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Paolo M. Ossi *Editor*

Advances in the Application of Lasers in Materials Science

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Preface

The influence of lasers in materials science continues to rapidly advance along with the progress in the development of laser sources. For example, ultrafast lasers once employed mainly in science for their ability to reveal the dynamics of excited atoms and molecules now have the average power and reliability needed for manufacturing, both additive and subtractive, from metals, to polymers, to biomaterials. From the exquisite control needed for laser surgery to the extreme power necessary for the laser propulsion of satellites to the outer reaches of the galaxy, understanding the interactions between laser radiation and matter is fundamentally central to emerging applications.

Laser interactions play a special role in materials science. Pulsed lasers effortlessly produce highly nonequilibrium conditions to synthesize new materials, permitting access to new states of matter that challenge our understanding based upon bulk phase diagrams. These states are transient, dynamically evolve, and are especially challenging to theoretically describe and computationally model. However, thanks to advances in the development of laser spectroscopic tools in materials science, we are gaining new insight at the necessary timescales in the form of time-resolved, in situ diagnostics provided by laser interactions with these excited states of matter. As new laser-based characterization techniques evolve, new understanding allows a more complete understanding of laser processes important to materials science.

With this perspective, this volume therefore presents a readable set of critical reviews meant to introduce both the fundamentals of laser–materials interactions and emerging applications of laser synthesis, processing, characterization, and modeling in materials science. Each chapter in the book was written by a lecturer at the 5th School on Lasers in Materials Science (SLIMS 2016) held July 10–17, 2016 at Venice International University. One of the goals of this biennial school is to provide Ph.D. students and young research scientists working in the field of laser–materials interactions with robust fundamental knowledge that is often lacking in their training, so that they may profitably interact with colleagues working in areas neighboring their own research fields. Although the laser community organizes several international conferences allowing focused exchange of information on similar topics, such a structured training opportunity that was specifically geared toward young researchers was lacking before the SLIMS series was established. The chapters reflect the content and didactic nature of the lectures as well as the spirited questions and ensuing discussions at the school. Active participation of the students and lecturers, sequestered together in the quiet and beautiful confines of San Servolo Island during the weeklong school, shaped the tone and scope of each chapter. Each chapter, written by an active researcher in their respective field, serves to provide both a didactic review of the relevant fundamental science and an overview of the emerging trends in applications and technology with current references. For similar reviews of emerging topic areas in the past few areas, the reader is strongly encouraged to refer also to two other volumes (Volumes 130 and 191) published in 2010 and 2014 by Springer in the same series that contain chapters originating from complementary sets of lectures from earlier schools.

The school directors are grateful to the lecturers for the attention they put in the preparation of truly didactic presentations at the school, for their valuable time spent at the school, and for the additional work spent writing comprehensive reviews of these topic areas into self-contained chapters designed for the general reader. The book is dedicated both to the pioneers in laser interactions in materials science, such as the late Roger Kelly (in honor of whom special student awards are presented at each school), but mainly to the new generation of students who are following in their footsteps.

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Chapter 1
Laser Synthesis, Processing, and Spectroscopy of Atomically-Thin Two Dimensional Materials

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Abstract Atomically-thin two-dimensional (2D) materials display widely varying electronic and vibronic properties compared to their bulk counterparts. Laser interactions with 2D materials are central to their development. Here we attempt to overview recent progress and define the current challenges in the broad range of laser interactions involved in the synthesis, processing, and optical characterization of 2D materials as the field has emerged from graphene and h-BN to encompass a multitude of other atomically-thin semiconducting, superconducting, thermoelectric, etc. 2D materials as "building blocks" for future energy applications and devices. Here, we first focus on challenges in the synthesis and processing of mainly semiconducting 2D layers for optoelectronics, and the advantages offered by non-equilibrium laser processing. Then, we review the optical characterization techniques that are being developed to serve as remote probes of their electronic and vibronic properties, as well as their structure, stacking, and atomistic alignment. Together, examples will be shown how these developments are already being merged to fulfill the promise for tailored synthesis and assembly of these exquisite materials with real-time in situ control of structure and optoelectronic properties.

1.1 Introduction

The discovery that the properties of layered materials such as graphite, boron nitride, and molybdenum disulfide can become radically altered when they are isolated in thicknesses of just one-, two-, or a few-layers [1] has generated an explosion of research over the past decade into atomically-thin two-dimensional (2D) materials. The revelation that certain transition metal chalcogenides (TMCs), (i.e., MX_2 where M is a metal, and X is a chalcogen) become direct band gap semiconductors when isolated as monolayers (e.g., ~1.9 eV for MoS_2) added the necessary "building blocks" of semiconductors to monolayered graphene (a pseudometal) and h-BN (an insulator) toward the fulfillment of a vision for stackable, flexible optoelectronics and other functional van der Waals (vdW) heterostructures [2, 3]. Figure 1.1 shows an example of such a vdW heterostructure combining two semiconducting TMC monolayers that self-align in reliable registry when GaSe (p-type) grows from the vapor phase on $MoSe_2$ (n-type) to form a photovoltaic p-n junction. Many other varieties of single-element (e.g., black phosphorus and silicene) and multi-element ultrathin layers (e.g., MXene) have been added to the growing list of atomically-thin building blocks that can be combined to form similar heterostructures [4–6].

Numerous excellent reviews of graphene [7] and materials 'beyond graphene' [8–10] including TMDs [11] have summarized their device [4] and broad energy applications [12] as well as challenges in their synthesis and preparation [13, 14],

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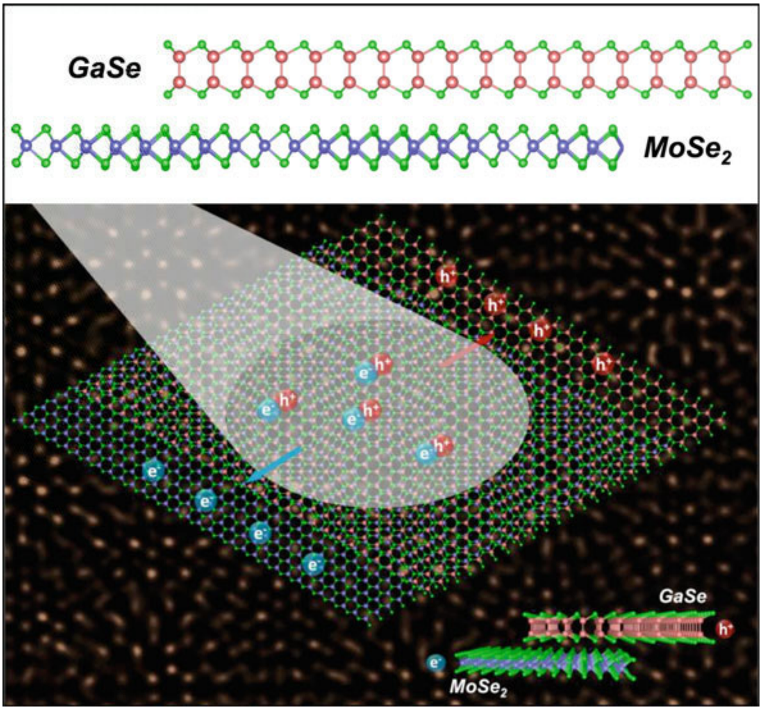

Fig. 1.1 Schematic showing two atomically-thin crystalline layers of GaSe and MoSe$_2$ that form a photovoltaic p-n junction, and exhibit photovoltaic behavior. The layers have different lattice constants but reliably align by van der Waals forces to form Moiré patterns when viewed by atomic-resolution Z-contrast scanning transmission electron microscopy (background) [38]

including their heterostructures and heterojunctions [15–18] and hybrids with other nanomaterials [19]. Bulk applications of TMC's for catalysis and composites are enabled by exfoliation techniques [20–22].

As for graphene (and single-wall carbon nanotubes), optical spectroscopy [23–25], including ultrafast dynamics [26] and Raman spectroscopy [27–32] has played a crucial role in revealing the electronic and vibronic properties of monolayers and stacked vdW heterostructures for refinement of theory and comparison with electronic transport measurements and photoresponse [33–38]. The TMCs are especially interesting because their optical properties are tunable with composition [39]. Optically-probing TMCs also reveals the strong role played by the substrate in determining their properties [40], and how strain can engineer their properties [41, 42].

Although 'top down' exfoliation of bulk crystals yields layers that are relatively free of defects, their lateral dimensions are typically smaller than those necessary for electronics. Reliable wafer-scale integration of these electronic materials requires 'bottom up' growth of atomically-thin layers of comparable quality to the 'top down' method, and as for graphene and h-BN such processes are currently an extremely active research area for the TMCs, other atomically-thin semiconductors, and topological insulators.

1.2 Key Challenges in the Synthesis of Atomically-Thin 2D Materials with Controllable Functionality

Understanding and controlling the growth of atomically-thin 2D materials with desired functional properties is hindered by the same fundamental gaps in synthesis science that crosscut many materials systems [43]. As outlined in a recent report by the U.S. Dept. of Energy on *Basic Research Needs for Synthesis Science*, tailoring the design and synthesis of materials for a desired functionality will require a new effort to "*Integrate emerging theoretical, computational, and* in situ *characterization tools to achieve directed synthesis with real-time adaptive control*" [43]. Nanomaterials with sensitive optoelectronic properties offer a golden opportunity for in situ optical characterization of both their structure and properties, both during and after synthesis. Such has been the case with single wall carbon nanotubes (SWCNT), where optical diagnostics coupled with atomic-resolution electron microscopy and predictive theory have stimulated world experts converge every 2 years to compare advances in characterization techniques, in situ diagnostics experiments, and modeling in order to redefine and publish a "top ten" list of remaining SWCNT synthesis science questions [44]. Atomically-thin 2D materials provide an even richer platform for directed synthesis of materials with designed functionality, and similar fundamental questions currently confront this challenge. Here we define a draft "top ten" list of crucial questions central to 2D materials synthesis.

A 'top ten' list of outstanding synthesis questions for 2D materials

1. What are the *chemical species and kinetic pathways* responsible for nucleation and for growth?
2. Is *nucleation* homogeneous or heterogeneous, and can it be suppressed to enable the growth of large single crystals?
3. What controls the *growth kinetics and shape* of the crystals during growth?
4. Why do *defects* form and how do they evolve during growth?
5. What is the role of *substrate interaction* (including van der Waals forces, covalent bonding, and hybrid orbital interactions determined by its crystallinity) in determining the shape, kinetics, defects, and termination of 2D crystals as they grow?
6. How does *strain* induced by the substrate or other crystalline layers influence growth?
7. Can *second layer* nucleation, growth, and orientation be understood to control size, stacking angle, and registry?
8. What are the roles of *dopants, 'catalysts', and adsorbates* in nucleation, growth, and crystalline perfection of 2D crystals? How do they affect defect formation?

9. What are the *collective effects* determining the growth of crystal ensembles and continuous layers (considering Ostwald versus Smoluchowski ripening)?
10. Which *growth method* (e.g., CVD, PLD, MOCVD, PECVD, MBE) is the most suitable to achieve directed synthesis of functional properties (e.g., electronic mobility, photoresponsivity, catalytic activity, etc.) consistent with practical issues of speed and scalability?

As implied by question 10, the most important practical challenge necessary to drive the field is an important question (#11) "*What is the "killer application" that will drive the development of 2D materials synthetic techniques"*? Currently, there are two main drivers and needs in 2D materials synthesis: (1) **Scalable synthesis** of wafer-scale 2D crystals with large-domain sizes for high electron mobility materials useful for electronics, or of loose 2D materials for bulk applications (e.g., for catalysis, batteries, composites), and (2) Control over heterogeneity in the crystals, meaning point defects and unwanted substitutional dopants, grain boundaries, and control over the number of layers and their orientation/stacking. The "top 10" questions above clearly focus on the fundamental problems in these two areas.

Laser interactions during and after synthesis of 2D materials provide the keys to answer these questions. Laser interactions can alter the synthesis of the crystals during their growth by providing well-defined bursts of energy to identify and control kinetic processes and control chemical species. Similarly, controllable laser processing treatments can modify the properties of existing crystals to alter the phase, composition, crystallinity, defect levels, and layer number. In addition to their use in synthesis and processing, laser interactions play an equal or larger role in the remote probing of 2D crystals through laser spectroscopy. Laser spectroscopy probes the most fundamental properties of atomically-thin 2D layers to remotely check theoretical predictions of their electronic band gap and band structure, vibrational modes, defects, and excited state dynamics. Practically, it can identify 2D materials, their number of layers, how they are stacked, and their quality as inferred from their Raman spectra, photoluminescence, and absorbance. When laser interactions are combined both in synthesis and processing, and as spectroscopic probes, they offer the capability to serve as in situ controls of the synthesis process.

This chapter will attempt to briefly review some of the laser synthesis and processing techniques that are rapidly evolving as non-equilibrium methods to explore these most exquisitely-thin films. It will also endeavor to summarize some of the most useful laser spectroscopy techniques. Along the way, examples of the applications of laser spectroscopy as in situ diagnostics of the growth environment and growing 2D crystals will be highlighted to illustrate the importance of laser interactions as real time probes to understand the essential links between synthesis, structure, and properties. This chapter cannot serve as a comprehensive review of atomically-thin 2D materials and their bright future for applications, for that the reader is referred to the excellent recent reviews referenced above. Instead it will attempt to review a few examples that illustrate the wide range of laser interactions in the synthesis, processing, and diagnostics of atomically-thin 2D materials that are key to developing and understanding these unique materials.

1.3 Laser-Based Synthesis and Processing of 2D Materials

1.3.1 Pulsed Laser Deposition of 2D Materials

Pulsed laser deposition (PLD) has been used for many years to explore the synthesis of thin films, offering the advantages of the transfer of stoichiometry from targets with complex compositions, epitaxial growth of films and superlattices with unit cell thickness control, suprathermal kinetic energy of plume species that allows the formation of metastable phases, and digital delivery of reactants. PLD would appear well suited to the synthesis of atomically-thin layers of two-dimensional crystals, however the high instantaneous fluxes that are typical for the process tend to result in high nucleation densities, resulting in the formation of networks of nanoscale domains. Instead, current research in the exploration of 2D materials has focused on techniques capable of growing single crystals of 2D materials with lateral dimensions >10 microns that are sufficient for the measurement of electronic transport (with lithographically-patterned contacts), optical measurements using micron-sized spot sizes in an optical microscope, and removal of the crystals to TEM grids or polymer stamps for alignment with other crystals. The growth of these single crystals is typically approached with continuous vapor transport techniques in order to slowly grow single crystals layer-by-layer from their edges in the manner that graphene crystals were grown to millimeter dimensions, using boats of precursor powders within a tube furnace, with molecular beam epitaxy, or by metal organic vapor deposition. Nevertheless, the commercialization of PLD systems in the past two decades has addressed some of the key objections to the technique for the synthesis of electronics-grade materials, including the ejection of particulates from the target, non-uniformity of the deposit, and lack of online process control. In addition, PLD does not introduce other reactants, or involve hazardous gases that are often associated with techniques such as MOCVD. In all of these techniques, the film stoichiometry is typically adjusted to compensate for the loss of more volatile elements during deposition, for example the loss of the chalcogen atoms in the family of 2D metal dichalcogenides.

Recently, a number of groups have explored the digital control of PLD to grow stoichiometric, atomically-thin 2D films of TMDs for optoelectronic applications, especially MoS_2. This builds from early work that demonstrated the viability of PLD for the stoichiometric deposition of MoS_2, which was first reported for tribological applications as early as 1988 using ns-pulse 532 nm lasers (~1 J/cm^2) in vacuum [45–47]. Today, very similar recipes have emerged for the PLD of stoichiometric MoS_2 with controllable number (1–10) of layers using ns-pulse 248-nm ablation (1–3 J/cm^2) of typically sulfur-rich [e.g., Mo:S (1:4)] mixed powder targets onto a variety of substrates (including typically (0001) Al_2O_3) at 700–850 °C in vacuum [48–53]. In these experiments, the base background pressure ($<1 \times 10^{-6}$ Torr) may rise to 0.1 mTorr during ablation, and films can be either cooled directly, or post-annealed in a sulfur atmosphere in order to repair sulfur vacancies and increase crystallinity [48]. Similar approaches have been developed for other 2D TMDs, such as WTe_2 [54]. The mobilities and small grain sizes of within the films (e.g., ~20 nm for MoS_2 [49], 20–50 nm for GaSe [55, 56]) need to be improved for electronic applications, yet are comparable to those grown by CVD. Therefore, PLD appears to be a promising method to digitally control the thickness of 2D TMDs over large areas with surprising reliability in stoichiometry. PLD has the additional advantage of reactive species in the ablation plasma that, in addition, have high kinetic energy capable of penetrating several centimeters through background gases at pressures up to 0.2 Torr. By varying the background gas pressure and target-substrate distance, the kinetic energy of the species arriving at the substrate can be adjusted, as well as the type of species, ranging from fast ions, to slower atoms and molecules, to clusters and nanoparticles. As shown in Fig. 1.2a, gated intensified CCD-array photographs or ion-probe current waveforms can be used to adjust the progression of the plasma plume in order to produce pure nanoparticle "building blocks" if desired, rather than atomic or molecular species, that can crystallize into different morphologies by the process of crystallization by particle attachment [57]. Such an approach was utilized to deposit amorphous GaSe nanoparticles at room temperature (Fig. 1.2b) that crystallized into highly photoresponsive 2D nanosheets in either lateral (at 600 °C, Fig. 1.2c) or vertical (at 550 °C, Fig. 1.2d) geometries, depending on deposition rate and temperature. These amorphous nanoparticles are formed by condensation during the thermalization of the gas-phase plume of reactants, and with proper tuning of the conditions have sufficient kinetic energy to impact the substrate to deposit at room temperature into nanoparticle aggregates, or crystallize at higher temperatures into different nanostructures [57]. These stoichiometric nanoparticles, deposited at room temperature, can be digitally delivered as precursors for the growth of very large monolayers, bilayers, and few-layers of 2D TMDs by post annealing within confined geometry between two substrates in "digital transfer growth", as shown in Figs. 1.2e–h [58]. Therefore, PLD has the potential to grow large 2D TMD crystals through the appropriate choice of deposition conditions.

1.3.2 *Laser Techniques for "Top-Down" and "Bottom Up" Defect Engineering of 2D Crystals*

The kinetic energy of plume atoms and ions in PLD is an advantage that can be used to controllably induce structural defects and compositional changes in the top-down processing of 2D crystals. Recently, pulses of KrF-laser irradiation vaporized a sulfur target in vacuum to deliver precise quantities of suprathermal sulfur atoms and molecules to $MoSe_2$ single crystals in vacuum at 700 °C in order to replace Se atoms to form $MoSe_{1-x}S_x$ alloys as shown in Fig. 1.3a. Photoluminescence and Raman spectra of the alloy crystals revealed a smooth transition in the photoluminescence peak wavelength and a corresponding change in the Raman spectra, confirming a smooth conversion from $MoSe_2$ to MoS_2 after 400 pulses. The technique was used in conjunction with lithographic patterning of SiO_2 protective ad-layers as shown in Fig. 1.3b to form the first patterned arrays of lateral semiconductor heterojunctions

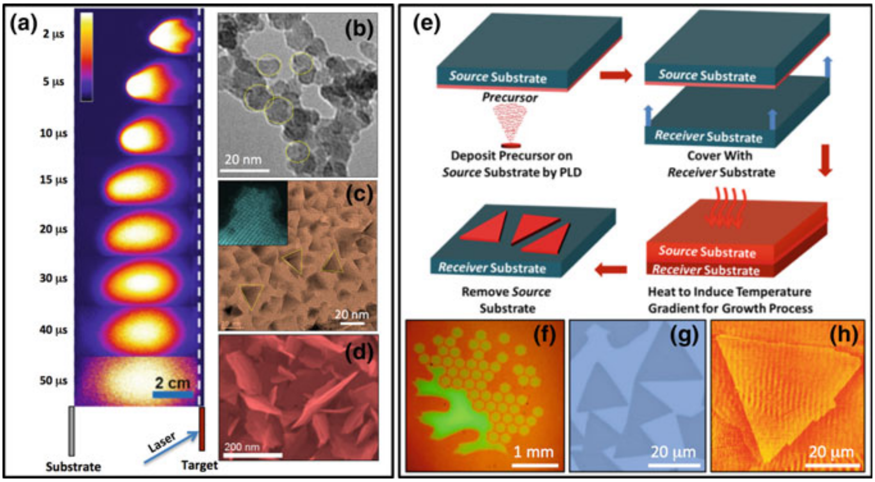

Fig. 1.2 Pulsed laser deposition of two-dimensional materials and digital transfer growth. **a** Gated ICCD-photography and other plasma diagnostics were adjusted [57] to deposit **b** primarily stoichiometric nanoparticles of GaSe and MoSe$_2$ at room temperature. Deposition at high temperatures and different repetition rates results in direct formation of either **c** small ~20 nm-grain, triangular, multilayered nanosheet networks at 600 °C or **d** vertically-standing nanoflakes at 550 °C. [56] These same amorphous nanoparticles can be **e** deposited onto *source* substrates at room temperature, then annealed between two substrates to grow large nanocrystals in confined spaces on a *receiver* substrate. The crystals grow directly opposite the regions where they are deposited, allowing **f** complex patterns of **g** large (20–100 µm) triangular crystals to grow as monolayer domains or **h** multilayers, depending on the amount of nanoparticle feedstock that was laser-deposited [58]

within monolayer 2D semiconductors—an essential step for the lateral integration of 2D semiconductor building blocks with different electronic and optoelectronic properties for high-density, ultrathin devices [59]. Laser plumes therefore can serve as sources of fast ions and neutrals to introduce defects and substitutional dopants in a top-down approach.

Alternatively, laser-vaporization can be used to controllably introduce defects from the 'bottom-up' during synthesis. A novel CO$_2$ laser-heater source was used to intentionally evaporate MoSe$_2$ powder non-stoichiometrically in order to grow single crystals of monolayer MoSe$_{2\text{-x}}$ on a substrate with tunable levels of Se vacancies up to very high levels (up to 20%) [60]. These highly-non-stoichiometric single crystals exhibited a remarkable transition in electrical transport properties from n-type to p-type character with increasing vacancy concentration. The vibrational modes of the crystal were also altered, and Raman spectroscopy of the crystals revealed the emergence of a new phonon mode, which was confirmed by theory and could then be used as a fingerprint of vacancy concentration in the crystals. Interestingly, laser evaporation of a selenium target could be used to repair the Se-vacancy sites introduced during synthesis to nearly recover the properties of pristine MoSe$_2$ crystals. Thus, laser vaporized fluxes can be used in both top-down and bottom-up synthesis

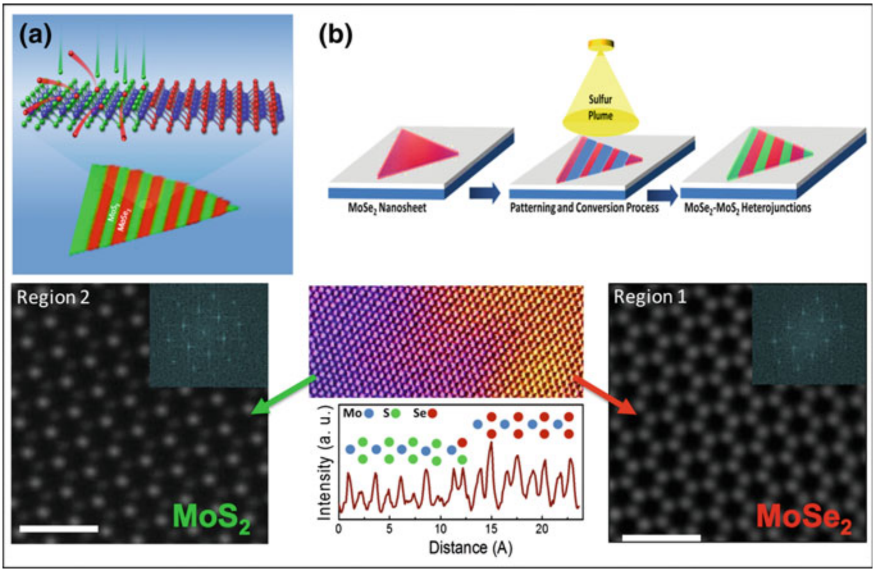

Fig. 1.3 Pulsed laser conversion of two-dimensional materials and the formation of multiple lateral semiconductor heterojunctions. **a** Energetic atoms of sulfur (green) replace selenium atoms (red) in a triangular single crystal of $MoSe_2$. After conversion, a map of the Raman spectrum reveals the regions of the crystal corresponding to MoS_2 and $MoSe_2$. **b** Schematic of the conversion process, starting with a triangular $MoSe_2$ single crystal monolayer domain. Laser ablation of a sulfur target produces energetic S atoms. Electron-beam lithography patterning/deposition of a protective SiO_2 layer (blue) shields regions of the $MoSe_2$ crystal. After 400 pulses at 700 °C, the stepwise conversion of $MoSe_2$ to MoS_2 is complete. The lower panels show atomic-resolution HAADF-STEM contrast images that confirm the transformation of the crystalline monolayer and the formation of lateral semiconductor heterojunctions within a single step induced by the energetic laser-generated plume of S atoms [59]

and processing strategies to digitally control the heterogeneity and properties of 2D crystals.

1.3.3 Substrateless Growth of 2D Materials by Laser Vaporization

The nonequilibrium conditions of laser ablation plasmas provide a versatile synthetic method to explore the condensation of novel clusters and nanoparticles, such as carbon fullerenes (e.g., C_{60}, C_{84}, etc.). Given sufficient time, temperature, and spatial confinement, larger nanostructures such as single wall carbon nanohorns (SWCNHs) can self-assemble in the laser plasma. Time-resolved growth experiments using pulsed laser plasmas have shown that these pure carbon SWCNH nanostructures grow at nm/ms rates (equivalent to microns per second) [61], which are as fast as the high growth rates measured for the catalyst-assisted synthesis of single-wall carbon nanotubes (SWCNTs), either in similar substrateless plasma conditions, or by CVD on substrates [62]. This synthesis process has been reviewed before [63, 64].

Recently, with the addition of either boron or hydrogen to the reaction environment, the assembly of carbon nanohorns was observed to shift from SWCNHs (in pure argon, Fig. 1.4a) to few-layer graphene-like flakes (GLFs) and thicker polyhedral graphene platelets (PGPs) as pictured in Fig. 1.4b–d [65, 66]. In this way, planar 2D materials can be synthesized in large quantities in the gas phase, without interacting with a substrate during growth and without the complication of removal from the substrate after synthesis. While boron is a well-known graphitization agent during carbonization treatments [67], its similar role to hydrogen in the stabilization of the planar GLFs in these studies is unclear, yet is thought to be related to the fact that boron remains loaded within the flakes (but not the SWCNHs) at 2–4% levels [65]. Interestingly, the boron-loaded graphene layers are not stacked as in graphite, but are arranged turbostratically at small angles with the adjoining layers, as revealed by selected area electron diffraction and Moiré fringes in STEM images (Fig. 1.4d) [65]. Note that similar graphene sheets can be grown without substrates in other types of plasmas at atmospheric pressure, such as arc plasmas [68] or microwave plasmas [69]. More generally, other 2D materials such as the transition metal dichalcogenides have been grown cleanly in microwave plasmas from just the base metals and chalcogens powders, without solvents, proving the generality of the technique [70]. Such so-called ‘high temperature’ synthesis routes that employ plasma torches or high-power lasers have been successfully developed to scale the production of SWCNTs and boron nitride nanotubes (BNNTs) [71–73] to tens of grams per hour in continuous flow reactors at high rates. So, as in the exploration of novel thin films by PLD, laser vaporization plasmas are well suited to explore the synthesis of pure and doped layered 2D materials that self assemble into flakes in the vapor phase.

1.3.4 Laser Thinning of Layered Two-Dimensional Materials

Control over layer number is often difficult to achieve during synthesis, so laser processing is currently being explored to selectively remove layers of 2D materials by laser thinning. Theoretically, Tomanek predicted that pristine monolayer graphene could be photoexfoliated intact from bulk graphite through the use of ultrafast (45 fs) laser pulses to rapidly produce an expanded electron gas capable of causing ejection of polarized layers by Coulomb ejection before the electron thermalization time [74].

Experimentally, however, success in laser thinning of few-layer crystals has relied upon selective ablation or etching of the topmost layers. Dhar, et al., showed that the ablation threshold of the topmost layers of few-layer graphene rises sharply as the number of layers is decreased, allowing processing windows to selectively leave a desired number of layers intact on a substrate. They proposed that the steep dependence of the threshold ablation energy arises from a dimensional crossover of the specific heat of a layered material for layers $N < 7$, where flexural modes

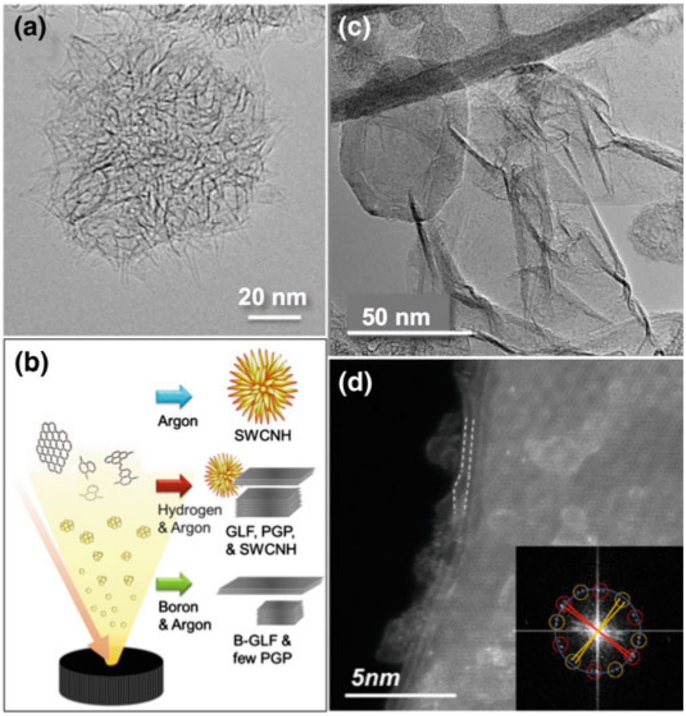

Fig. 1.4 Large volume laser vaporization synthesis of 2D materials: B-doped graphene. **a** Single-wall carbon nanohorn (SWCNH) aggregate produced by high-power laser vaporization of pure carbon in argon. **b** Schematic showing the shift in product distribution as hydrogen or boron is added to the growth environment, either in the gas phase (5% H_2 in Ar mix) or in the target (5% B in C). Ablating carbon into 5%H_2/Ar at 760 Torr shifts the product distribution to predominantly polyhedral graphite platelets (PGP) and graphene like flakes (GLF) as pictured in the TEM image of **c**. Boron is even more effective at shifting the products to few-layer GLF which incorporate boron at levels of 2–4 at.% and are turbostratically rotated as indicated by the Moiré patterns in atomic-resolution HAADF-STEM images shown in **d**

in thin-layered materials overwhelm bulk acoustic modes, leading to flaking of the topmost layers—a process that should occur in other layered materials with weak interlayer coupling [75]. Recently, similar layer-by-layer exfoliation of graphene has been achieved in air using picosecond laser thinning in a scanning fashion, as indicated in Fig. 1.5, where each 30 μm laser spot receives ~600 picosecond pulses at 2 MHz repetition rate [76]. However, even continuous wave sources such as those found within commercial micro-Raman spectroscopy apparatus can achieve selective layer-by-layer thinning as shown by Castellanos-Gomez, et al., for MoS_2 in air [77]. The ability to utilize the unique Raman spectroscopy signatures of the different layers in situ is an enabling diagnostic in these studies to assess the layer number, quality, and defects as outlined below.