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Soft Synthesis of Single-Crystal Silicon Monolayer Sheets**

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Silicon-based nanoscale materials, such as nanotubes,[1] nanowires,[2] and nanoparticles,[3] have remarkable electronic and optical properties and are suitable for nanodevice applications owing to their extraordinary structures. While zero- or one-dimensional nanomaterials may be suitable for nanoscale fabrication, two-dimensional nanomaterials can bridge the gap between the quantum world and three-dimensional bulk because of their nanoscale thickness and microscale area. To synthesize two-dimensional nanomaterials, chemical exfoliation is performed artificially for several classes of layered materials by certain soft-chemistry procedures.[4] In a previous study,[5] we tried to prepare the two-dimensional silicon backbone of siloxene nanosheets (composition: $Si_6H_3(OH)_3$),[6] but the silicon skeleton was partially oxidized. Moreover, epitaxial films of siloxene are obtained on the silicon (111) surface by topochemical transformation of $CaSi_2$ (111) films.[7] Although many researchers have attempted to prepare two-dimensional silicon sheets, there have been no reports of a successful fabrication of silicon monolayer sheets.

We tried to prepare silicon sheets by chemical exfoliation of calcium disilicide, $CaSi_2$, which has a hexagonal layered structure consisting of alternating Ca layers and corrugated Si (111) planes in which the Si_6 rings are interconnected (Figure 1 a). One of the most important techniques to exfoliate precursor-layered crystals into their elementary layers is the adjustment of the charge on the silicon layer. Because $CaSi_2$ is ionic (i.e. $Ca^{2+}(Si^-)_2$) the electrostatic interaction between the Ca^{2+} and Si^- layers is strong and so it is very important to reduce the charge on the negatively charged silicon layers. Thus, we prepared Mg-doped $CaSi_2$ (mixture composition: $CaSi_{1.85}Mg_{0.15}$) in which Mg was doped successfully into the $CaSi_2$ (see Supporting Information). Then, we tried to prepare silicon monolayer sheets (Figure 1 b,c) through chemical exfoliation of $CaSi_{1.85}Mg_{0.15}$. When

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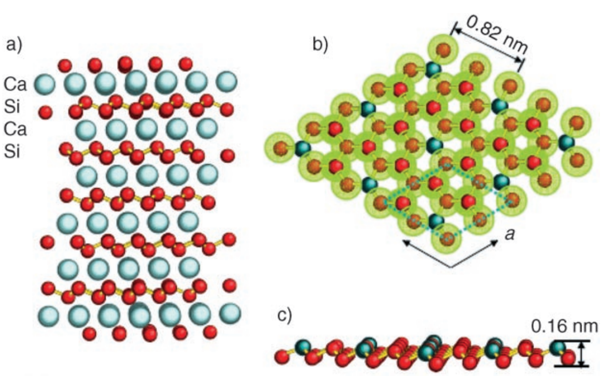

Figure 1. a) Structural model of $CaSi_2$. b) Top view of Mg-doped silicon sheet capped with oxygen; the axis notation follows that for the hexagonal crystal structure of the parent layered silicon. c) Side view of the core of the silicon sheet; the large yellow-green circles represent oxygen atoms, small red (Si) and green (Mg) circles represent the Si(111) plane in the layer below.

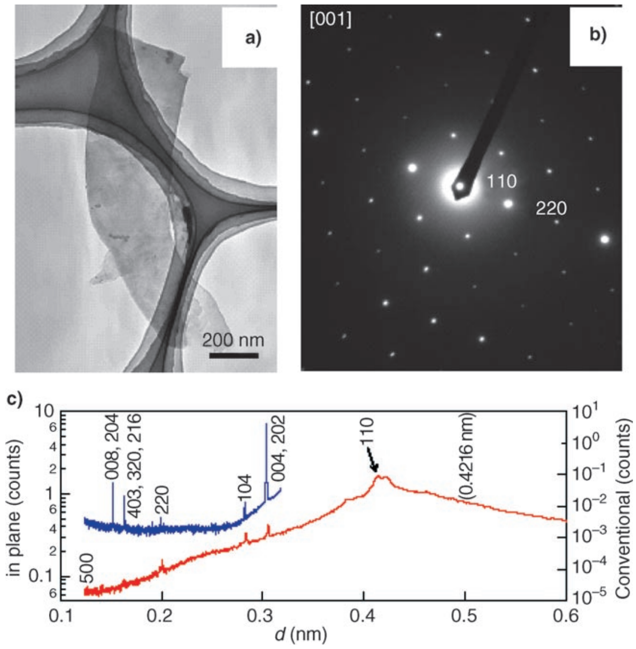

Figure 2. a) TEM image of the sheet. b) ED pattern recorded along the [001] zone axis perpendicular to the surface of the sheet. c) In-plane XRD scans with an incident angle of 0.2° (red line) and conventional θ-2θ scans (blue line) of the silicon sheets. The data was recorded at SPring-8 (BL16XU).

bulk $CaSi_{1.85}Mg_{0.15}$ is immersed in a solution of propylamine hydrochloride (PA·HCl), the calcium ions are deintercalated, which is accompanied by the evolution of hydrogen, and $CaSi_{1.85}Mg_{0.15}$ is converted into a mixture of silicon sheets and an insoluble black metallic solid. A light-brown suspension containing silicon sheets was obtained after the sediment was removed from the bottom of the flask.

To determine the binding energy and composition of silicon sheets, X-ray photoelectron spectroscopy (XPS) of the Si 2p orbitals on silicon sheets adsorbed on a positively charged graphite substrate was measured (see Supporting Information). The Si 2p peak has a binding energy of 102 eV. This energy is close to that of the Si^{II} oxidation state. From the XPS data, the molar ratio of Si:O is roughly 1:1, which is in good agreement with previous reports.[8] The composition of the adsorbed monolayer silicon sheets was determined to be Si:Mg:O = 7.0:1.3:7.5 by XPS measurement. The Si:Mg ratio is appreciably smaller in the starting material, $CaSi_{1.85}Mg_{0.15}$, which indicates that exfoliation into individual silicon sheets occurred preferentially in a section of the silicon layer where magnesium atoms were present. The bonding of oxygen onto the surface of the silicon sheets was confirmed by Fourier transform infrared spectroscopy (FTIR). The bands at 1050 cm^{-1} correspond to Si-O-Si stretching, which indicates that the sheets are capped with oxygen.[9] The overall exfoliation reaction comprises the following steps: 1) the oxidation of $CaSi_{1.85}Mg_{0.15}$ is initiated by the oxidation of the Ca atoms with PA·HCl, accompanied by the liberation of PA; 2) the resulting Mg-doped SiH is presumably very reactive and thus easily oxidized with water to form gaseous hydrogen; 3) Mg-doped layered silicon with capping oxygen atoms is exfoliated by the reaction with aqueous PA solution, which results in a stable colloidal suspension of silicon sheets.

The structure of the silicon sheets was confirmed by transmission electron microscopy (TEM). A TEM image of the silicon sheets, dropped on a carbon grid, which shows their general characteristics, reveals a two-dimensional structure with lateral dimensions in the range of 200 to 500 nm (Figure 2a). The sheet is almost transparent, thus indicating a high degree of exfoliation of the $CaSi_{1.85}Mg_{0.15}$ crystals, and it exhibits uniform and homogeneous contrast, which reflects its uniform thickness. A selected-area electron diffraction (ED) pattern of the *hk*0 layer is shown in Figure 2b. ED confirmed that the sheet is single-crystalline and gives a spot pattern. All the diffraction spots could be indexed as *hk* reflections of a hexagonal lattice with $a = 0.82$ nm, which corresponds to approximately twice that of the (111) plane structure of bulk silicon (0.38 nm). The arrangement is attributable to either a superlattice structure or a delamination effect. Figure 2c shows the in-plane X-ray diffraction (XRD) scan of the sheets with an incident angle of 0.2°. The sheets give rise to fundamental peaks at $d = 0.422$ nm that correspond to the (110) plane, which is also observed in the ED (Figure 2b). Moreover, although the in-plane diffraction pattern of the silicon sheet was compared with that of siloxene,[10] this diffraction pattern could not be assigned to any siloxene structures (see Supporting Information). Thus, these results can be explained by the silicon sheets having a superlattice structure with twice the period of the (111) plane structure of bulk silicon. Energy-dispersive X-ray spectroscopy (EDX) combined with TEM revealed the presence of Si and Mg atoms, which suggests successful Mg doping of the sheets. Taken together with the superlattice structure and the XPS data, the evidence shows the structure of the sheets to be that of the theoretical structure shown in Figure 1b, and the molar ratio of silicon sheet is consequently Si:Mg = 7:1. However, the position of the Mg site is questionable and will be investigated in more detail.

Atomic force microscopy (AFM) provided further evidence of monolayer sheets. Figure 3a shows a noncontact

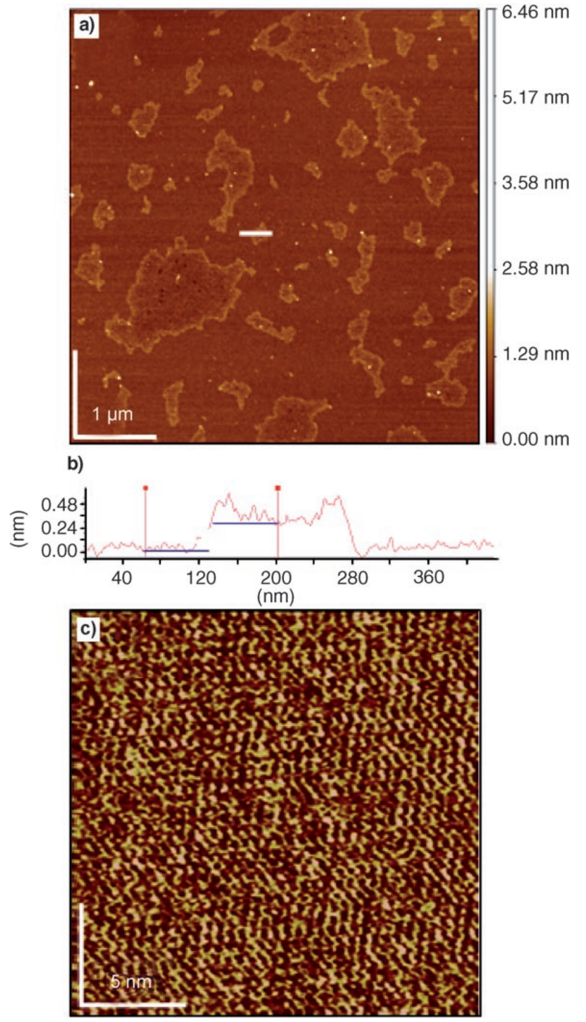

Figure 3. a) Noncontact mode AFM image of the silicon sheets, and b) its line profile taken along the white line in (a). c) Atomically resolved AFM image of silicon sheets.

mode AFM image of silicon sheets adsorbed electrostatically onto a positively charged mica substrate as the silicon sheets have a negative charge. The observation of breaks at the edges of the sheets suggests that they are ultrathin. The thickness of the sheets was measured at intervals between the sheets and the substrate surface and yielded an average value of 0.37 nm (Figure 3b). A thickness below 1 nm clearly demonstrates that the sample was composed of monolayer sheets. The crystallographic thickness of the silicon sheet was calculated to be 0.16 nm on the basis of its atomic architecture (Figure 1c). The difference between this value and that obtained by AFM indicates that the surface of the silicon sheet was stabilized by capping oxygen atoms, silicon nanowires,[2] and silicon nanoparticles.[3]

An atomically resolved AFM image of an individual sheet provided further insight into the structure (Figure 3c). The quality of the image was neither affected by the long duration of the experiment during which the sample was exposed to air nor by exposure of the sheet to air for several days before measurement. Thus, the oxygen-capped silicon sheets are resistant to air oxidation. A high-resolution AFM image reveals that the closest distance between the dotlike "atoms" is 0.41 ± 0.02 nm (Figure 3c). The lattice period of the sheet determined by this measurement is in agreement with that of the TEM observation. A structural model for the surface of the sheet is shown in Figure 1b. In this model, each silicon atom in the plane below is bonded to an oxygen atom, which may be accounted for by considering the resolution of AFM and the actual surface structure. Thus, the periodicity of the surface of the sheet is 0.41 nm, which is slightly larger than the distance between Si atoms in a Si (111) plane of bulk crystal, that is, 0.38 nm. On the basis of the high-resolution AFM image and the TEM observation, we conclude that the sheet cores consist of a single-crystalline silicon monolayer with the thickness of a slightly squashed Si (111) plane.

The absorption spectrum of the silicon sheets (Figure 4a) has a peak at 268 nm (4.8 eV) that corresponds to the L→L critical point in the silicon-band structure, which is strongly blue-shifted with respect to the bulk indirect band gap of 1.1 eV. The silicon sheets are thought to be predominantly ⟨110⟩ oriented. Normally, ⟨110⟩-oriented silicon nanowires exhibit a single sharp absorbance at 3.7 eV.[11] This difference in energy of about 1 ev maybe associated with the subnanometer thickness of the silicon sheets, which is about one order of magnitude smaller than the thickness of silicon nanowires (5 nm). The position of the absorbance was observed to be linearly dependent on the silicon content and excludes a possible association of nanosheets in this concentration range. The photoluminescence (PL) spectrum was obtained by using an excitation wavelength of 350 nm (Figure 4b). The emission has a peak at 434 nm (2.9 eV),

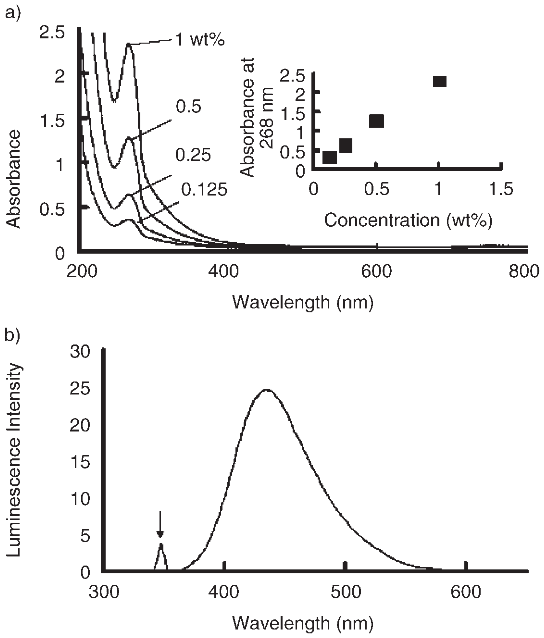

Figure 4. Room-temperature optical properties of the silicon sheets. a) UV/Vis spectra of suspensions of silicon sheets at various concentrations. Inset: the absorbance at 268 nm is plotted against the concentration of the sheets. b) PL spectra dispersed in water with an excitation wavelength of 350 nm (indicated by an arrow).

which is direct evidence that the two-dimensional silicon backbone is maintained because the PL of the silicon quantum dots, with diameters smaller than 2 nm, has a peak at 3 eV and shifts to the red by as much as 1 eV after exposure to oxygen.[12] Moreover, the absence of PL from defect or trap-state recombination, which typically occurs near 600 nm, supports the notion that the observed PL is due to direct electron–hole recombination in the silicon sheets as occurs in silicon nanocrystals.[13]

In conclusion, we have obtained unique silicon sheets, whose thickness is an order of magnitude smaller than that previously reported for silicon nanomaterials. The ability to synthesize silicon sheets under the conditions presented will presumably broaden the applicability of these sheets in future optoelectronic devices.

Experimental Section

A stoichiometric mixture (Ca:Si:Mg = 1:1.85:0.15) of CaSi (99 %), Si (99.99 %), and Mg (99.9%) was melted by using a water-cooled copper crucible with radio-frequency (RF) heating under an Ar atmosphere and then slowly cooled to room temperature.

Preparation of silicon monolayer sheets through chemical exfoliation of $CaSi_{1.85}Mg_{0.15}$: PA·HCl (10 g) and water (50 mL) were added to platelike crystals of $CaSi_{1.85}Mg_{0.15}$ (0.1 g) several millimetres in width. The reaction mixture was stirred (100 rpm) at room temperature for ten days to yield a mixture of silicon sheets and an insoluble black metallic solid. A light-brown suspension containing silicon sheets was obtained after the sediment at the bottom of the flask was removed. The total yield of silicon sheets based on the starting materials ($CaSi_{1.85}Mg_{0.15}$) was less than 1 %.

The monolayer sheets for the XPS and AFM measurements were prepared by a self-assembling layer-by-layer technique. The substrate was primed by treatment with a poly(diallyldimethylammonium chloride solution (PDADMAC, $M_w > 200000$; 1.0 g dm^{-3}) for 20 min to introduce a positive charge to the substrate surface. The substrate was deposited into a suspension of silicon sheets (0.5 g dm^{-3}) and after 20 min, the excess silicon sheets and other ions (e.g., PA and Ca^{2+} ions) were removed thoroughly by washing with water.

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