monolayer with minimal bilayers. Under these conditions, a uniform monolayer was obtained across the 2" diameter wafer (Fig. 2(a)). Undulations in the surface morphology of the monolayer arise from steps on the sapphire surface. Small triangular bilayers are also present at a surface coverage of <15%. Room temperature PL spectra (Fig. 2(b)) obtained at the center and the edge of the 2" sapphire contain an emission peak at 1.91 eV associated with the A exciton [6]. Raman spectra (Fig. 2(c)) obtained at the center and edge of the wafer show characteristic modes for MoS_2.

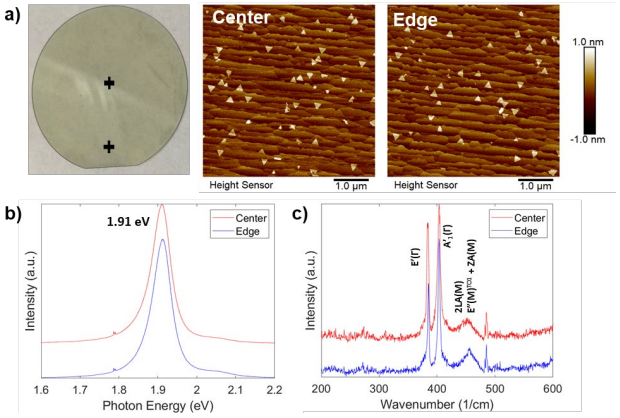

Fig. 2: (a) Surface morphology of MoS_2 monolayer grown on 2" c-plane sapphire at center and edge of wafer (locations indicated by + in photo); Room temperature (b) PL and (c) Raman spectra obtained at the center and edge of the wafer.

A three-step nucleation-ripening-lateral growth process [1] at 850-1000°C was used for the epitaxial growth of WS_2 on 2" c-plane sapphire. The three-step process is beneficial for the growth of tungsten-containing TMDs as it enhances the surface diffusivity of W-containing species leading to a reduction in the in-plane misorientation of domains [2]. $W(CO)_6$ and H_2S were used as precursors in a H_2 carrier gas at a reactor pressure of 50 Torr. Lateral growth times ranging from 10-15 mins were required to achieve a fully coalesced monolayer. The WS_2 monolayer (Fig. 3(a)) exhibits a similar morphology to that of MoS_2 (Fig. 2) characterized by sapphire step undulations and a small number of bilayers. The room temperature PL spectrum (Fig. 3(b)) obtained at the

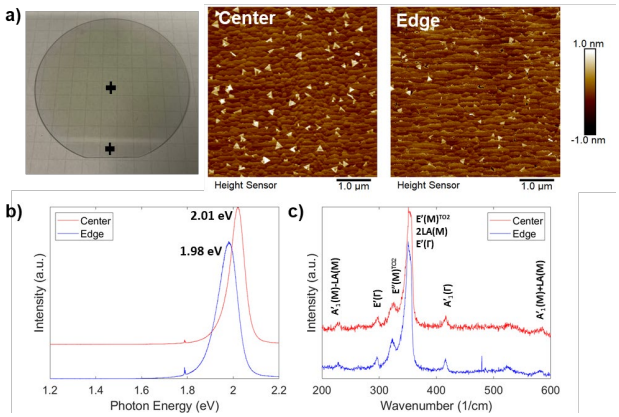

Fig. 3: (a) Surface morphology of WS_2 monolayer grown on 2" c-plane sapphire at center and edge of wafer (locations indicated by + in photo); Room temperature (b) PL and (c) Raman spectra obtained at the center and edge of the wafer.

center of the 2" sapphire contains a peak at 2.01 eV which is red-shifted to 1.98 eV near the edge. Raman spectra (Fig. 3(c)) obtained at the center and edge show characteristic modes for WS_2.

MOCVD growth of WSe_2 was also carried out in the horizontal cold-wall reactor using $W(CO)_6$ and H_2Se in a H_2 carried gas at 200 Torr. Similar to WS_2 on sapphire, a three-step process at 850-1000°C was used to promote epitaxy of WSe_2. Lateral growth times ranging from 22-30 minutes were required to obtain a coalesced monolayer. The surface morphology of WSe_2 on sapphire consists of undulations due to steps on the sapphire, (Fig. 4(a)), however, the undulations are less uniform than that of the MoS_2 and WS_2 monolayers. The WSe_2 monolayer also contains small pinholes due to incomplete coalescence and triangular bilayers which are

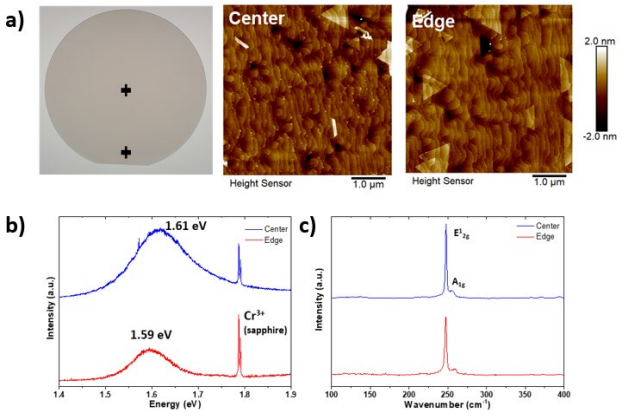

Fig. 4: (a) Surface morphology of WSe_2 monolayer grown on 2" c-plane sapphire at center and edge of wafer (locations indicated by + in photo); Room temperature (b) PL and (c) Raman spectra obtained at the center and edge of the wafer.

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generally larger in size (hundreds of nanometers) than the bilayers present on MoS_2 and WS_2 (tens of nanometers). The room temperature PL spectrum (Fig. 4(b)) obtained at the center of the 2" sapphire contains a peak at 1.61 eV which is red-shifted to 1.59 eV near the edge. The PL intensity from the WSe_2 monolayers is generally lower than that of the MoS_2 and WS_2 films as evidenced by the presence of the sharp peak at 1.79 eV associated with Cr^{3+} emission from the sapphire substrate which is barely visible in the PL from MoS_2 (Fig. 2(b)) and WS_2 (Fig. 3(b)). Raman spectra (Fig. 4(c)) obtained at the center and edge of the wafer show characteristic modes for monolayer WSe_2.

The difference in the growth and properties of wafer-scale WSe_2 on c-plane sapphire compared to the sulfide-based TMDs (MoS_2 and WS_2) can be attributed, at least in part, to lattice mismatch. While both exhibit hexagonal symmetry, there are significant differences in the lattice constants of the TMDs and sapphire (Table 1). However, there is commensurability between 2 units cells of α-Al_2O_3 and 3 units cells of the TMDs [2]. Based on this, the effective lattice mismatch of (MoS_2, WS_2)/sapphire is reduced to ~0.569% compared to a much larger lattice mismatch (~4.89%) for WSe_2/sapphire. This translates into increased strain/defects in WSe_2 which impacts the optical and transport properties of the coalesced monolayers. In addition to lattice mismatch, the metal-sulfide bond strength is greater than that of metal-selenide which imparts additional thermal and chemical stability to the sulfide TMDs.

Table 1. Lattice parameter (a) and effective lattice mismatch between TMDs and sapphire assuming $3x(a_{TMD})/2x(a_{Al2O3})$

Material Substrate/Film	Lattice parameter* (a, Å) [7]	Effective mismatch (%) to sapphire
α-Al_2O_3	4.758	-
MoS_2	3.190	0.569
WS_2	3.191	0.569
WSe_2	3.327	4.89

Conclusion

Epitaxial growth of wafer-scale MoS_2, WS_2 and WSe_2 monolayers on c-plane sapphire is demonstrated by MOCVD. Uniform films are achieved across the 2" wafer diameter. The sulfide TMDs exhibit fewer defects and improved optical properties compared to WSe_2 which is attributed, in part, to reduced lattice mismatch on sapphire.

Acknowledgments

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