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Topical Review

Laser synthesis and functionalization of nanostructures

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Abstract

This article summarizes work at the Laser Thermal Laboratory and discusses related studies on the laser synthesis and functionalization of semiconductor nanostructures and two-dimensional (2D) semiconductor materials. Research has been carried out on the laser-induced crystallization of thin films and nanostructures. The *in situ* transmission electron microscopy (TEM) monitoring of the crystallization of amorphous precursors in nanodomains is discussed herein. The directed assembly of silicon nanoparticles and the modulation of their optical properties by phase switching is presented. The vapor–liquid–solid mechanism has been adopted as a bottom-up approach in the synthesis of semiconducting nanowires (NWs). In contrast to furnace heating methods, laser irradiation offers high spatial selectivity and precise control of the heating mechanism in the time domain. These attributes enabled the investigation of NW nucleation and the early stage of nanostructure growth. Site- and shape-selective, on-demand direct integration of oriented NWs was accomplished. Growth of discrete silicon NWs with nanoscale location selectivity by employing near-field laser illumination is also reported herein. Tuning the properties of 2D transition metal dichalcogenides (TMDCs) by modulating the free carrier type, density, and composition can offer an exciting new pathway to various practical nanoscale electronics. *In situ* Raman probing of laser-induced processing of TMDC flakes was conducted in a TEM instrument.

Keywords: laser nanofabrication, laser crystallization, nanowire growth, near field scanning optical microscopy, transition metal dichalcogenides

(Some figures may appear in colour only in the online journal)

1. Nanoscale melting and crystallization

1.1. *In situ* observation experiments

Laser-based processing enables a wide variety of device configurations comprised of thin films and nanostructures on sensitive and even flexible substrates which are not possible with traditional thermal annealing schemes [1]. The

crystallization of amorphous thin films is a critical fabrication step for enhancing the performance of thin-film transistors [2, 3] and thin-film solar cell devices [4]. Typical thin-film materials offer cost-effective device fabrication routes but intrinsically suffer from a low degree of crystallinity and hence require improvements by subsequent thermal annealing. Using a furnace to increase crystallinity not only requires a large thermal budget but also limits the adoption of inexpensive substrates, such as pyrex, soda-lime glass, or polymer substrates [5]. Annealing by pulsed lasers can significantly mitigate these issues by taking advantage of precisely localized heating [6]. Laser-induced crystallization is a promising



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Figure 4. (a) Schematics of the LIMA nanoparticle assembly process flow and SEM images of assembled nanoparticle arrays. (b) LiMA results using different laser processing parameters. (c) LiPS of Si nanoparticle crystallinity and its effect on color appearance. A second pulse changed the color of a preassembled nanoparticle canvas through from ‘green’ to ‘red’ through amorphization of crystalline Si. The scale bars are 300 nm for (a) (iii)–(iv) and (b) (iv)–(iv) and 5 μm for (c) (ii). Reprinted with permission from [58]. Copyright (2018) American Chemical Society.

application of Fano resonance [60, 61] and spectroscopy [62]. In a broader context, the concept of Si as ‘phase change’ material may find applications in storage and reconfigurable metasurfaces.

2. Directed laser nanomaterial growth

2.1. Laser-aided vapor–liquid–solid (VLS) nanowire (NW) growth

Nanoscale-synthesized materials are the key to building future generation devices in diverse fields, including NW-based applications in energy conversion [63, 64], energy storage [65, 66], optoelectronics [67, 68], and biotechnology [69, 70]. To realize this promise, new techniques must be developed to enable the precise layout and assembly of heterogeneous components into functional ‘superblocks.’ Even though a high level of compositional and orientational control in NW growth has been achieved, the post-synthesis assembly steps, even by state-of-the-art optical or optoelectronic tweezing [71, 72], are not sufficient to allow high spatial and directional precision. As a route towards this goal, several studies have attempted site-selective growth of NWs [73, 74] or nanotubes [75, 76] by local laser illumination. Laser-assisted NW (nanotube) growth broadly falls into the category of laser CVD which has been actively explored for a few decades [77] as a versatile materials synthesis technique enabling the

formation of microstructures of well-defined dimensions in a single-step maskless process [78].

The VLS crystal growth approach is utilized for the fabrication of high aspect ratio nanoscale semiconductor materials. In the VLS mechanism, the gold (Au) catalyst forms a liquid alloy with Si that preferentially adsorbs onto the catalyst surface at the eutectic temperature of 363 °C or higher and then diffuses into the Au–Si liquid alloy droplet. After reaching the solubility limit at the liquid–solid interface, Si precipitates inducing NW growth. Actual growth begins after an elapsed time, typically called the *nucleation time* (or *incubation time*). The shortest nucleation time reported was in the range of 15 s at 650 °C growth temperature (for an ~ 30 nm diameter Au catalyst) and extended to ~ 180 s at 450 °C [79]. Considering that the possible contributing factors to this elapsed time are reaction and diffusion, mediated by phase change of the silicon species through molten catalyst of only tens of nm in diameter, these times appear to be too long.

The laser-assisted growth mechanism of silicon nanowires (SiNWs) has been investigated via the heating of deposited catalysts [80]. Figure 5 shows vertical growth of SiNWs on a homoepitaxial c-Si film. The heterogeneity in length that is controlled by the laser duration is notable. Conductive heat transfer analysis shows that the induced, nearly steady, temperature in the time regime of seconds exhibits a linear relationship with respect to the laser power applied. The NW growth follows typical Arrhenius behavior with an activation energy of ~ 66.8 (kcal mol⁻¹). Laser-assisted multielement

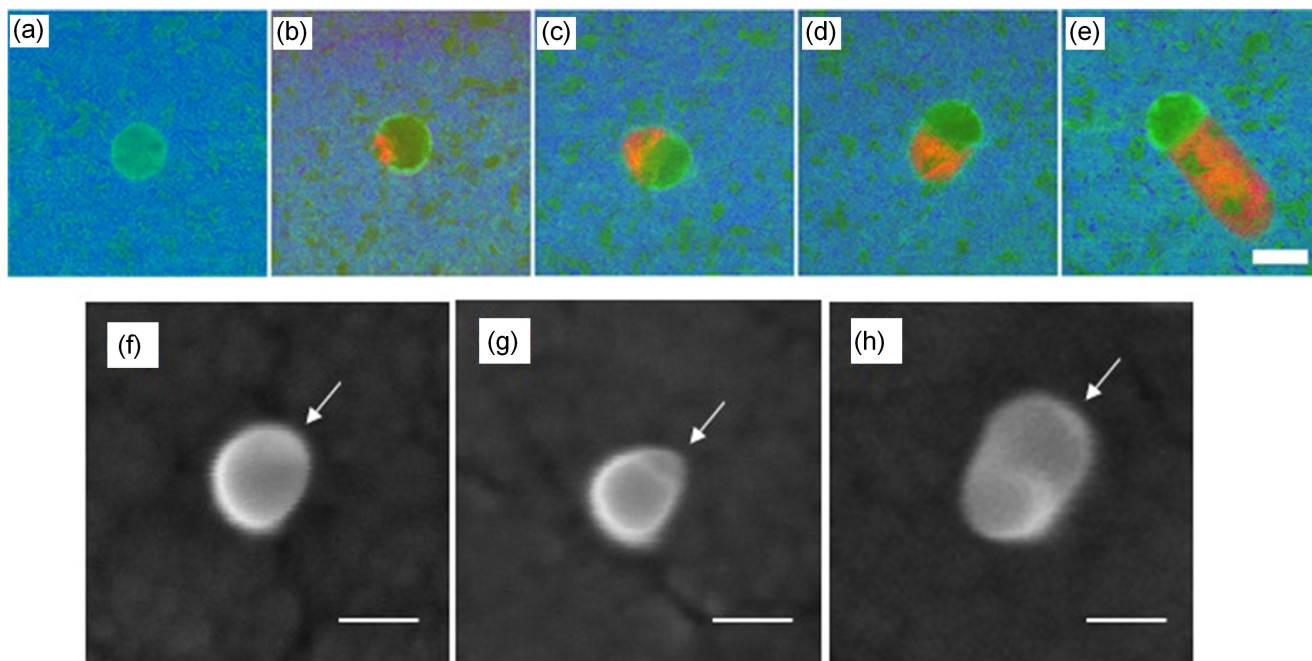


Figure 6. (a)–(e) Composite chemical maps for various growth times: (a) just prior to nucleation at 8 ms, (b) just after nucleation at 10 ms, (c) 40, (d) 80, and (e) 400 for 50 nm AuNP catalysts. Laser power was fixed at 7.5 mW (calibrated growth temperature of 918 K) and a partial pressure of SiH_4 maintained at 6 Torr with a flow rate of 600 sccm. The scale bar is 50 nm. (f)–(h) SEM images showing early stage growth behavior of SiNW: (f) just after nucleation at 10 ms, (g) 20 ms, and (h) 100 ms for 50 nm AuNP catalysts. The laser power was fixed at 7.5 mW (calibrated growth temperature of 918 K) and a partial pressure of SiH_4 maintained at 6 Torr. The scale bar is 50 nm. Reprinted from [83], with the permission of AIP Publishing.

on a single selected Au nanocatalyst in order to initiate nucleation and then drive the subsequent SiNW growth, as shown in figure 8(a). Figure 8(b) shows a scanning electron microscope image of discrete SiNWs selectively grown among randomly distributed Au nanocatalysts while the neighboring catalysts remained intact. Far-field indirect illumination was first provided onto the film, inducing no evident reaction within the heat-affected zone. Following a temporal delay, near-field direct illumination was superimposed onto the far-field radiation providing the impetus for the nanowire growth. The near-field illumination can induce an extra temperature increase in a AuNP at the very early growth stage when the AuNP is still under direct near-field illumination. The directionality of the NW could be improved by placing an electrically biased AFM tip over the catalyst during the laser-induced growth process [86].

3. Laser processing of atomic layered films

3.1. Localized doping

Two-dimensional (2D) transition metal dichalcogenide (TMDC) semiconductors with the general chemical formula of MX_2 ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}, \text{Te}$) have attracted much interest due to their finite direct band gaps, rich excitonic dynamics, and valley polarization (valleytronics) associated with the broken inversion symmetry. These layered semiconductors, composed of vertically stacked layers held together by van der Waals interactions, are emerging as

alternatives to Si-based electronics. The TMDC devices exhibit exceptional characteristics that are particularly suitable for next generation optoelectronic and electronic device applications [87–89]. They are excellent candidate materials for transistors [90–92], photodetectors [93, 94], electroluminescent devices [95], and sensors [96]. Despite the potential in electronics and optoelectronics, reliable and stable processing methods are needed for transition to practical applications [97]. More specifically, controlled doping of semiconductors is vital for integration into devices. However, previous efforts have mostly focused on doping TMDCs by means of charge transfer from adsorbed molecules [98], electrostatic [99] or physisorption gating [100], defect engineering [101], and substitutional doping during growth [102]. Site-specific doping with precise doping level control becomes essential, especially for nanoscale devices using ultrathin TMDCs in order to minimize random dopant fluctuation and ensure device performance reproducibility. A versatile method was reported for widely tunable, site-specific doping of ultrathin TMDCs (molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2)) through focused laser irradiation in a phosphine environment [103]. A schematic diagram of the laser-assisted doping process is shown in figure 9(a).

The laser serves two major functions: (i) creation of chalcogen vacancies in the TMDC materials and (ii) simultaneous dissociation of the dopant molecules. The released dopant molecules were incorporated into the vacancy sites. The phosphine (PH_3) doping of Si has been extensively studied, both experimentally and through theoretical modeling

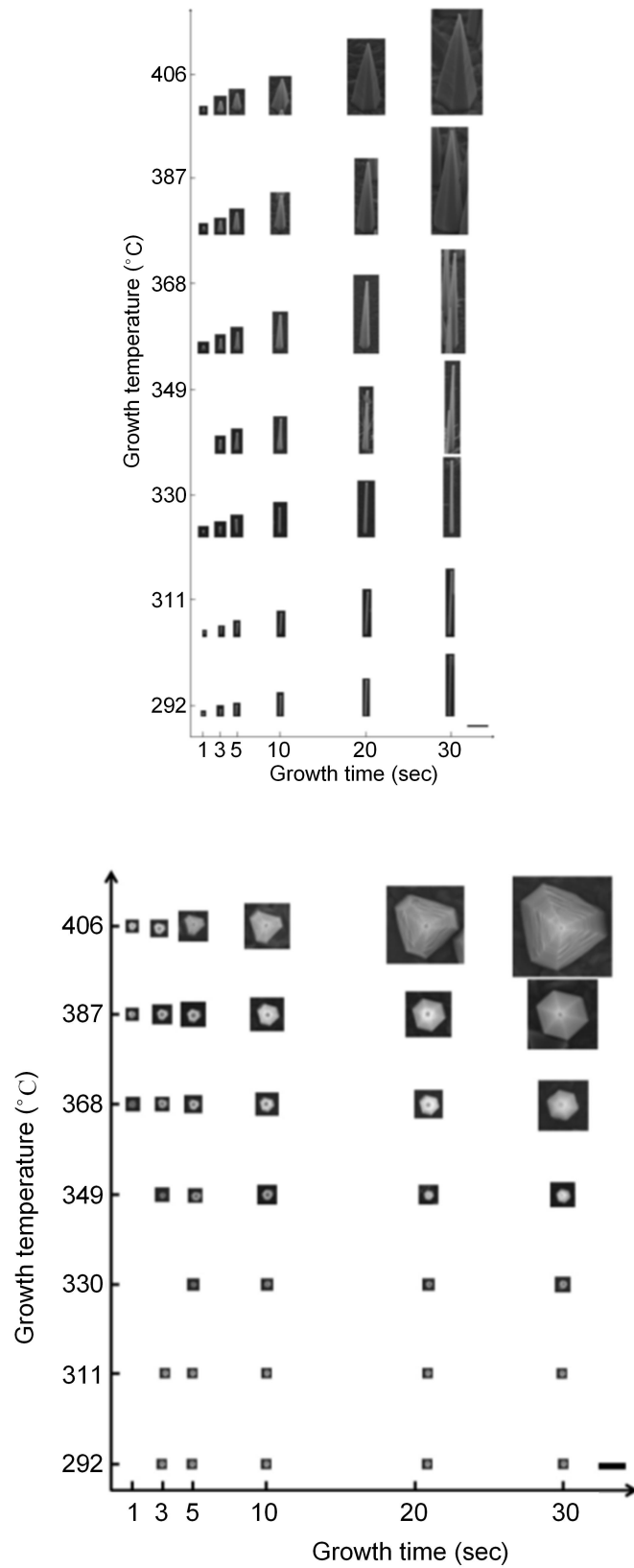


Figure 7. (Top) Field-emission scanning electron microscopy (FE-SEM) images at a 45° tilted angle of vertically grown GeNWs on Si(111). All NWs were grown on a single 4 μm thick c-Si bonded on quartz. The growth temperature ranged from 292 °C to 406 °C and the growth time from 1 to 20 s. The scale bar is 500 nm. (Bottom) Planar view images of vertically grown GeNWs on Si(111). The growth temperature ranged from 311 °C to 406 °C and the growth time from 1 to 30 s. The scale bar is 50 nm. Reprinted with permission from [84]. Copyright (2013) American Chemical Society.

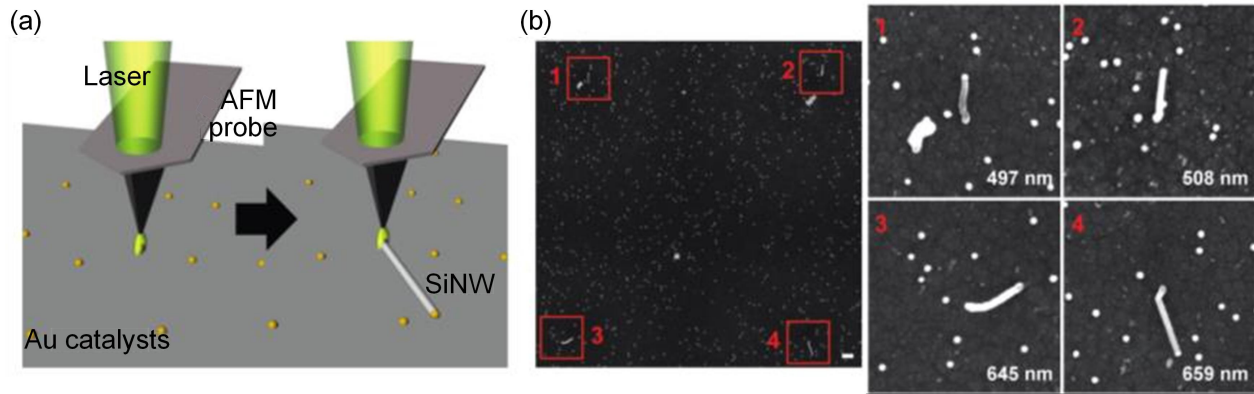


Figure 8. Highly selective growth of single SiNWs by near-field direct illumination over the AuNP, aided by supportive film heating by far-field indirect illumination. (a) Single catalysts were selected from randomly distributed AuNPs via the AFM mapping process for growth into a SiNW. Length control was implemented by adjusting the near-field laser irradiation power. (b) Each of two single NWs on top (1), (2) and at bottom (3), (4) were individually grown with 1.5 and 2.0 mW in laser input power for 5 s, respectively. The corresponding axial lengths were 503 (1), (2) and 652 nm (3), (4) on average. The scale bar is 500 nm. Reproduced from [85] (2014). With permission of Springer.

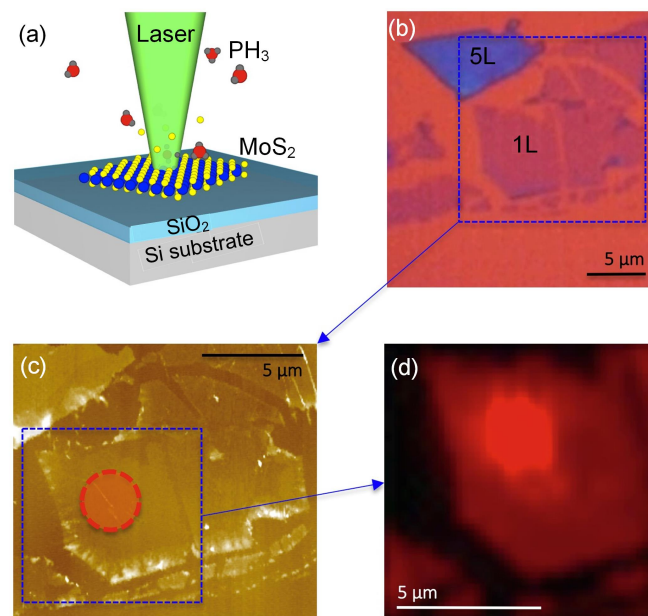


Figure 9. (a) Schematic diagram of the laser-assisted doping method. (b) Optical image of as-prepared monolayer MoS₂ on SiO₂/Si substrates. (c) Atomic force microscopy image of the zoomed area in (b). Its thickness is around 0.7 nm, in good agreement with the thickness of monolayer MoS₂. The circle in (c) is the laser spot area in the laser doping. (d) Photoluminescence (PL) mapping of the zoomed area in (c) that clearly shows the PL intensity enhancement of the laser-assisted doped area. [103] John Wiley & Sons.

[104]. Despite differences between Si and TMDCs, it is reasonable to adopt the substitutional doping mechanism. Considering that the dissociation temperature of TMDCs is in the range of 1200–1400 K, a laser power slightly below this range is enough to break the PH₃ molecules whose dissociation temperature is 685 K. Figure 9(b) shows an optical image of a mechanically exfoliated monolayer and five-layer MoS₂ flakes. The monolayer MoS₂ flake in figure 9(c) was ~0.7 nm thick. The PL map shown in figure 9(d) was taken from the laser-irradiated region indicated in figure 9(c). The laser doping process did not cause detrimental structural damage to these TMDCs at the given conditions.

Previous studies have already achieved both n- and p-type doping by surface charge transfer mechanisms, mostly through chemical physisorption [105]. However, physisorption doping is unstable and decays almost completely within an hour [106] or is retained for longer periods only if the doping environment is maintained or protected [92]. Among the various doping methods, substitutional doping of foreign elements is an effective and stable doping strategy for TMDCs. Accordingly, the laser was used to create sulfur vacancies and locally heat up the material to crack the precursor molecules, enabling the substitution of sulfur with phosphorus. The laser-assisted doping was shown to be irreversible and stable, even after

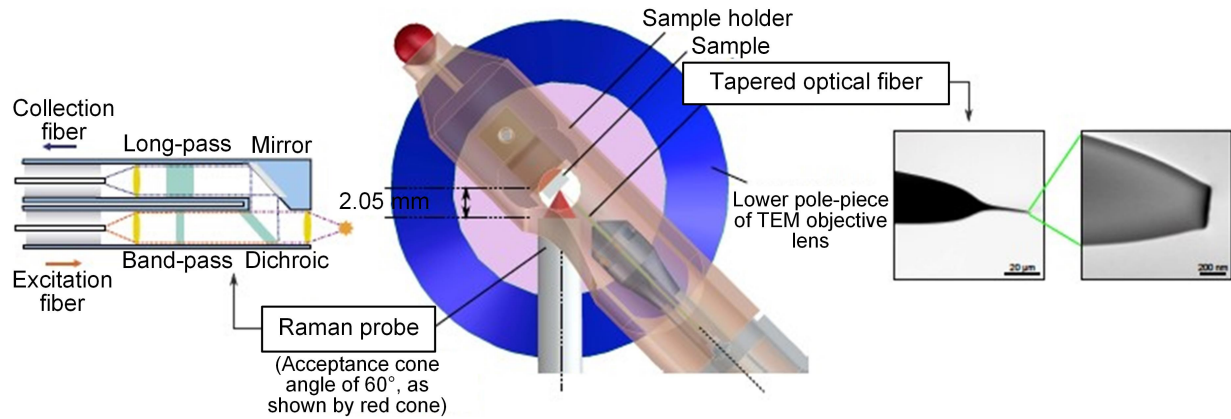


Figure 10. Layout of *in situ* Raman assembly in the sample chamber of the TEM (middle), schematic of Raman probe (left), and TEM images of tapered optical fiber (right). Reprinted from [115], Copyright (2017), with permission from Elsevier.

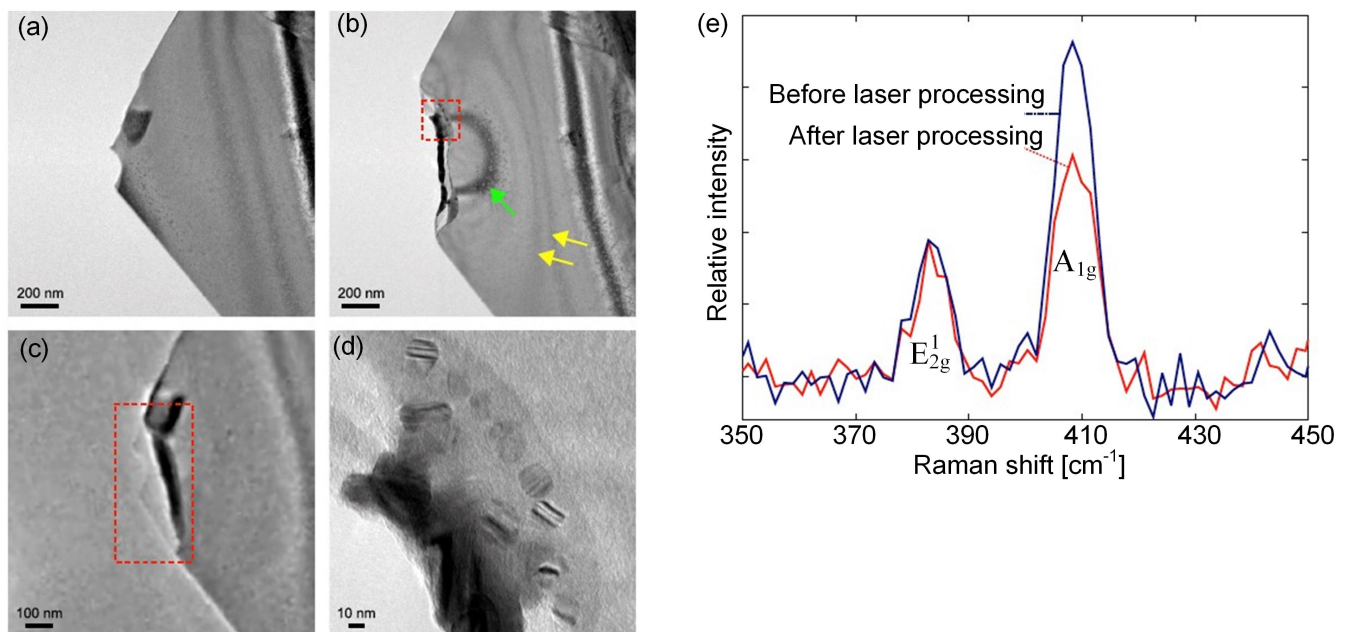


Figure 11. Bright-field TEM of MoS₂ flake (a) before and (b) after pulsed laser ablation. (c) Bright-field TEM snapshot from movie of the MoS₂ flake acquired during laser processing. (d) Higher magnification view of (b) showing spherical crystallites formed as a result of the pulsed laser processing. (e) Raman spectra of MoS₂ flake acquired before (blue) and after (red) laser processing, normalized to the *E_g* 21 peak and background subtracted. Reprinted from [115], Copyright (2017), with permission from Elsevier.

exposure in air for a month. In parallel to strong modification of the luminescent properties, the laser-assisted doping also drastically affected the electrical properties of the ultrathin TMDCs. This was investigated using field-effect transistor devices incorporating the locally doped TMDC layers as current channels.

This approach effectively introduced electronically active phosphorus atoms into the TMDCs. The precise level, temporal, and spatial control of the doping was achieved by varying the laser irradiation power and time, demonstrating wide tunability and high site selectivity. Future investigation on the choice of dopant, the dopant concentration, and the contact engineering should be conducted. The high stability and effectiveness of the laser-assisted doping method combined

with the site selectivity and tunability demonstrated here may open a new avenue for functionalizing TMDCs for customized nanodevice applications.

Irradiation with a single continuous laser beam of Gaussian profile induces spatially nonuniform doping and, therefore, limits the potential of laser processing of TMDCs as a well-controlled tool for a wider range of applications. Advanced laser configuration is, therefore, required for decoupling the fundamental phenomena associated with the doping mechanism: (1) the dissociation of dopant molecules to provide dopant radicals, and (2) the laser treatment and ensuing structural modification on the TMDCs. These can be separately controlled via a dual laser beam configuration combining different pulse lengths and wavelengths. Furthermore, the dopant gas for laser doping can

be selected according to the desired p- or n-type doping effect. This approach represents a new concept for fabricating PN junctions on 2D materials, offering distinct advantages with respect to reducing the process time and minimizing random fluctuation of doping. To further expand the potential of TMDCs towards novel optoelectronic devices, bandgap tuning by laser alloying is a promising candidate and will be achieved by introducing atoms of another chalcogen (S, Se, and Te). Local replacement of Se by S atoms in TMDCs was demonstrated via a laser-assisted chemical modification process [107]. Furthermore, laser-induced selective decoration of few- and multilayer MoS₂ has been demonstrated with silver (Ag) NPs via the photo-excitation of the semiconductor material exposed to silver nitrate (AgNO₃) solution [108]. This route enables control of p-type doping by varying the laser irradiation time.

3.2. *In situ* observation of laser processing of MoS₂ layers

The unique and highly promising characteristics of TMDCs depend on their thickness, which is typically in ultrathin format of a few layers or monolayers. Monolayer MoS₂ has a direct bandgap of ~1.85 eV instead of the indirect bandgap of 1.2 eV for the bulk counterpart. Thus, control of the TMDC layer thickness in arbitrary patterns should add flexibility to fully explore their exotic properties and push forward potential applications. However, TMDC few or monolayer flakes that are typically exfoliated from bulk crystals can have high crystallinity but rely on the spatially random van der Waals force between flakes and substrate resulting in uncontrollable thickness and shape. A tightly focused continuous-wave laser beam was utilized to thin MoS₂ down to a single layer [109]. The semiconducting properties of the thinned layers were found to resemble the properties of pristine MoS₂ single layers. Evidently, the laser light absorption into the semiconducting material changes dynamically during the thinning process. Moreover, the thermal conductivity of TMDC materials varies with the number of layers and is influenced by the backing substrate [110]. Consequently, the laser thinning represents a self-regulated process. A photochemical variance of the laser thinning process was presented in [111], utilizing adsorbed H₂O molecules on molybdenum (IV) telluride (MoTe₂) layers from the humidity present in the atmosphere to effect thinning under very low laser powers. Laser excitation at ultralow laser power in vacuum was shown to induce irreversible changes in the optical properties of TMDC materials [112]. An *in situ* study of void formation upon CW laser irradiation, with the assistance of temporal Raman evolution, yielded an empirical formula relating void size to laser power and exposure time [113]. Ultrafast laser-based thinning of MoS₂ through a two-photon absorption process was reported [114]. The interaction of laser radiation with TMDC material involves complex nanoscale physicochemical phenomena and, therefore, calls for further investigation. An *in situ* Raman instrument extending the capability of the TEM apparatus described in section 1.1 was utilized to quantitatively probe the laser thinning process of a MoS₂ flake (figures 10 and 11). Further studies are needed to understand the precise mechanism of the

laser interaction and modification of these exotic materials and push their applications, including in optoelectronics, flexible electronics, and sensors.

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