Cubic Lattice Nanosheets: Thickness-Driven Light Emission

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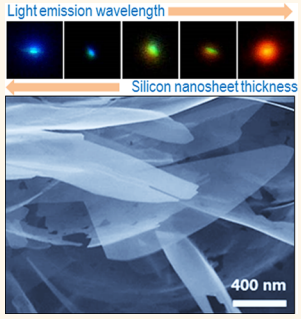
ABSTRACT Silicon has a diamond-like cubic crystal lattice for which two-dimensional (2D) nanometer thickness nanosheet crystallization appears not to be trivial. However, in this issue of *ACS Nano*, the group led by Heon-Jin Choi demonstrates the gas-phase dendritic growth of Si nanosheets, only 1 to 13 nm thick. Moreover, such nanosheets display strong thickness-dependent photoluminescence in a visible range with red, green, and blue emission each documented.



If one hears the term "nanosheets", he/she probably imagines graphene-like nanostructures, that is, either graphene itself, or its sister system of layered boron nitride, or metal dichalcogenides (MoS_2, WS_2, *etc.*). In fact, the family of layered crystal lattice nanosheets, so-called van der Waals two-dimensional (2D) structures, is growing rapidly, steadily, and successfully, as evidenced by a number of recent reviews and perspectives.[1,2] However, the term "nanosheet" is not solely limited to graphene-like 2D materials but is also applicable to any sort of layered crystals, like oxide and hydroxide nanosheets of TiO_2, $Ca_2Nb_3O_{10}$, MnO_2, TaO_3, *etc.*,[3] which may be assembled in complex layered geometries through solution-based processing (*e.g.*, flocculation, electrostatic sequential deposition, or the Langmuir–Blodgett method). By contrast, intuitively, it is rather difficult to guess that this sort of 2D structure would be possible in cubic lattice materials, due simply to crystallographic constraints; however, it was indeed theoretically calculated and experimentally demonstrated that materials having nonlayered structures (*e.g.*, cubic, monoclinic, *etc.*) may also be shaped as single-crystalline nanosheets or nanotubes.[4–6]

Silicon, the second most abundant element in the earth's crust (after oxygen), represents the typical example of a cubic, diamond-like crystal. Silicon has been the most important element for the semiconducting industry over the last 50 years. Its lattice is fully isotropic and could hardly be expected to reveal selective 2D anisotropic growth. However, layered Si-based materials, like those covered with organic groups, have been fabricated using layered polysilane (Si_6H_6).[7,8] In addition, free-standing pure Si nanosheets were also produced utilizing graphene oxide as a template[9] or using chemical vapor deposition on Si substrates with $SiCl_4$ as the Si precursor and H_2 as a carrier gas.[10] Moreover, the existence of silicene—the purely sp^2-hybridized (or sp^2–sp^3-hybridized) graphene-like Si honeycomb 2D structure—has recently become a subject of intense theoretical[11,12] and experimental[13,14] interests.

In this issue of *ACS Nano*, the group of Heon-Jin Choi extend their earlier work on dendrite-based growth[10] and report free-standing Si nanosheet fabrication under full control of the cubic sheet thicknesses and lateral dimensions.[15] The dimensions of nanosheets were varied by extending or shortening the synthesis time. Then, the authors analyzed photoluminescence and photocurrents from the prepared nanosheets of various thicknesses and sizes and found a clear correlation of a nanomaterial's optical band gap and emission wavelength

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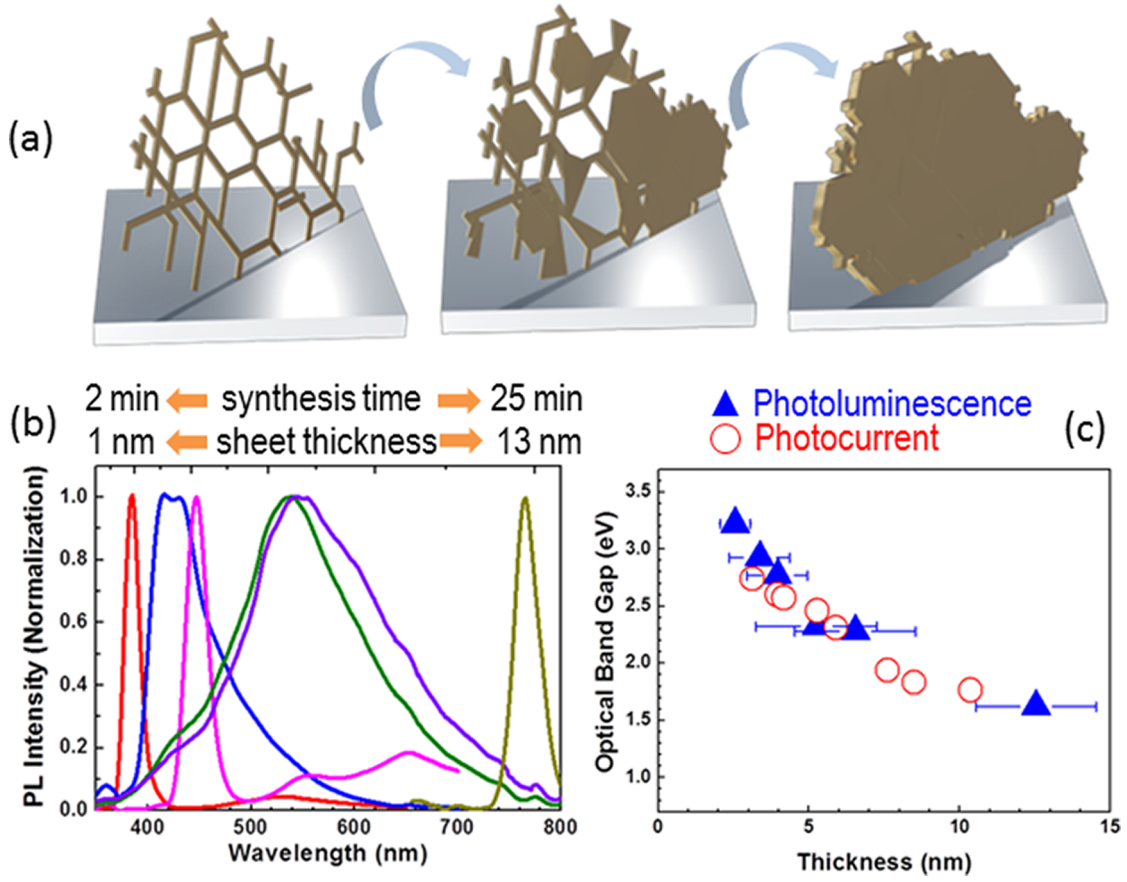

Figure 1. (a) Nanosheet growth. (b) Dependence of a photoluminescence wavelength upon the synthesis time of free-standing single-crystalline Si nanosheets. A decrease in the synthesis time leads to the nanosheet thinning and decrease in the emission wavelength in line with the confinement effect. (c) Optical band gap as a function of the nanosheet thickness determined from photoluminescence and photocurrent measurements. Adapted from Figures 1−3 of ref 15. Copyright 2014 American Chemical Society.

with its geometry (Figure 1). The authors thus confirmed the confinement effect in nanoscale Si previously noted for Si quantum dots.[16] They attributed the observed behavior to excitonic recombinations (*i.e.*, the formation of excitons by the recombination of electrons in the conduction band and holes in the valence band). The Si nanosheet optical band gaps ranged between 1.8 and 3.2 eV for Si nanosheet thicknesses ranging from 2 to 13 nm, therefore notably exceeding the figures previously documented for Si quantum dots (1.7−2.7 eV)[16] and comparable with Si nanowires[17] (1.1−3.5 eV for wire thicknesses of 1−7 nm). These results provide intriguing possibilities for smart optical engineering: the color of light emitted from Si nanosheets corresponds well to the synthetic time, which is the easiest experimental parameter to control, even for an inexperienced operator. In addition, the mixtures of sheets of various thicknesses should produce white light analogous to broad-band solar radiation. In fact, the authors were able to construct prototypes of white or blue light-emitting diodes with Si nanosheet ensembles as active layers.

The German group led by M. Stutzmann became interested in the luminescence and optical properties of Si-based compounds, namely, siloxenes, more than 20 years ago.[18] Such interest should be intensifying due to the new availability of pure single-crystalline Si nanosheets that reportedly reveal tunable photoluminescence. Not only optical properties but also thermoconducting properties of Si nanosheets might be of interest.[19]

The growth of cubic Si nanosheets begins from the formation of one-dimensional (1D) free-standing Si nanowires on Si substrates along the ⟨110⟩ crystallographic direction. Then, branching of seed nanowires along six directions leads to the crystallization of 2D dendrites followed by filling of the spaces between them

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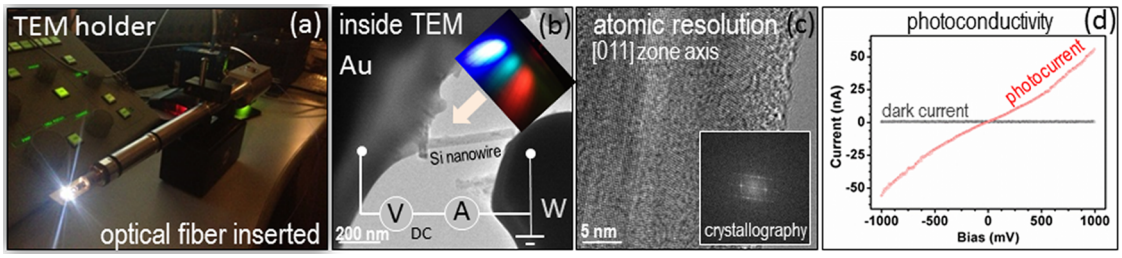

Figure 2. Pilot *in situ* transmission electron microscope optoelectronic experiment on an individual single-crystalline Si nanowire. (a) Photo of the TEM holder with a white light shining from its frame tip end. (b) Individual Si nanowire stretched between two electrical contacts inside TEM. (c) Atomically resolved high-resolution transmission electron microscope image of the wire (viewed along the $[011]_{fcc}$ zone axis) with the corresponding fast Fourier transform pattern revealing its true single-crystalline nature. (d) *I*−*V* curve recorded under 405 nm light illumination.

(Figure 1a). The final stage is actually thickening of the ensembles along the ⟨111⟩ direction which leads to the possibilities of thickness tuning as a function of growth time and, as a result, emission wavelength variations, as shown in Figure 1b. The proposed mechanism, as evidenced by Choi *et al.*, should not be restricted solely to Si; it appears to be possible for any materials with diamond-like lattices, like cubic boron nitride, for instance, giving rise to the opportunity to document analogous discoveries in other important cubic systems in the near future. The simplicity of the method is appealing, and real commercial applications for multiband lighting may be awaited.

OUTLOOK AND FUTURE CHALLENGES

The experiments described above highlight the importance of lateral dimensions of nanoscale Si for its photoluminescence properties and technological usage in lighting. Taking into account this experimental finding and our personal views and experience with Si nanostructures, we think further development in this field may ultimately lead to downsizing the structures and increasing the range of optical band gaps toward the deep UV. However, once the structures get smaller and thinner, one needs a proper instrument to visualize and to study them. In this regard, it is noteworthy that, among the many scientific instruments available on the market, a high-resolution transmission electron microscope (HRTEM) has one of the highest spatial resolutions, going down to 80 pm or even less for aberration-corrected HRTEMs. Modern methods of *in situ* transmission electron microscopy (TEM) allow one not only to achieve the deepest insights into the atomic ordering and elemental compositions of these tiny nanoscale materials (down to single-atom imaging) but also to probe their electrical, mechanical, and/or thermal properties simultaneously.[20] Recently, our team at the National Institute for Materials Science (NIMS) has been able to widen the *in situ* TEM possibilities toward dedicated optical measurements on individual inorganic nanostructures, for example, diverse nanotubes, nanowires, nanobelts, nanoparticles, nanoheterostructures,[21] and graphene-like nanosheets. Among those, Si nanostructures deserve attention.

Therefore, for the most informative future analysis of nanoscale Si (in its various nanoshapes and nanomorphologies), one may think of predesigned opto-compatible HRTEM operations using various wavelength light sources or tunable wavelength light and corresponding optical fibers protruding into the TEM column and shining light of a given color on the nanostructures (Figure 2). Simultaneous nanomaterial bending/stretching and/or electrical probing inside HRTEM may be accomplished in tandem with illumination. The key advantage of the proposed challenging experiments is that direct measurements of photocurrent, photovoltage, photoluminescence, and cathodoluminescence spectra may be accomplished on the smallest individual nanostructures possible under full control of their exact crystallography, atomic ordering, pre-existing and/or appearing (under light absorption, current flow, and Joule heating) structural defects, and spatially resolved chemistry, and at the highest spatial and temporal resolutions achievable with HRTEM.

For example, Figure 2 shows one of our recent pilot experiments on an individual Si nanostructure. The frames in a−d, respectively, show a view of the side entry TEM holder with an optical fiber thread inside it; this fiber passes a bright white light to the nanosample location; the light may then be chopped to a desired pulse frequency or continuous wavelength tuned using a monochromator; an individual Si nanowire stretched between gold and tungsten electrical contacts thus forming a two-terminal electrical circuit; a direct atomic lattice image of the wire taken at 500 000× magnification revealing its single-crystalline nature and a thin amorphous silica layer on its surface; and finally, a resultant photocurrent measured.

This technique may be of use for the analysis of photoluminescence and photocurrent spectroscopy not only for Si nanosheets and other Si nanostructures, as briefly illustrated here, but also for a diverse range of other inorganic nanomaterials of different crystallinity, either layered or nonlayered. Most importantly, the full crystallography-related and nanostructure defect status information (*i.e.*, stacking faults, dislocations, grain and antiphase boundaries, interfaces between various structural

domains, individual vacancies and their agglomerates, surface quality, and oxidation states) may be obtained *in situ* before, during, and after the measurements in real time, and thus the true structure—property relationship, which is the Holy Grail of material science, may be unambiguously determined.

Conflict of Interest: The authors declare no competing financial interest.

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