Tuning laser interactions for the synthesis and processing of atomically-thin 2D materials and heterostructures

David B. Geohegan[1*], Sumner Harris[2], Alex Puretzky[2], Gerd Duscher[1], Kai Xiao[2] *et al.*

[1] Department of Materials Science and Engineering, University of Tennessee at Knoxville, TN, USA
[2] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA
*Corresponding author email: geohegan@utk.edu

Photoexcited processes are key to the development and applications of atomically-thin two-dimensional (2D) materials and their heterostructures, which are being developed as novel optically-active quantum materials. Here we will review recent developments in the laser synthesis, characterization, and processing of atomically-thin 2D materials using real-time *in situ* diagnostics which take advantage of their unique optical signatures (e.g., Raman or photoluminescence spectra) as feedback to detect their formation and evolution.

For the precision synthesis of such atomically-thin materials, we explore tuning the kinetic energies of species in nanosecond pulsed laser ablation plasmas from their already uniquely advantageous sub-50 eV/atom regime to < sub-eV/atom using background gas collisions and *in situ* gated-ICCD imaging and ion probe diagnostics. Using a unique, fully automated and computer-controlled pulsed laser deposition (PLD) chamber equipped with not only *in situ* plasma diagnostics but also optical diagnostics of the substrate (reflectivity, Raman spectroscopy, and photoluminescence) we show how the hyperthermal implantation of atoms into monolayer 2D materials can be understood and controlled for the doping of semiconductor transition metal dichalcogenides (TMDs), the formation of Janus monolayers[1,2] (e.g., Se conversion of WS_2 to WSSe), or the complete transformation of one material into another(e.g., WS_2 to WSe_2). Raman spectra of these transformations provide a map of the material evolution, which can be halted and characterized by *ex situ* atomic resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy, providing key inputs for computational simulations of the material transformations. By applying machine learning and artificial intelligence to explore different synthesis pathways, such *in situ* diagnostics can explore autonomous synthesis – not only in PLD[3], but in laser processing. We show that laser processing within a TEM can be used to explore atomistic mechanisms of crystallization and metastable phase formation. Using PLD to deposit amorphous clusters by 'soft landing' without damage to suspended 2D monolayers, laser processing within the TEM reveals how they assemble into epitaxially-aligned, layered 2D crystals bonded by van der Waals interactions (i.e., van der Waals epitaxy)[4] or how metastable phases form. Selected examples of the resulting impact on ultrafast quasiparticle dynamics and other photoexcited processes in these unique materials will also be shown.

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