

Large area growth of transition metal dichalcogenides for photonics and optoelectronics

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Interest in transition metal dichalcogenides (TMDs), such as WS_2 , MoS_2 and related compounds, has been renewed by the discovery of emergent properties when reduced to single, two-dimensional (2D) layers.^{1,2} These atomically thin layers of TMDs form a versatile and vast library of 2D materials.³ On the one hand, they allow to study novel condensed matter phenomena, such as strong excitonic many-body interactions or topological phases,^{4,6} while on the other, they hold great promise for applications in electronics, optoelectronics, or catalysis.⁷⁻⁹ A major bottleneck to this research is the lack of reproducible and large scale synthetic methods for high quality, consistent monolayer TMD samples. The dominant growth method is the vaporization and subsequent chalcogenization of solid metal oxides in the presence of gaseous chalcogen precursors. This process is commonly referred to as chemical vapor deposition (CVD) or powder vaporization.¹⁰⁻¹³ Due to its simplicity, CVD is extensively used by the TMD community to produce high quality, micron-sized single crystals.^{10-12,14-18} However, for technological realization of the fundamental advances made in the TMD field, the creation of large area coverage materials is critical.

In this presentation I will show our recent work on developing new growth processes for creating large area and conformal coatings of bulk and 2D transition metal dichalcogenides. This work includes the direct conversion of atomic layer deposition grown metal oxides into sulfides and selenides which can produce a variety of structures from nanowires to continuous nanocrystalline 2D films (Figure 1) or bulk conformal films which are used for photonic applications (figure 2), and novel CVD methods for van der Waals epitaxy of high density single crystal TMDs (figure 3) on graphene for advanced characterization such as angle resolved photoemission spectroscopy (ARPES, figure 4) and scanning tunneling microscopy (STM, figure 5).

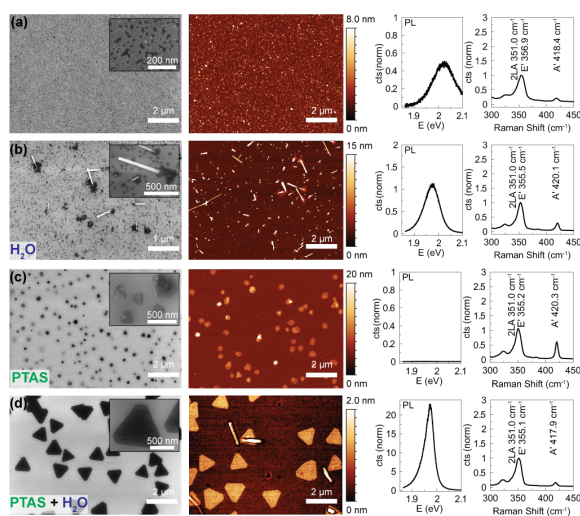


Figure 1. Characterization of WS_2 nanostructures grown under various conditions. The nanostructures are characterized by SEM and AFM (first and second column), as well as Raman and photoluminescence spectroscopy (third column). The spectra are normalized to the Raman mode intensity at $\sim 351\text{ cm}^{-1}$. Conversion of 1 nm thick WO_3 films into WS_2 at $T = 800\text{ }^\circ\text{C}$, H_2S flow of 5 sccm and Ar flow of 250 sccm (a) in dry Argon atmosphere, (b) in the presence of 100 ppm water vapor, (c) with seeding molecules on the substrate and (d) with both 100 ppm water vapor and seeding molecules on the substrate.

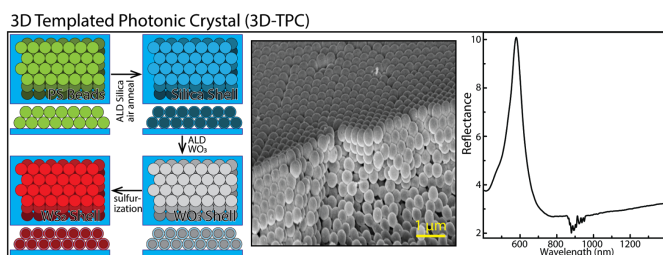


Figure 2. WS_2 inverse opal photonic crystal. Self-assembled polystyrene beads are coated with SiO_2 and WO_3 and then converted into WS_2 . Full infiltration of the 3D structure is achieved, yielding a large reflectance feature at 45° off normal incidence.

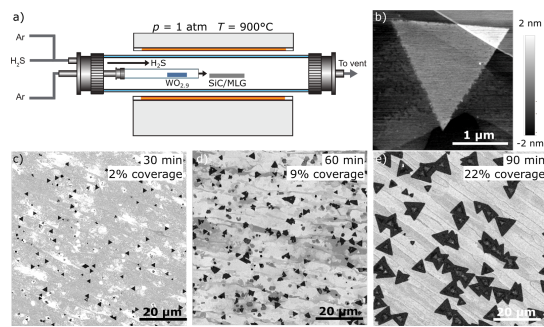


Figure 3. (a) Modified tube furnace system with separate gas supply for outer 1-inch tube and inner 1/4-inch tube. Tungsten oxide powder ($\text{WO}_{2.9}$) serves as the metal source, and it is loaded into the smaller inner tube. Hydrogen disulfide (H_2S) and Argon (Ar) serve as chalcogen source and carrier gas, respectively. (b) Atomic force microscopy image of monolayer WS_2 domain on epitaxial graphene. (c-d) Electron microscope images of CVD-grown WS_2 islands.

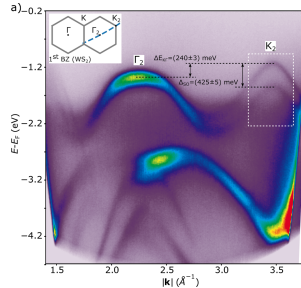


Figure 4. Band structure of a single triangular domain of monolayer WS_2 on epitaxial graphene. ARPES spectrum of monolayer WS_2 on SiC/graphene. The spectrum was measured outside of the 1st Brillouin zone.

References

- Frindt, R. F. Optical Absorption of a Few Unit-Cell Layers of MoS_2 . *Phys. Rev.* **1965**, *140*, A536–A539.
- Mak, K. F.; Shan, J. Photonics and Optoelectronics of 2D Semiconductor Transition Metal Dichalcogenides. *Nat. Photonics* **2016**, *10*, 216.
- Wilson, J. A.; Yoffe, A. D. The Transition Metal Dichalcogenides Discussion and Interpretation of the Observed Optical, Electrical and Structural Properties. *Adv. Phys.* **1969**, *18*, 193–335.
- Barja, S.; Wickenburg, S.; Liu, Z.-F.; Zhang, Y.; Ryu, H.; Ugeda, M. M.; Hussain, Z.; Shen, Z.-X.; Mo, S.-K.; Wong, E.; *et al.* Charge Density Wave Order in 1D Mirror Twin Boundaries of Single-Layer MoSe_2 . *Nat. Phys.* **2016**, *12*, 751.
- Yao, K.; Yan, A.; Kahn, S.; Suslu, A.; Liang, Y.; Barnard, E. S.; Tongay, S.; Zettl, A.; Borys, N. J.; Schuck, P. J. Optically Discriminating Carrier-Induced Quasiparticle Band Gap and Exciton Energy Renormalization in Monolayer MoS_2 . *Phys. Rev. Lett.* **2017**, *119*, 087401.
- Fei, Z.; Palomaki, T.; Wu, S.; Zhao, W.; Cai, X.; Sun, B.; Nguyen, P.; Finney, J.; Xu, X.; Cobden, D. H. Edge Conduction in Monolayer WTe_2 . *Nat. Phys.* **2017**, *13*, 677.
- Fiori, G.; Bonaccorso, F.; Iannaccone, G.; Palacios, T.; Neumaier, D.; Seabaugh, A.; Banerjee, S. K.; Colombo, L. Electronics Based on Two-Dimensional Materials. *Nat. Nanotechnol.* **2014**, *9*, 768–779.
- Pospischil, A.; Mueller, T. Optoelectronic Devices Based on Atomically Thin Transition Metal Dichalcogenides. *NATO Adv. Sci. Inst. Ser. E Appl. Sci.* **2016**, *6*, 78.
- Parzinger, E.; Mitterreiter, E.; Stelzer, M.; Kreupl, F.; Ager, J. W.; Holleitner, A. W.; Wurstbauer, U. Hydrogen Evolution Activity of Individual Mono-, Bi-, and Few-Layer MoS_2 towards Photocatalysis. *Applied Materials Today* **2017**, *8*, 132–140.
- Lee, Y.-H.; Zhang, X.-Q.; Zhang, W.; Chang, M.-T.; Lin, C.-T.; Chang, K.-D.; Yu, Y.-C.; Wang, J. T.-W.; Chang, C.-S.; Li, L.-J.; *et al.* Synthesis of Large-Area MoS_2 Atomic Layers with Chemical Vapor Deposition. *Adv. Mater.* **2012**, *24*, 2320–2325.
- Liu, H. F.; Wong, S. L.; Chi, D. Z. CVD Growth of MoS_2 -Based Two-Dimensional Materials. *Chem. Vap. Depos.* **2015**, *21*, 241–259.
- Kang, K.; Xie, S.; Huang, L.; Han, Y.; Huang, P. Y.; Mak, K. F. High-Mobility Three-Atom-Thick Semiconducting Films with Wafer-Scale Homogeneity. *Nature* **2015**, *520*, 656–660.
- Das, S.; Robinson, J. A.; Dubey, M.; Terrones, H.; Terrones, M. Beyond Graphene: Progress in Novel Two-Dimensional Materials and van Der Waals Solids. *Annu. Rev. Mater. Res.* **2015**, *45*, 1–27.
- Liu, Z.; Amani, M.; Najmaei, S.; Xu, Q.; Zou, X.; Zhou, W.; Yu, T.; Qiu, C.; Birdwell, A. G.; Crowne, F. J.; *et al.* Strain and Structure Heterogeneity in MoS_2 Atomic Layers Grown by Chemical Vapour Deposition. *Nat. Commun.* **2014**, *5*, 5246.
- Bao, W.; Borys, N. J.; Ko, C.; Suh, J.; Fan, W.; Thron, A.; Zhang, Y.; Buyanin, A.; Zhang, J.; Cabrini, S.; *et al.* Visualizing Nanoscale Excitonic Relaxation Properties of Disordered Edges and Grain Boundaries in Monolayer Molybdenum Disulfide. *Nat. Commun.* **2015**, *6*.
- Eichfeld, S. M.; Hossain, L.; Lin, Y.-C.; Piasecki, A. F.; Kupp, B.; Birdwell, A. G.; Burke, R. A.; Lu, N.; Peng, X.; Li, J.; *et al.* Highly Scalable, Atomically Thin WSe_2 Grown via Metal–Organic Chemical Vapor Deposition. *ACS Nano* **2015**, *9*, 2080–2087.
- Lee, Y.; Park, S.; Kim, H.; Han, G. H.; Lee, Y. H.; Kim, J. Characterization of the Structural Defects in CVD-Grown Monolayered MoS_2 Using near-Field Photoluminescence Imaging. *Nanoscale* **2015**, *7*, 11909–11914.
- Gong, Y.; Ye, G.; Lei, S.; Shi, G.; He, Y.; Lin, J.; Zhang, X.; Vajtai, R.; Pantelides, S. T.; Zhou, W.; *et al.* Synthesis of Millimeter-Scale Transition Metal Dichalcogenides Single Crystals. *Adv. Funct. Mater.* **2016**.