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Forum

Laser synthesis and processing of atomically thin 2D materials

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Recent advances in laser synthesis and processing of 2D materials are described that address key issues of scalable synthesis, precise heterogeneity control, and transformative manufacturing. Laser spectroscopy is used to remotely characterize and optimize the structure and functionality of 2D materials, enabling their *in-situ* diagnostic-based synthesis and processing.

Addressing key synthesis challenges of 2D materials by laser-based approaches

Realizing novel electronic and quantum properties in atomically thin 2D materials requires control over their structural and chemical heterogeneities within individual layers, including defects, dopants, edges, layer stacking, and localized strain [1]. However, due to their atomically thin thickness and vulnerable structure, many conventional synthesis and processing tools developed to process bulk materials, such as ion implantation for chemical doping of semiconductors, are no longer applicable. Tailoring such synthesis and processing techniques for atomically thin 2D materials is essential. In this forum article, we present trending laser-based synthesis and processing approaches for the growth, doping, thinning, conversion, direct writing, and phase modification of atomically thin 2D materials [2]. Because laser energy can be discretely pulsed and wavelength-tuned, electronic transitions and vibronic modes of 2D crystals can be excited and spectroscopically probed to enable the creation of point defects, enable phase transitions by conversion to heat, and at higher intensities, achieve atomic layer-by-layer exfoliation for thinning. Conversely, laser ablation plasmas can be intentionally created to supply novel species and conditions for synthesis, for example, **hyperthermal kinetic energy (KE) clusters** (see Glossary) for low-energy implantation [3] or amorphous ultrasmall nanoparticles as precursors for **laser crystallization** and assembly of 2D crystals with different phases [4]. In combination, the strong light–matter interactions in 2D materials enable lasers to serve not only as synthesis and processing tools but as remote optical spectroscopic diagnostics to directly measure and monitor the structural quality, grain orientation, strain, and defect evolution *in situ* by Raman scattering, photoluminescence (PL), second harmonic generation, and ultrafast pump-probe techniques.

Precisely managing the layer number and phase of 2D materials by laser processing

Due to the significant light absorption of 2D materials, **laser thinning** is being developed as an effective post-growth method to precisely control layer thickness, which is crucial for the physical properties of layered 2D materials, such as optical, electronic, vibrational, and magnetic properties. Both continuous-wave (CW) and pulsed lasers offer a variety of photochemical and thermal options to directly and cleanly remove layers of **van der Waals (vdW) crystals** on substrates by controllably heating or inducing photochemical etching reactions in oxidative, wet, or chemical environments [2,5]. Due to the strong thermal coupling of the bottom-most layer to the substrate, atomic layer-by-layer thinning can be reliably accomplished in transition metal dichalcogenide (TMD) materials, such as MoS_2, by heating with CW lasers [6]. In addition, because the band gap and vibrational modes of TMD flakes depend strongly on thickness, Raman and PL spectral peak positions can monitor *in situ* the optical fingerprints of different layer numbers, promising on-demand fabrication of monolayer/multilayer 2D materials with any desired patterns for device applications.

Glossary

Domain rotation: a crystalline grain rotates on another crystalline grain or substrate.

Hyperthermal kinetic energy (KE) clusters: clusters of atoms with translational kinetic energies well in excess of k_bT (e.g., 1–100 eV/atom in PLD plasmas).

Laser crystallization: laser heating or photolysis to crystallize an amorphous precursor into a crystalline state.

Laser-induced structural phase transitions: a structural change of a material from one phase to another by laser irradiation.

Laser thinning: exfoliation of layered materials using laser heating, ablation, or etching.

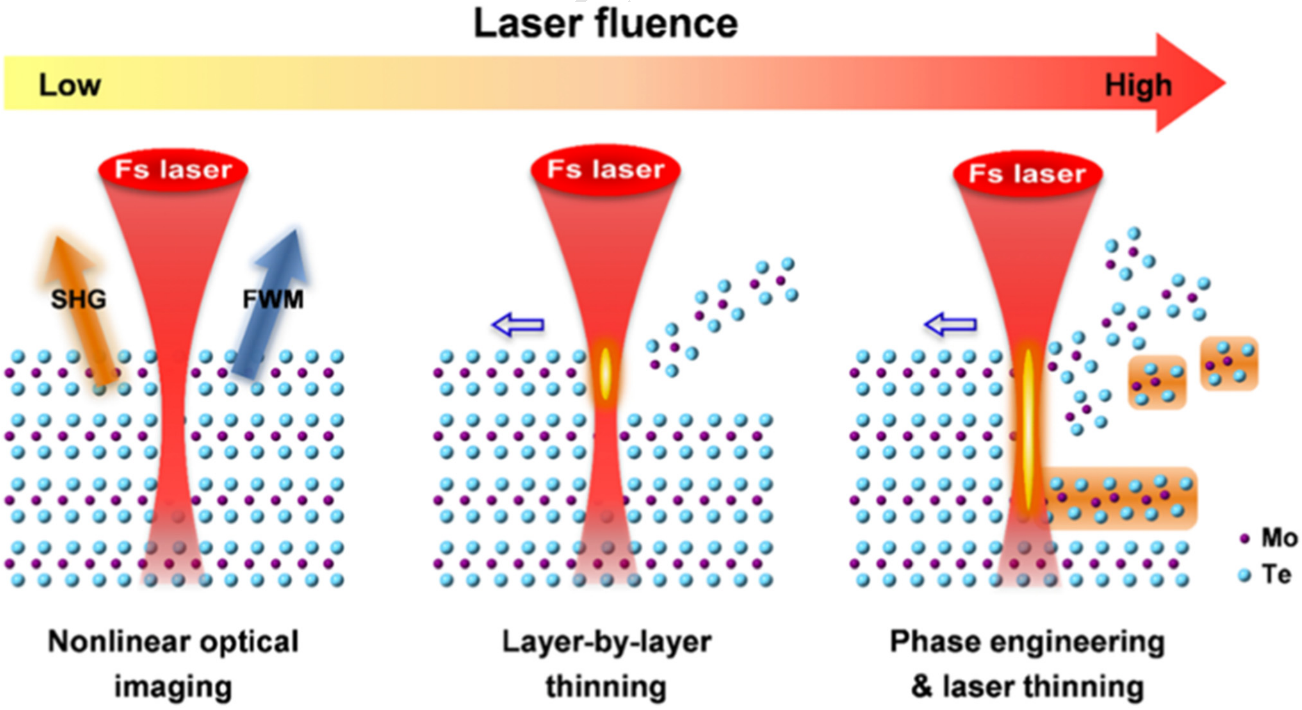
Van der Waals (vdW) crystals: strongly bonded 2D layers that are bound in the third dimension by weaker vdW forces between the layers.

Laser crystallization of predeposited amorphous precursors is another pathway to form 2D crystals. Liu and colleagues revealed within the transmission electron microscope (TEM) how ultrathin amorphous WSe_x precursors on suspended graphene and $MoSe_2$ substrates stepwise laser-crystallize into aligned vdW epitaxial heterostructures [7]. The *in* situ TEM studies revealed a surprising variety of nonclassical crystallization pathways by which nanoscale domains of the crystals assemble into large 2D WSe_2 flakes driven by interactions with the monolayer substrates, including directed diffusion, **domain rotation**, and grain boundary migration. These results are promising for laser direct writing/crystallization as a transformative approach for the rapid synthesis and processing of 2D materials.

Laser-induced structural phase transitions and metastable phases in 2D materials can be triggered by the highly nonequilibrium conditions of laser irradiation. Controlling how 2D layers stack with precise atomic configurations is crucial for a particular stoichiometry since each polymorph usually has distinctly different electronic and quantum properties. For instance, in few-layer $MoTe_2$, the atomic configuration of a semiconducting hexagonal 2H phase can be reorganized to a topological distorted octahedral 1T′ phase by CW-laser irradiation that creates Te vacancies [8]. This approach has been used to fabricate an ohmic heterophase homojunction by accurately controlling micron-scale patterning. Alternatively, the extremely high intensities of pulsed ultrafast lasers enable nonlinear optical processes and spectroscopic characterization, for layer-by-layer thinning, or inducing the 2H-to-1T′ phase transition in few-layer $MoTe_2$ crystals (Figure 1) [9]. Therefore, while mechanisms responsible for such nonequilibrium processes are still being revealed, it is clear that ultrafast laser processing holds promise to enable the simultaneous optical characterization, phase engineering, and nanomanufacturing of 2D TMDs for fabricating nanoelectronics devices.

Precisely controlling the growth and doping of 2D materials by laser synthesis

The nonequilibrium processing advantages of laser-based synthesis approaches, including pulsed laser deposition (PLD), are emerging for growth and layer-by-layer implantation of dopants. PLD provides a versatile approach to stoichiometrically laser vaporize and deposit prototype 2D materials from bulk targets to substrates with digital thickness control, substrate-scale uniformity, and with controllable KE [10]. Moreover, the 'building blocks' for growth can be tuned in PLD from atomic and molecular species to nanoparticles for the stoichiometric growth of crystalline 2D materials on substrates, as shown for GaSe nanosheets grown on insulating substrates with high spatial uniformity and thickness control [4]. This approach uses controlled spatial confinement and thermalization of the ablation products, adjusted with time-resolved imaging and plasma diagnostics of the fast-moving laser plasma, to form and deposit stoichiometric nanoparticle precursors of 2D materials with sufficient flux and KE to efficiently nucleate triangular ~20-nm domain GaSe nanosheets across the substrate that coalesced to form interconnected networks. Simple *in situ* laser reflectivity diagnostics can provide real-time control over the growth kinetics during PLD growth of 2D TMDs and achieve sub-monolayer thickness precision [11]. Alternatively, the same amorphous nanoparticle precursors laser-deposited onto room temperature substrates can be evaporated to grow large monolayer crystals onto a nearby substrate just microns away, as demonstrated for

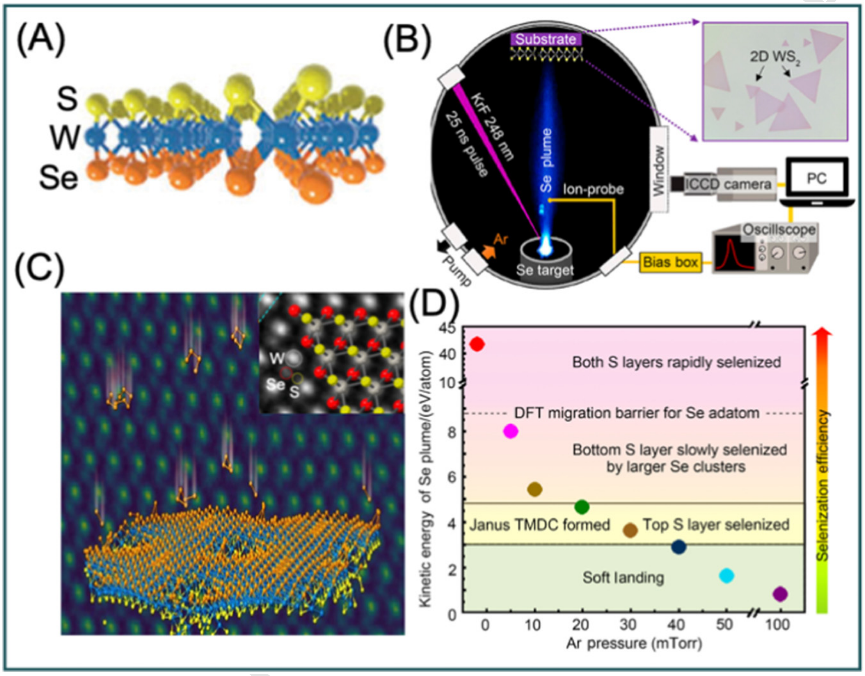


Trends in Chemistry

Q1 Figure 1. Schematic view showing different interactions between $MoTe_2$ layers and fs laser by varying the laser fluence. (A) Nonlinear optical characterization, (B) precise layer thinning with no phase change, and (C) phase engineering and laser thinning [9]. Abbreviations: FWM, four-wave mixing; SHG, second harmonic generation.

monolayer GaSe and $MoSe_2$ in a 'digital transfer growth' approach [12]. This versatile and digital technique allows lithographic prepatterning of the precursors and then transfer of this pattern via subsequent confined growth onto a substrate of choice. In addition, lasers can simply provide remote heating for evaporation to grow 2D materials with engineered defect densities. For example, by nonstoichiometrically evaporating TMD powders, single-crystalline, monolayer $MoSe_2$ can be grown with Se vacancy concentrations up to 20%, far beyond intrinsic values [13]. Interestingly, these Se vacancies can also be repaired reliably by a follow-on treatment supplying Se by PLD from a selenium target [13].

Laser-ablation plasmas provide a new opportunity for implanting dopants into atomically thin 2D materials and transforming them. The KE of species in typical PLD plumes is <100 eV/atom and this can easily be moderated by inert background gas collisions into the 1–10 eV/atom range necessary for interacting with monolayer TMDs, energies far below typical ion implantation techniques. As shown in Figure 2, by controlling the KE of Se species arriving to a WS_2 crystal using an Ar background and *in situ* plume diagnostics, a very narrow 3–5 eV/atom range allows Se to be selectively implanted into just the plasma-facing side of a WS_2 monolayer, forming Se-rich nanoscale domains and causing the ejection of sulfur dimers as the crystal recrystallizes. This selective hyperthermal implantation permits the low-temperature synthesis of novel Janus monolayers of WSSe with different chalcogens on either side [14]. More generally, the tunable KE/Se atom and digital nature of PLD enables precise layer-by-layer implantation to control the Se/S ratio in $WS_{2(1-x)}Se_{2x}$ alloys. With this technique, multiple lateral heterojunctions of MoS_2-$MoSe_2$ were formed by selectively converting $MoSe_2$ to MoS_2 in lithographically masked regions [15]. This technique presents a low-temperature, single-step processing route utilizing hyperthermal implantation for the synthesis of many predicted Janus monolayers and, more generally, new regimes to implant dopant atoms for the formation of 2D Janus materials and alloys using the wide variety of source atoms available by PLD with controlled KE in this virtually unexplored <20 eV range.



Trends in Chemistry

Figure 2. Controlled formation of Janus monolayers using hyperthermal implantation of species in pulsed laser deposition (PLD). (A) Schematic structure of Janus monolayer of WSSe. (B) Gated intensified charge-coupled device (ICCD) imaging and ion probe current measurements are used to record and adjust the kinetic energy (KE) and flux of species arriving at existing, freestanding 2D WS_2 crystals through the use of inert background gas (Ar) collisions that slow the species from 42 eV/Se atom to sub-eV. (C) Molecular dynamics (MD) simulations reveal how Se_2-Se_9 clusters in the plume implant in the suspended monolayer crystals. The background and inset show a tilted scanning transmission electron microscopy image for a WSSe Janus monolayer created at 4.5 eV/atom, confirming all the Se atoms are on 'top' and S atoms on the 'bottom' chalcogen layers. (D) Summary diagram of KE regimes for selenization of WS_2 monolayer by implantation using Se PLD showing KE effects. For lower KE's < 3 eV/atom, a nondamaging 'soft-landing' regime allows encapsulation of the WS_2 crystal in Se. This same approach of soft-landing transition metal dichalcogenide amorphous precursors on as-grown 2D layers, then followed by laser annealing, is promising to epitaxially grow van der Waals heterostructures. For higher KE's > 5 eV/Se atom the WS_2 crystal can be completely converted to WSe_2 [14].

Concluding remarks

Laser-induced nonequilibrium processes offer unique advantages to precisely deposit, thin, etch, dope, direct-write, and tune the phases of atomically thin 2D crystals. In each case, the digital delivery of energy and layered nature of vdW 2D crystals enables the development of selective processes. Indeed, the low-energy, yet hyperthermal kinetic energies inherent to typical PLD plasmas illustrated how precisely atoms can be implanted layer-by-layer in 2D TMDs to make metastable crystals such as Janus monolayers with novel functionalities, including charge separation, piezoelectricity, Rashba effects, and new quantum states. Laser spectroscopy during and after processing not only provides an essential characterization method to remotely understand the structure and properties of laser interactions of 2D materials, but it also provides the key *in situ* diagnostic to provide real-time feedback control to optimize laser processing approaches required for reliable manufacturing. This emerging evolution of combined laser synthesis, processing, and diagnostics promises not only approaches for the scalable synthesis of 2D materials with controlled heterogeneity, but transformational manufacturing approaches for laser-based direct write and additive manufacturing of atomically thin materials.

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Declaration of interests

No interests are declared.

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