
Kevin Bogaert

Song Liu, Na Guo, Tao Liu, Jordan Chesin, Denis Titow, Martial Duchamp, Chun Zhang, Silvija Gradecak, Slaven Garaj

National University of Singapore, 6 Science Drive 2, Singapore

Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts, USA

bogaert@mit.edu

Transition Metal Dichalcogenides with Spatially Controlled Composition

Two-dimensional transition metal dichalcogenides (TMDs) possess a variety of properties that make them attractive for applications in electronic, energy, and sensing applications. In analogy to conventional semiconductors, more complex heterostructures or alloys based on 2D TMDs would expand the realm of possible device architectures by, for example, promoting directed charge carrier transport. Therefore, controlled synthesis of complex TMD structures with nanometer or atomic precision is required to unlock their full potential.

Here, we present a two-step chemical vapor deposition (CVD) synthesis method to control the spatial composition of the MoS₂-WS₂ material system and produce structures ranging from an abrupt heterostructure between pure species [1] to a composition-graded or spatially uniform alloy [1,2]. The composition configuration is determined by temperature-dependent and S-vacancy-assisted diffusion of Mo atoms through the WS₂ lattice.

For the synthesis of all three configurations, the starting material is CVD-grown single crystal WS₂ on its native SiO₂ substrate followed by the growth of MoS₂. We show that in-plane diffusion of Mo atoms can play a significant role in the chemical vapor deposition of MoS₂/WS₂ lateral heterostructures leading to a variety of non-trivial structures whose composition does not necessarily follow the growth order. The diffusion can be controlled by the growth temperature of MoS₂ and point defect concentration in the starting WS₂ crystals. Optical, structural, and compositional studies of TMD crystals captured at different growth temperatures and in different diffusion stages suggest that compositional mixing vs. segregation are favored at high and low growth temperatures, respectively.

Computational analysis of various mechanisms for Mo incorporation into WS₂ indicate that Mo atoms, after adsorbing to edge sites of the WS₂ lattice, can diffuse toward the interior of the crystal to displace a W atom and this process is mediated by S vacancies. This pathway is energetically favorable with an activation energy barrier that can be readily overcome at CVD growth temperatures.

In addition to affecting the ability for atoms to diffuse, the CVD growth temperature also dictates the equilibrium crystal structure. At lower growth temperatures, an enthalpy-dominated equilibrium leads to phase segregation with a MoS₂ core surrounded by a WS₂ ring. At higher growth temperatures, an entropy-dominated equilibrium leads to homogeneous alloy. However, at sufficiently high and heterogeneous defect densities, the distribution of S vacancies will drive the system to create an alloy such that the MoS₂ distribution resembles the original distribution of S vacancies in the WS₂ lattice. *In-situ* transition electron microscopy investigation of these temperature-driven processes [3] as well as composition-dependent quantum yield properties of the resulting compositionally-tuned TMD structures will be discussed.

References

- [1] Bogaert, K.; Liu, S. Chesin, J.; Titow, D.; Gradecak, S.; Garaj, S., *Nano Lett.*, 16 (2016) 5129-5134.
- [2] Bogaert, K.; Liu, S.; Guo, N.; Zhang, C.; Gradecak, S.; Garaj, S., *To Be Submitted*.

Figures

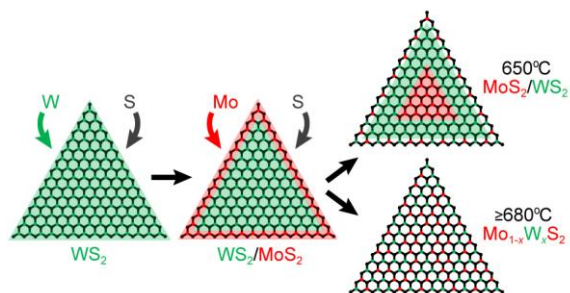


Figure 1: Schematic demonstrating the high and low growth temperature structures achieved by two-step chemical vapor deposition synthesis of transition metal dichalcogenide structures. In both pathways, the original WS_2 crystal has a uniform distribution of defects.

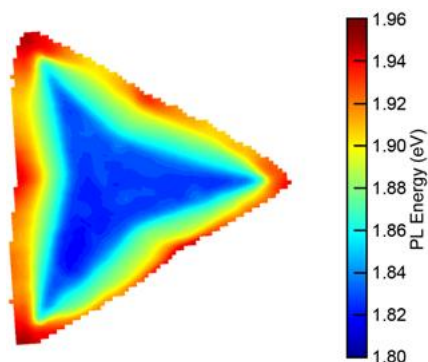


Figure 2: Photoluminescence peak emission energy of a $Mo_{1-x}W_xS_2$ composition-graded alloy crystal. The lower energy emission from the crystal core corresponds to higher Mo concentration. Conversely, the higher energy emission from the crystal edge corresponds to higher W concentration. The original WS_2 crystal has radial distribution of S vacancies which manifests itself in the final distribution of Mo atoms due to the S-vacancy-assisted Mo diffusion mechanism.