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
tool for realizing melt-mediated growth of crystalline silicon (Si). However, the localized heat-affected area can suffer rapid heat loss; and the subsequent severe undercooling can instigate numerous nucleation events. Accordingly, the crystallization process can end up with a myriad of crystalline grains, i.e. polycrystalline silicon (pc-Si). When un-melted crystallites exist in the initial stage of crystallization, these seeds also provide active growth sites, leading to crystallization into pc-Si. However, the pc-Si grain boundaries degrade the electronic performance. These issues have motivated development of various crystallization techniques (including superlateral growth [2], grain filter [7, 8], and crystal-seeded growth [9]) to enlarge the grain size and reduce the density of grain boundaries.

Researchers have reported on the synthesis of one-dimensional (1D) nanostructures in electron microscopy instruments by far-field optics [10, 11]. It has been demonstrated that laser-induced nanoscale melting of amorphous silicon (a-Si) can effectively lead to the formation of single-crystalline nanodomains after re-solidification on single-crystal Si substrates [12, 13]. An in situ transmission electron microscope (TEM) monitoring technique was implemented to observe the crystallization of a-Si during laser irradiation by directly coupling a laser beam into a TEM using a fiber optic probe [14, 15]. In contrast to prior in situ TEM observations of laser-induced phase transformations [16, 17], this approach uses a near-field technique.

Figure 1 shows a schematic of a near-field scanning optical microscopy (NSOM) probe coupled into a TEM. The fiber probe tip is precisely positioned to illuminate a-Si precursors prepared by focused ion beam (FIB) processing. Figure 2 shows the results from laser-induced crystallization of an a-Si pillar structure with a nanosecond (ns) laser where the entire sample width is within the spot size of the laser. Progressing from a-Si (figure 2(a)) to pc-Si (figure 2(b)) to a final cap of single-crystal Si (sc-Si) (figures 2(c) and (d)).

The transient temperature evolution during crystallization has a critical influence on the resulting microstructure [18–20]. In order to gain insight into the crystallization of a single-crystal Si cap, a 3D transient heat transfer simulation combined the classical homogeneous and heterogeneous nucleation mechanisms [21], based on the finite difference method [19, 20, 22]. Heterogeneous nucleation prevails over the homogeneous mechanism at a relatively higher temperature, not allowing deeper undercooling. Quasi-steady state (QSS) estimates of the nucleation rate were assumed in the simulation. More elaborate nucleation kinetics, such as athermal [23, 24] and non-QSS [24] nucleation, may emerge during the relatively fast cooling rate. However, several theoretical papers confirm that the calculated cooling rate ($\sim 7 \times 10^9$ K s$^{-1}$) is in the QSS regime (or moderately close to QSS [23]). The simulations showed that the nucleation commenced at a temperature of 1240–1330 K. The nucleation rate dramatically increased with the degree of undercooling. Hence, growth of single crystal happened when the recrystallization due to the latent heat release was sufficient to quench subsequent nucleation events.

Massively parallel lithography techniques (possibly nanoimprint lithography or e-beam lithography) could be configured to fabricate the base structures. Subsequent laser crystallization steps would form nanoscale crystalline dot arrays to serve as controlled seeds for polycrystalline or even epitaxial film growth by chemical vapor deposition (CVD) [25]. Such an approach could lead to polycrystalline films with tailored grain distribution.

Experiments on the crystallization of long a-Si nanopillars were performed on the same TEM-based setup discussed above [26]. In this case, Si nanopillars (diameter: 300–400 nm, length: 1.7–2.5 μm) consisting of a-Si—silicon oxide ($\sim 100$ nm)—crystalline Si layers were fabricated by an FIB technique. In contrast to the previously discussed study where a confined a-Si fully melted, the laser heat could only affect the phase of the pillar extremity. As shown in figure 3, the initial a-Si pillar was crystallized into pc-Si but with an unusually large sc-Si grain at the tip. Electron diffraction patterns confirmed single crystallinity of the large tip grain. The confined lateral (or radial) dimension prevented additional grains from growing into columnar structures [27]. Moreover, growth of the diverging secondary grains was preferentially frustrated by lateral confinement. The formation of the large tip crystal is reminiscent of the argument of Im et al [2] on the formation of large sc-Si from a-Si thin films and also of a study by Leung et al [27]. Large-area laser irradiation, including expanded/homogenized beam scanning, could incur efficient crystallization of pillar arrays. The resulting pillar arrays and the exposed single-crystalline surface may serve as a growth template and crystalline seeds for the controlled growth of sc-Si.

1.2. Assembly and phase switching of silicon nanoparticles (NPs)

Patterned periodic nanostructures serve as building blocks in electronics [28], spintronics [29], chemical catalysts [30], plasmonic and photonic devices [31–33], and memory devices [34–36]. Various efforts have been made to write nanostructures into well-defined configurations. Electron-beam lithography and helium-FIB processing represent ultrahigh resolution, top-down approaches. On the other hand,
bottom-up, self-assembly relies on fundamental chemical processes offering a scalable nanomanufacturing path. Pattern-guided laser [37–39] and thermal [40, 41] dewetting, as well as liquid assembly [42, 43], can produce periodic metallic and dielectric nanostructures combining pattern fidelity and low cost. Advancements in structural color [44–48], optical data storage [49, 50], and active nanophotonic devices [51–53] rely on tuning of the patterned geometrical features. Optical field patterning is a promising route [54–56]. The laser-induced forward transfer (LIFT) method has been employed to print Si resonators with tunable size [57].

A laser-based method that can tune the size, number, symmetry, and crystallinity of Si NP arrays was recently reported [58]. Laser-induced modulated assembly utilizes nanosecond laser pulse irradiation as a source modulating the assembly of a prepatterned a-Si film to a periodic NP array (figures 4(a) and (b)) The LiMA process relies on modulation of the local laser absorption due to the near-field optical energy coupling. Due to the near-field interaction, LiMA does not require elaborate focusing of the laser beam and is easily scalable. The modulation entails polarization-dependent particle sizing, fluence-dependent particle number selection, and deliberate particle subtraction. Amorphization of crystalline Si NPs follows via laser-induced phase switching (LiPS), due to the fast cooling rate upon nanosecond irradiation. Phase switching has usually been observed in compound phase change materials, such as germanium antimony tellurium (GeSbTe). The ensuing structural modification leads to dielectric constant switching.

In Wang et al’s study, LiMA and LiPS could program the Si Mie resonator combination as well as the resonance peak position and the dielectric constant of selected resonators in three different scales. The complex NP arrangement modulated by the laser pulse energy and polarization produced particle sizes ranging from 60 to 330 nm. The number of Mie resonators as well as the resonance peaks and dielectric constants of selected resonators can be programmed. Optical metasurfaces [59], structural color, and multidimensional optical storage devices could be fabricated using this approach. Dielectric NPs exhibit a significant advantage over plasmonics due to low loss and compatibility with conventional semiconductor processing and manufacturing. The present method can ultimately produce monoperiodic, biperiodic and triperiodic patterns, directly facilitating the

Figure 2. (a) As-prepared nanoscale a-Si pillar fabricated by FIB. (b) TEM image of pc-Si observed after irradiation by several ns laser pulse shots. (c) Bright-field TEM image of single-crystalline, nanoscale sc-Si cap achieved after the pc-Si cap shown in (b) irradiated by a single-pulse shot of ns laser beam. Inset: electron diffraction pattern of the nanoscale sc-Si as shown in (c), zone axis is [0 1 1 2]. (d) The corresponding dark-field TEM image of the nanoscale sc-Si grain as shown in (c), using the [2 2 0] reflection to illuminate only the lone Si grain. Reprinted with permission from [14]. Copyright (2012) American Chemical Society.

Figure 3. The figure (a) shows the NSOM probe against an a-Si pillar. The figure (b) shows the crystal structure obtained upon irradiation of laser pulses. Reproduced from [26] (2014). With permission of Springer.
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 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
(and hence multibandgap) semiconductor NW direct growth has been demonstrated on a single platform [81]. The reaction size can be tailored depending on the specific target application by regulating the laser power or by temporally/spatially modulating the laser irradiation. Arbitrary patterning of single element or compound NWs can be achieved on demand simply by switching the precursor gases.

A critical difference is identified in the growth time resolution as the furnace growth was \( \sim 15 \) s. The relatively lower activation energy in laser-assisted growth is partly attributed to the difference in time resolution. However, localized CVD or growth by confined laser spot is advantageous in driving three-dimensional gas transport over a smaller reaction zone (CVD gas delivery and exchange of reaction byproducts such as hydrogen) versus 1D transport in wider reaction area cases [82]. Due to competing solid–liquid and vapor–liquid interfacial energy effects, the catalyst size affects SiNW growth kinetics and, therefore, the diameter and growth rate. In contrast to conventional furnace experiments that are of limited temporal resolution, regulating the duration of the laser illumination can precisely control the laser-driven NW growth [83]. Energy filtered transmission electron microscopy-based chemical mapping was employed to investigate the commencement of the laser-driven nucleation process (figure 6). In the regime of rapid and sustained growth, nucleation occurs in the time range of 10–100 ms depending on the catalyst diameter and growth temperature. The precise measurements of nucleation times elucidate the early stage behavior of catalyzed growth and reveal that the activation energy for the NW nucleation diminishes as the catalyst size is reduced. In a more general point of view, the laser heating methodology provides useful clues to a wide range of phenomena spanning from synthesis to phase change of nanomaterials.

The highly controlled spatial and temporal laser irradiation distribution enabled growth of discrete semiconductor NWs having precisely tunable dimensions on heteroepitaxial substrates [84]. Figure 7 shows VLS growth of vertical germanium nanowires (GeNWs) with deliberately varying shapes on a single Si(111) substrate by controlling the laser power (i.e. growth temperature) and illumination time. The irregular cross-sectional shape obtained at high temperatures was due to the anisotropy induced by the crystallographic orientation. Despite the lack of buffer layers to mitigate the lattice mismatch, the quality of the interface between the nanowire root and the substrate is excellent.

2.2. NSOM enabled selective nanowire growth

Highly selective growth of single SiNWs was achieved by means of an optical near-field technique [85]. Supportive, indirect heating of the catalyst provided to the underlying substrate via far-field laser irradiation lowered the level of direct near-field illumination onto the catalyst and also sustained the nanometer-scale heat source confinement. The actual exposure of the direct illumination beam on the catalyst was limited to the early stage of the growth and was followed by heat conduction to the catalyst through the nanowire stem. Damage-free, nanoscale spatial selectivity under the reactant gas was possible using a dielectric atomic force microscopy (AFM) tip. The optical near-field laser radiation was applied
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$_2$ (M = Mo, W; X = S, Se, 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. (Left) 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. (Right) 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.
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 PH$_3$ molecules whose dissociation temperature is 685 K. Figure 9(b) shows an optical image of a mechanically exfoliated monolayer and five-layer MoS$_2$ flakes. The monolayer MoS$_2$ 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...
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

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 $E_2$ 21 peak and background subtracted. Reprinted from [115], Copyright (2017), with permission from Elsevier.
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 MoS$_2$ has been demonstrated with silver (Ag) NPs via the photo-excitation of the semiconductor material exposed to silver nitrate (AgNO$_3$) 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 MoS$_2$ 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 MoS$_2$ has a direct bandgap of $\sim$1.85 eV instead of the indirect bandgap of 1.2 eV for the bulk counterpart. Thus, control of the TMDC layer thickness in arbitrary patterns should add flexibility to fully explore their exotic properties and push forward potential applications. However, TMDC few or monolayer flakes that are typically exfoliated from bulk crystals can have high crystallinity but rely on the spatially random van der Waals force between flakes and substrate resulting in uncontrollable thickness and shape. A tightly focused continuous-wave laser beam was utilized to thin MoS$_2$ down to a single layer [109]. The semiconducting properties of the thinned layers were found to resemble the properties of pristine MoS$_2$ 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 H$_2$O molecules on molybdenum (IV) telluride (MoTe$_2$) 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 MoS$_2$ 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 MoS$_2$ 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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