

Supplementary Information

Controllable conversion of liquid silicon from high-density to low-density towards amorphous silicon nanospheres on a wafer-scale

Qiang Liu,^a Ruifeng Qi,^a Shuang Song,^b Zhihui Yan and Qingsong Huang*^a

^aSchool of Chemical Engineering, Sichuan University, Chengdu 610065, China

^bCollege of Architecture & Environment, Sichuan University, Chengdu 610065, China

Corresponding e-mail: qshuang@scu.edu.cn

1. Fabrication of a-Si or c-Si particles on 6H-SiC (0001) by PMG method

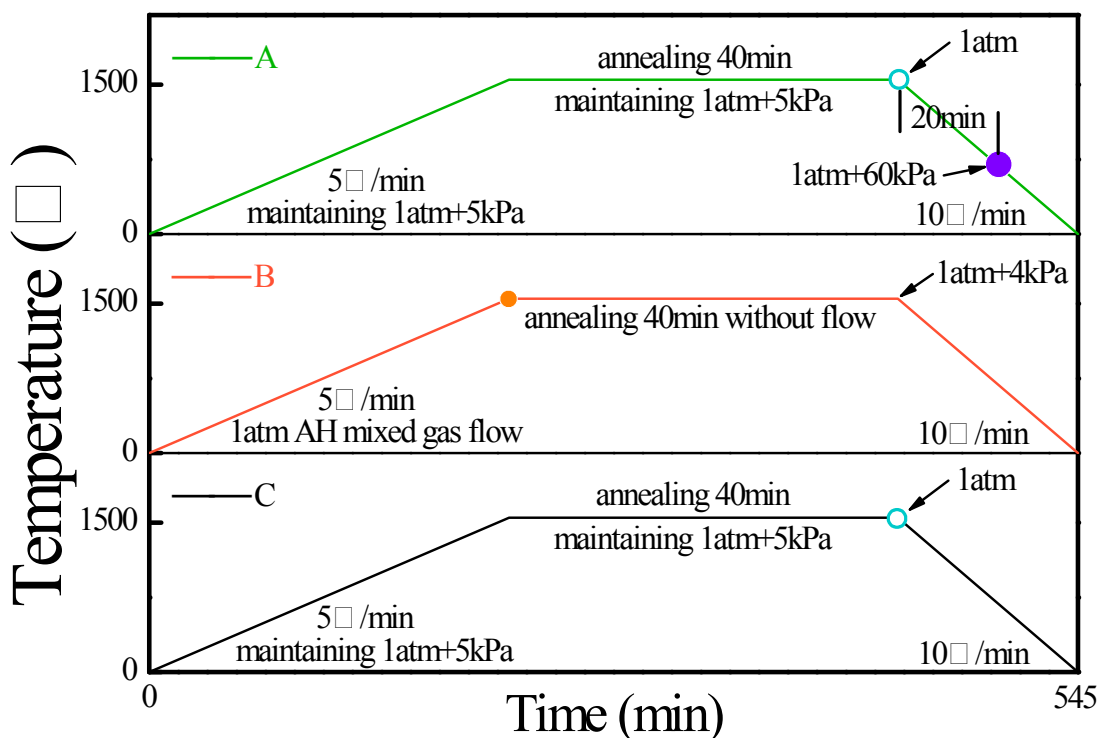


Fig. S1 Three kinds of technique process to prepare a-Si or c-Si particles on SiC by PMG method. (A) Monodisperse a-Si nanospheres by PMG1. (B) Controllable-size a-Si spheres in array by PMG2. (C) Nucleation of hexagonal pyramid-like c-Si particles by PMG3. The solid circle

indicates that the pressure begins to increase at this time, and the circle indicates that the pressure begins to decrease.

Commercially available nitrogen-doped 2-inch and on-axis ($0 \pm 0.5^\circ$) 6H-SiC wafers (TankeBlue Semicon. Co. Ltd., Beijing), were chemically-mechanically polished on Si-terminated face, and mechanically polished on C-terminated face.

The 6H-SiC substrates, cutting into small pieces of 10 mm * 20 mm, were first dipped into concentrated HF ($\geq 40\%$) for 30 min. Furthermore, they were ultrasonically rinsed in high-purity deionized water, acetone, and ethanol for 10 min, respectively, to remove oxides on the surfaces^{1, 2}. After that, the substrates were blown dry by nitrogen gas, and put into a graphite crucible successively. Top surface of SiC wafer is set as SiC (000-1), and then loaded into tube furnace with alundum tube.

(1) PMG1 route (Fig. S1A)

The mixture gas comprising by argon gas (95% v) and hydrogen (5% v) (AH mixed gas) was introduced into furnace, and kept the pressure as 1 atm + 5 kPa. Upon heating, Si atoms decomposed and sublimated from the surface of SiC, and the heating rates were sustained 5 °C/min. By adjusting the pressure every 10 minutes, the furnace pressure was kept from changing. When the temperature was raised to 1550 °C and kept for 40 minutes, the concentration of Si vapor reached a balance value.

Upon cooling, the pressure in the furnace was adjusted to 1atm, and kept for 20 min. After that, the pressure was promoted to 1 atm + 60 kPa, and kept for 10 min. After repeating the above process several times, the furnace temperature dropped to 500 °C. After the tube furnace was cooled via furnace cooling to room temperature, monodisperse a-Si nanospheres were formed on the SiC surface. In the cooling process, typical cooling rates were 10 °C/min. Upon pressurization, the AH mixed gas flow was maintained at 250 mL/min. The SEM morphology of the sample is surveyed from 6H-SiC (0001) surface (Fig. 2(b) and Fig. S2(a, b)). AFM topography of the sample is shown in Fig. 1(d, e) and Fig. S2(c).

(2) PMG2 route (Fig. S1B)

6H-SiC wafer was introduced into a tube furnace, lying on its Si-terminated. The AH mixed gas flow was introduced, and the pressure in the furnace was maintained under 1 atm. Upon heating, the

heating rate was maintained around for 5 °C/min, and the AH mixed gas flow was around 100 mL/min. When the temperature rose to 1550 °C, the mixed gas AH was stopped from flowing by closing the valve. After holding temperature for 40 minutes, the concentration of Si vapor reached a balance value, i.e. saturate vapor pressure. With the annealing time elongating, the pressure in the furnace would increasing and beyond 1 atm finally (around 1atm+4kPa). The furnace was scheduled to cool down, lowering the balance Si pressure down to as well. The Si particles nucleated on the 6H-SiC (0001) substrate, and grew up by driving force of silicon pressure difference. Typical cooling rate was 10 °C/min. The improved or optimized process towards preparation of a-Si nanosphere arrays is illustrated in Fig. S3(a). 6H-SiC (0001) surface were checked by SEM (Fig. S3(b, c)), demonstrating a-Si nanospheres with a more pronounced array shape.

(3) PMG3 route (Fig. S1C)

The substrates were heated to 1550 °C and maintained for 40 min in an atmosphere of AH mixed gas with a pressure of 1 atm + 5 kPa. Upon cooling, the pressure in the furnace was adjusted to 1atm, and typical cooling rates were 10 °C/min. Once the temperature drops, the hexagonal pyramid-like submicron c-Si particles nucleated immediately. These particles further agglomerated to silicon oligomers (dimers, trimers, tetramers, etc.) over the margin of the SiC surface, which could exhibit typical anisotropy optical properties³⁻⁵, referring to Raman scattering (Fig. 3(a)). The SEM morphology of the sample is shown in Fig. S5.

Characterization of the samples: The morphologies of a-Si nanosphere arrays were examined by SEM (JEOL, JSM-7610F) at 5 kV. AFM (Asylum Research, MFP-3D-BIO) was used to observe the topographies and heights of monodisperse a-Si nanospheres in tapping mode. HRTEM (FEI, Titan G2 60-300) samples were prepared by focused ion beam process (FEI, Helios 450S dual Beam). The morphology and structure of the a-Si nanospheres were investigated by HRTEM, with the EDS (Bruker, super-X) and the EELS line scanning by Enfinium-EREELS. Raman spectra were measured with a Raman spectrometer (Thermo Scientific DXR) using 455 nm laser light at room temperature. Ultraviolet visible diffused reflectance spectrum were measured by UV-vis spectrophotometer (Shimadzu, UV-3600).

2. Preparation of monodisperse a-Si nanospheres by PMG1

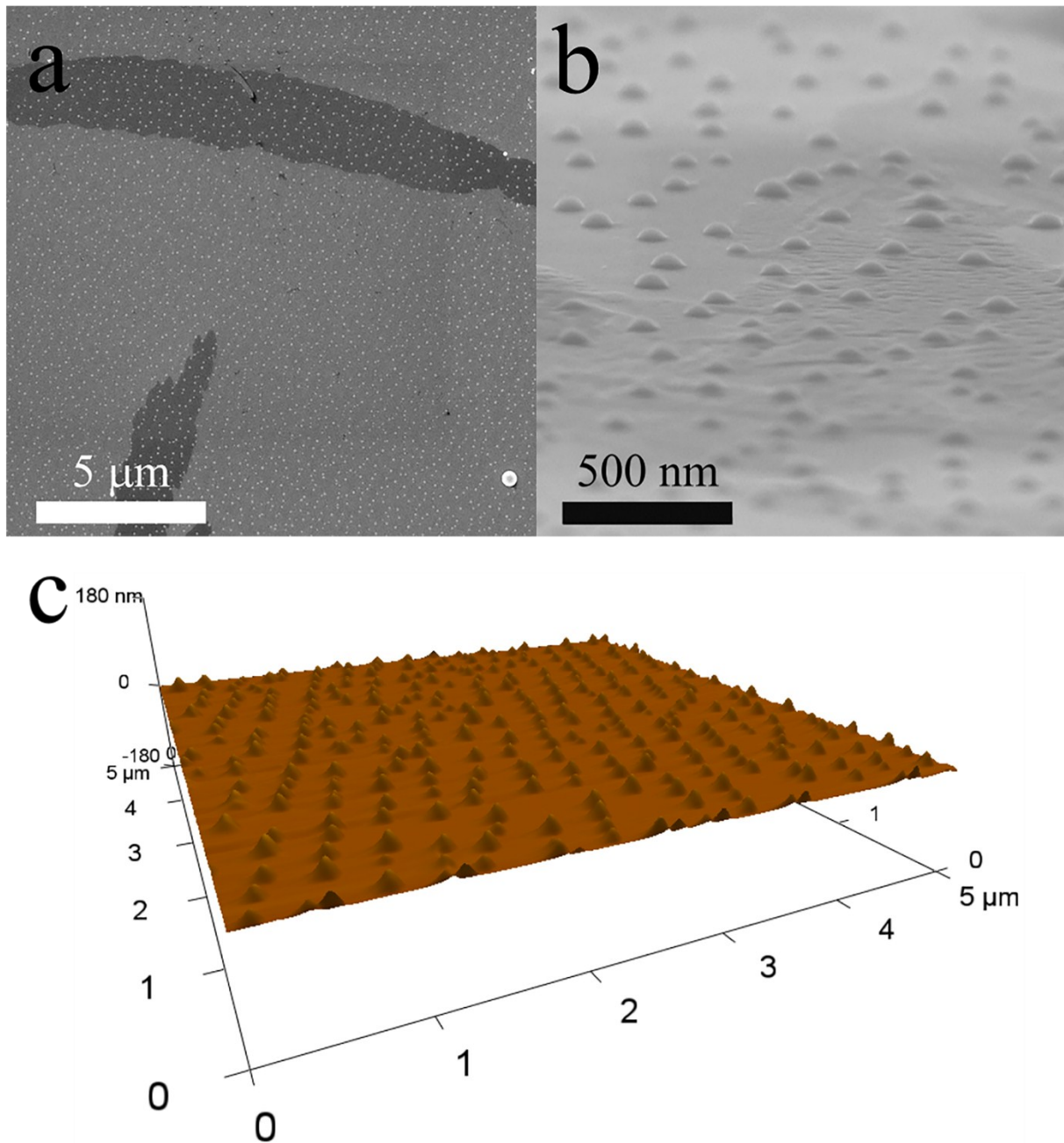


Fig. S2 (Color online) Morphologies of monodisperse a-Si nanospheres. (a) Planar top-view SEM images of monodisperse a-Si nanospheres on 6H-SiC (0001). (b) Side-view image of a-Si nanospheres. (c) Three-dimensional AFM image of Fig. 1(d).

3. The optimized experiment for a-Si nanospheres with a better-pronounced array shape by PMG2

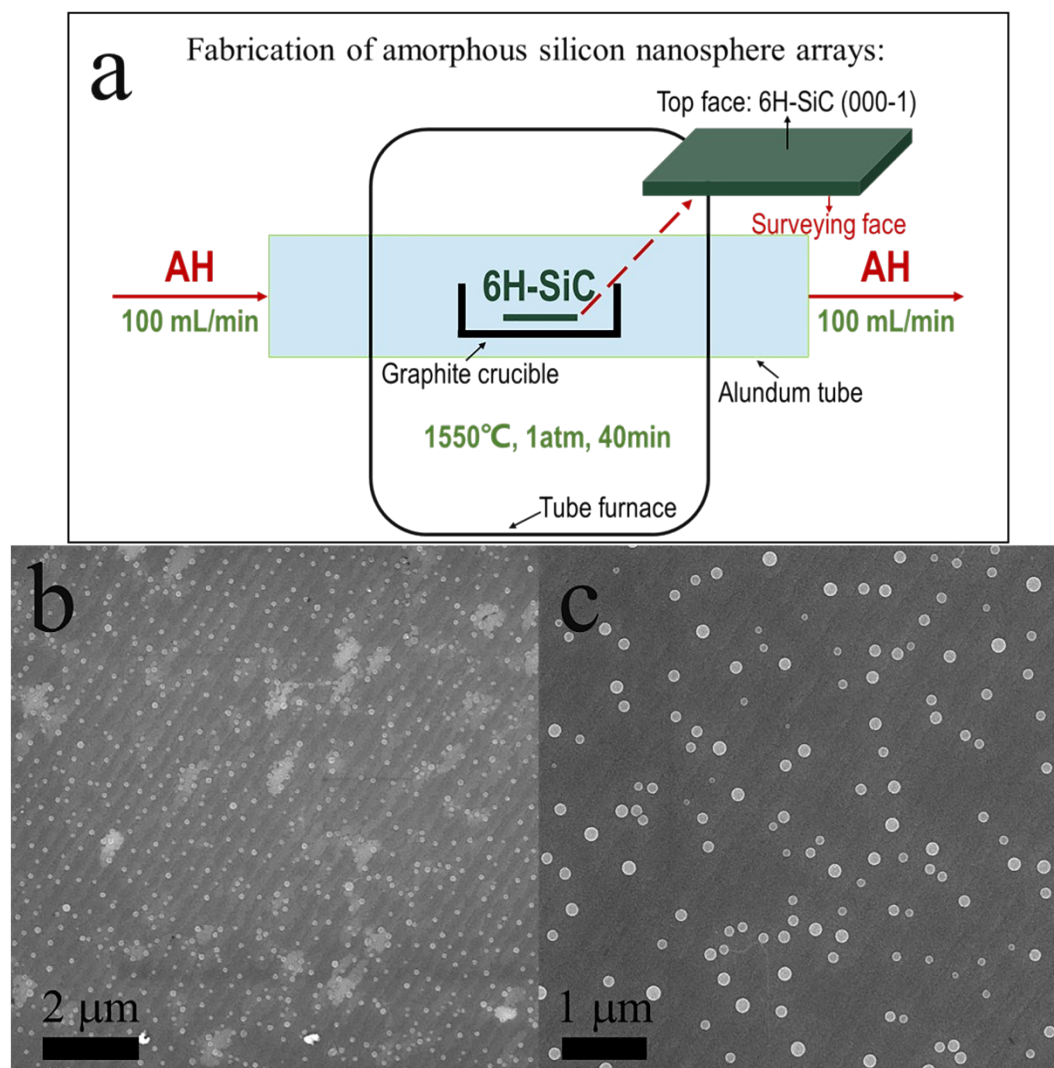


Fig. S3 (Color online) Optimized process towards preparation of a-Si nanosphere arrays on 6H-SiC (0001). (a) Schematic diagram of fabrication of a-Si nanosphere arrays by optimized experiment. (b, c) Top-view SEM images of a-Si nanosphere arrays with more obvious array shape on 6H-SiC (0001).

4. Controlling a-Si nanosphere size by PMG2

Amorphous silicon nanospheres in array were prepared on 2-inch 6H-SiC(0001), purchased from Tanke Blue Co. LTD. After rinsing with buffered HF acid, acetone, and deionized water successively, the substrate was put into a graphite crucible, and transferred to an alumina tube chamber. In an atmosphere of AH mixed gas (95 vol% Ar + 5 vol% H₂), the wafers are heated to 1550 °C and maintained for 40 minutes. During the cooling process, Si particles nucleate on the surface of the SiC wafer via a PMG process.

Referring to PMG2 route (Fig. S3), SiC wafer was put into the graphite crucible, lying on 6H-SiC

(0001) (LP1), suggesting the top face is 6H-SiC (000-1). Upon cooling, the rate was set as 10 °C/min, and a-Si nanospheres arrays were detected on the 6H-SiC (0001) (Fig. S4(b)). We controlled the size of Si nanoparticles by decreasing the cooling rate, equating to elongate annealing time, such as 20 °C/min (Fig. S4(a)), 10 °C/min (Fig. S4(b)), and 1 °C/min (Fig. S4(c)). If SiC wafers was lying on SiC (000-1) (LN1), the size of nanospheres on SiC (0001) was normally larger than those derived from LP1 technique, suggesting the size of a-Si nanospheres could be controlled by limiting ripening time.

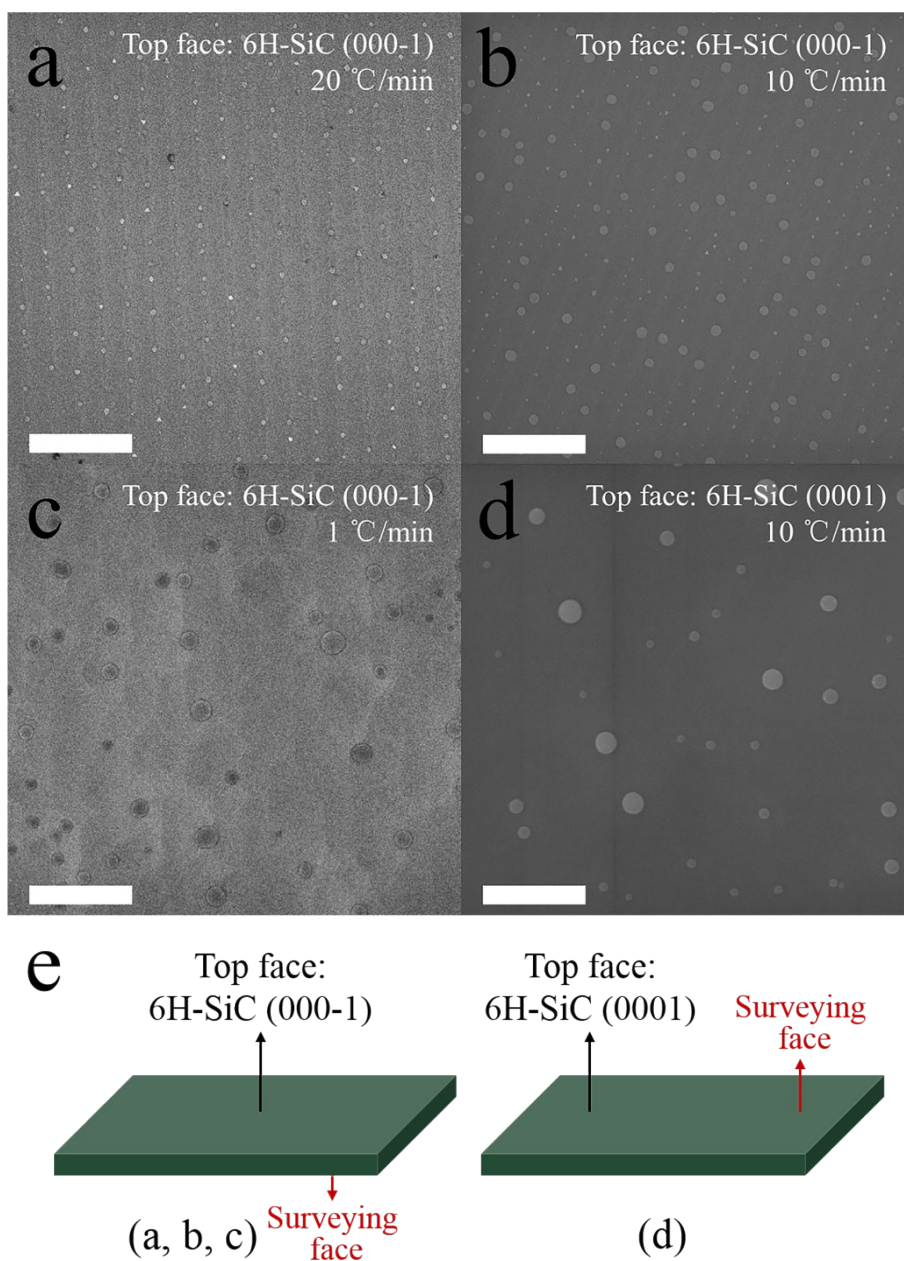


Fig. S4 The distribution of a-Si nanospheres on Si-terminated 6H-SiC (0001) surface. (a-c) The a-Si nanoparticles by adjusting growth conditions, including changing cooling rate or top face of SiC wafers lying on the graphite crucible during the experiment. Scale bars are 1 μm . C-terminated

face upwards during the experiment and the cooling rate is controlled as 20 °C/min (a), 10 °C/min (b), or 1 °C/min (c). (d) Si-terminated face upwards during the experiment, the cooling rate is 10 °C/min. (e) Schematic diagrams of surveying face in SEM characterization and its upward/top face of wafers lying on the graphite crucible in the reaction process.

5. Nucleation process of hexagonal pyramid-like c-Si particles by PMG3

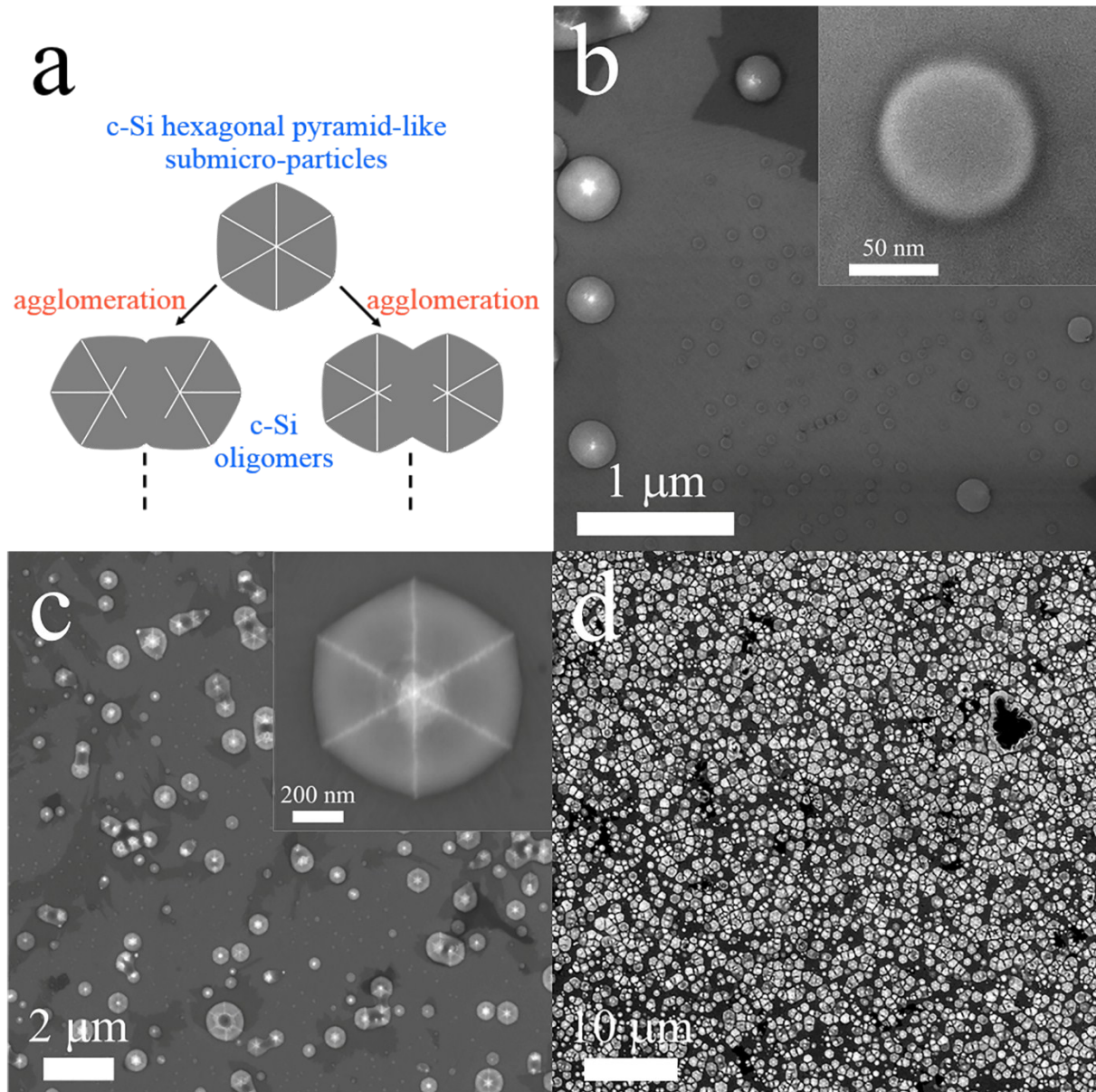


Fig. S5 (Color online) Nucleation process of c-Si particles. (a) Schematic diagram of gradually growth process of c-Si particles. (b) Both a-Si nanospheres and c-Si are available. The inset show single a-Si sphere. (c) The c-Si particles are majority. (d) The c-Si propagates on the full of 6H-SiC(0001).

6. High resolution TEM analysis of a-Si nanospheres

Some specific a-Si spheres are checked by TEM. Three Si hemispheres (black arrows) grow on

the surface of 6H-SiC(0001) (Fig. S6(a)). One of the particles marked “SP” in Fig. S6(a) is enlarged in Fig. S6(b), whose high-resolution image is listed in Fig. S6(c). Fig. S6(d-f) are magnified TEM images, selecting from green, sky blue, and purple frames in Fig. S6(c). The lattice fringes in Fig. S6(d) represent the 6H-SiC substrate, and the middle area of Fig. S6(e) represents the amorphous buffer layer (BFL), where the a-Si nanospheres, marked by violate frame, can be observed as well, connecting with BFL.

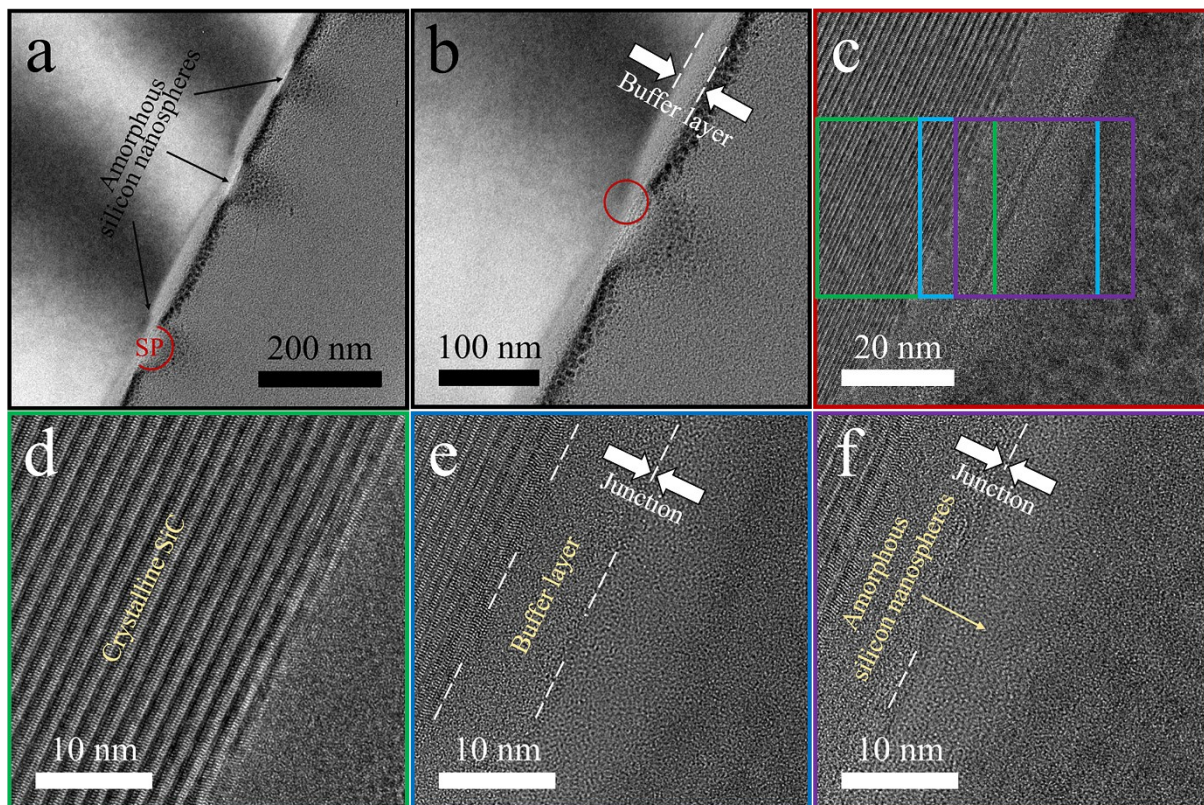


Fig. S6 (Color online) High-resolution TEM analysis of a-Si nanospheres grown on 6H-SiC (0001). (a, b) Low-resolution TEM images, the left side of the images are 6H-SiC substrate. (c-f) HRTEM images of single a-Si nanosphere. (c) TEM photograph of the red circle area of (b), (d-f) magnified TEM images of the green, sky blue, and purple squares in (c), respectively.

7. EELS analysis of single a-Si nanosphere

Amorphous silicon nanospheres were subjected to FIB sectioning. Before FIB process, Cr powders were deposited as a protective layer on the surfaces of the hemispheres to fix the spheres and surface of substrate. The prepared sample was covered with conductive carbon powders to enhance the test signal. We first find a sphere (Fig. S7(a)) and perform the EELS sweep from bottom to top, and the results are shown in Fig. S7(b). The blue, red, and black lines depict the

changes in the Si, carbon (C), and oxygen (O) elements of the green line in Fig. S7(a). The SiC substrate is initially scanned, and then the intensity of Si and C gradually decreased, which represent the buffer layer Si_xC_y . When scanning to the hemisphere, the C intensity is minimized and the scan line of Si intensity has a convex peak, suggesting the hemisphere is silicon. For comparative analysis, we performed an EELS analysis on the non-hemisphere (Fig. S7(c)). The EELS line scan is shown in Fig. S7(d). From the bottom to the top, the substrate is SiC, the buffer layer is Si_xC_y . The line scan is continued, the Si intensity is reduced to the lowest value, and the C intensity is increased due to conductive carbon. In summary, the nanosphere is Si, and the buffer layer between the sphere and the substrate is Si_xC_y .

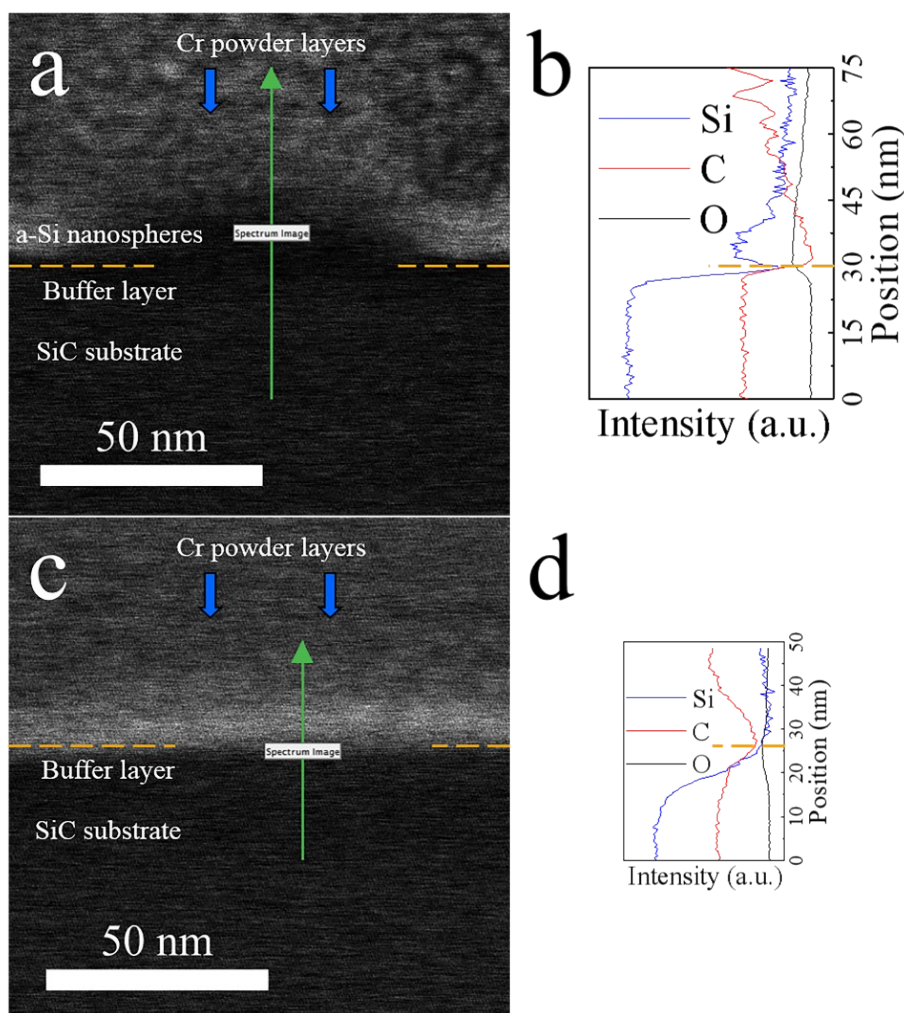


Fig. S7 (Color online) EELS analysis of single a-Si nanosphere. EELS profile for Si, C and O elements of with (a, b) and without (c, d) a-Si nanosphere, respectively. Blue, red and black line in (b, d) indicate the three elements of Si, C and O, respectively.

8. Formation mechanism of buffer layer and junctions between hemisphere and buffer layer

When the SiC wafer is heated in the tube furnace with the program, the amorphous buffer layer is formed on the SiC surface with the gradual sublimation of silicon (Fig. S8(a)). During the annealing process, the silicon vapor by sublimation reaches a balance pressure. Once the temperature drops, the silicon particles nucleate immediately. The initial annealing pressure determines the nucleus size (Fig. S8(b)), and successive growth should be limited by the total silicon vapor. If the density is high and size of nuclei is small, the growth should fail to proceed upon depletion of Si vapor, where the total vapor is determined by temperature (Fig. S8(c)). As a result, the pressure determines the nucleus size and density, whereas the temperature determines the total Si vapor. Since the nanospheres are formed by deposition of silicon vapor, suggesting the nanosphere is connected by junction to BFL. The continuous sublimation of the silicon underneath the particles would be inhibited by particles (Fig. S8(c)). The greater the pressure at cooling, the smaller the size and higher density of the silicon spheres (Fig. S8(b)).

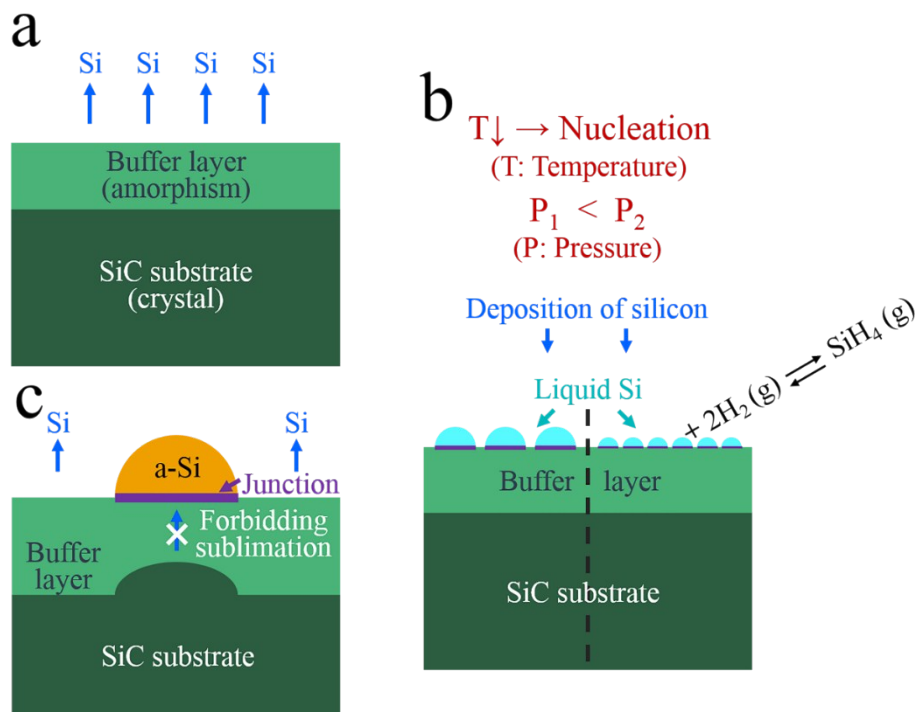


Fig. S8 (Color online) Formation mechanism of silicon hemisphere, junction, buffer layer. Schematic diagram of the formation of buffer layer (a), the nucleus size and densities depending on pressure (b), the nucleation initiation depending on temperature reduction and the thickness of the buffer layer depending on the presence or absence of Si spheres (c).

9. The application of mono-dispersed a-Si nanocavities in light absorption

The reflectance mechanism is illustrated in Fig. S9. Upon the surface of the ABS structure (Fig. S9, bottom square, corresponding to the black spectrum), the incident light irradiation can focus on the a-Si sphere surface, scattering part of the incident light out of the array forest, and part of it in the array forest (Fig. S9, arrow 1), mimicking a black body absorber. After removal of the a-Si spheres from the ABS structure, the incident light can focus on the surface of the BS structure (Fig. S9 upper square, corresponding to the red spectrum), reflecting even more light back (Fig. S9, arrow 2) than the ABS surface.

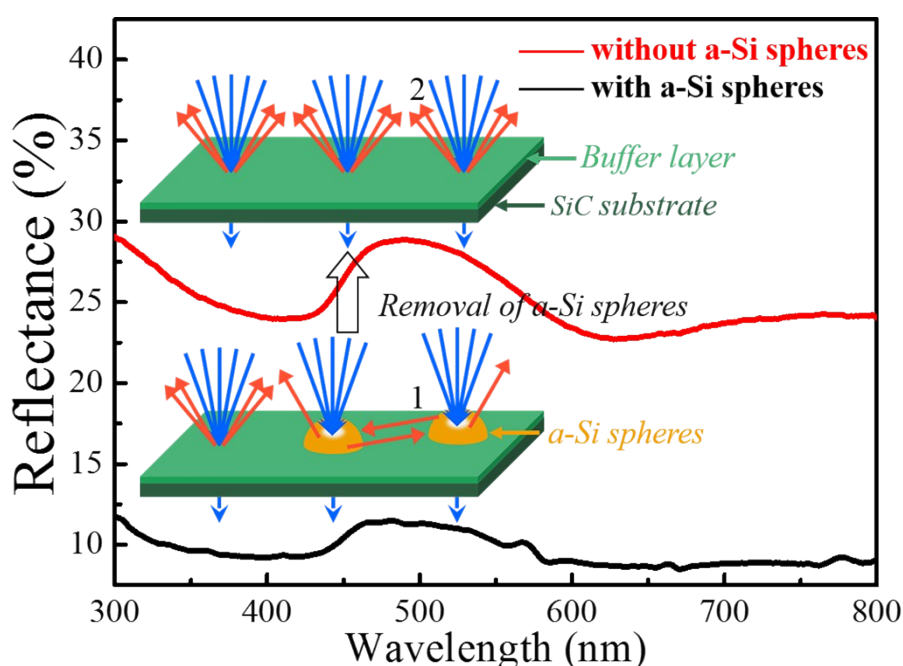


Fig. S9 The application of mono-dispersed a-Si nanocavities in light absorption. The ultraviolet-visible diffused reflectance spectrum of a-Si nanosphere arrays obtained from optimized experiments (black line) and the removal of a-Si spheres by simple acidification (red line).

10. Removal of a-Si spheres by simple acidification

Amorphous Si nanosphere arrays prepared by optimized experiments were placed in a Polytetrafluoroethylene beaker, and then 50 mL of concentrated HF ($\geq 40\%$) and 0.045 g of NH_4F were added for acidification. After soaking for 60 minutes at room temperature, the samples were blown dry with a nitrogen gun. The morphologies of the sample of removal of a-Si spheres by simple acidification were examined by SEM (JEOL, JSM-7610F) at 5 kV. Prior to acidification, the a-Si nanospheres are arranged along the surface steps (Fig. S4(b)). After adding HF acid, Si reacts

with HF. After the reaction, the Si nanospheres are removed and leaving the trail on the surface of SiC. The low to high magnification SEM images of the sample of removal of a-Si spheres refer to Fig. S10.

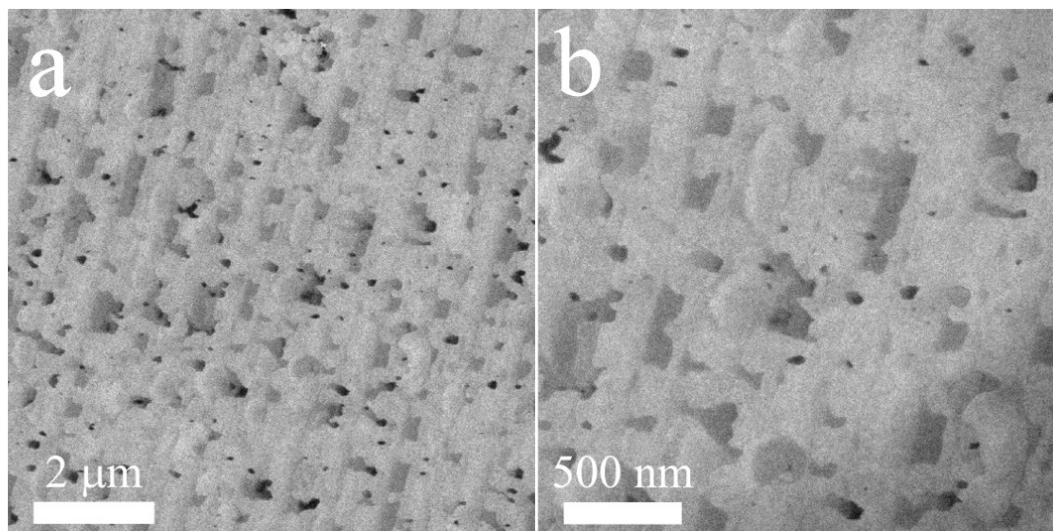


Fig. S10 Morphologies of removal of a-Si spheres by simple acidification. SEM images of the sample of removal of a-Si spheres from low to high resolution at 20,000X (a), 40,000X (b), confirming a-Si spheres were indeed removed.

References

1. Q. Huang, X. Chen, J. Liu, W. Wang, G. Wang, W. Wang, R. Yang, Y. Liu and L. Guo, *Chem. Commun.*, 2010, **46**, 4917-4919.
2. Q. Huang, G. Wang, L. Guo, Y. Jia, J. Lin, K. Li, W. Wang and X. Chen, *Small*, 2011, **7**, 450-454.
3. J. Yan, P. Liu, Z. Lin, H. Wang, H. Chen, C. Wang and G. Yang, *ACS Nano*, 2015, **9**, 2968-2980.
4. U. Zywietz, M. K. Schmidt, A. B. Evlyukhin, C. Reinhardt, J. Aizpurua and B. N. Chichkov, *Acs Photonics*, 2015, **2**, 913-920.
5. J. van de Groep, T. Coenen, S. A. Mann and A. Polman, *Optica*, 2016, **3**, 93-99.
6. K. Mizuno, J. Ishii, H. Kishida, Y. Hayamizu, S. Yasuda, D. N. Futaba, M. Yumura and K. Hata, *Proceedings of the National Academy of Sciences*, 2009, **106**, 6044-6047.