Supporting Information

Nature of Hexagonal Silicon Forming via High-Pressure Synthesis: Nanostructured Hexagonal 4H Polytype

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1. Detailed HP-HT Synthesis Procedure

For the high-pressure synthesis, a 10/5 multianvil assembly was employed. Experimental setup is analogous to the one already reported in [1]. The sample pellet (1.95 mm diameter, 2.12 mm height and prepared in an Ar-filled glovebox) was surrounded by an *h*BN sleeve (2.75 mm outer diameter (OD), 1.96 mm inner diameter (ID), 2.12 mm height) and a Ta foil (25 μ m thickness, 2.90 mm OD) resistance furnace. The use of a Ta foil heater over a graphite one allowed us to increase the sample volume due to the significantly thinner furnace. The Ta foil was inserted into a 10 mm octahedron edge length (OEL) Cr₂O₃-doped MgO octahedral pressure medium, along with ZrO₂ plugs. The cross-section of the octahedron that shows the placement of the different components of the assembly is reported in Figure S1a.

MgO octahedron was positioned between eight truncated 25 mm tungsten carbide cubes (ha7, Hawedia) with 5 mm truncation edge length (TEL) equipped with pyrophyllite gaskets. Along the beam direction two cylindrical 2 mm OD amorphous SiBCN X-ray windows and ~4 mm wide amorphous boron epoxy rectangles were inserted into the octahedron and gaskets respectively, as shown in Figure S1b.



Figure S1. Schematic view of the HP assembly. (a) Cross-section of the MgO/Cr₂O₃ octahedron used as pressure medium. (b) Scheme showing the arrangement of WC cubes, gaskets and the octahedron during the experiment. X-Ray transparent windows of amorphous boron epoxy and amorphous SiBCN ceramic were inserted along the direction of the beam in the gaskets and in the octahedron respectively.

The assembly was subsequently compressed at a rate of 0.04 GPa/min up to 13 GPa and heated in a Voggenreiter modified-cubic press located at the beamline ID06-LVP, ESRF [2]. During compression pressure was estimated using d-Si equation of state (EOS) [3] before starting the heating and was then assumed quasiconstant during the heating.

Temperature evolution during the heating is reported in Figure S2. Heating was performed at a rate of 26 K/min up to 604 K and then rate was decreased to 13 K/min up to 833 K. The temperature was then dwelled for 20 minutes to check the transformation Si-I→Si-II. To observe the complete disappearance of Si-I peaks,

temperature was raised up to 870 K (rate 16 K/min) and then dwelled for other 20 minutes. During the dwell, hydraulic primary pressure in the main RAM was increased of 20 bar to compensate the pressure loss during Si-I→Si-II transformation and maintain the sample pressure at 13 GPa. As soon as the reaction was complete, the system has been quenched to ambient temperature. Temperature was evaluated using Si melting temperature to calibrate the Power-Temperature curve.



2. Electron Diffraction Patterns and FFT-TEM proof of Si-4H stacking faults



Figure S3. TEM image and Electron Diffraction pattern of the sample (zone 15). Green dots are simulated Si-4H diffraction pattern along [010] and [100] direction respectively.



Figure S4. FFT-TEM patterns of zone 3 of the sample, shown also in the main text. Green dots are simulated Si-4H diffraction pattern along [2 - 2 3] and [0 0 1] direction respectively. As visible in the upper panel, the spots of [2 - 2 3] pattern are deformed along one precise direction; looking at the projection on the right, we see that this direction corresponds to the [0 0 1], i.e. the *c* axis. The deformation of the spots can thus be interpreted as due to stacking faults, that cause the superposition of several domains along the [0 0 1] direction. On the contrary, looking at the [1 0 0] pattern, that is perpendicular to the *c* axis, no deformation of the spots is observed.



Figure S5. FFT-TEM patterns are compared with simulated electron diffraction patterns for Si-2H, Si-4H and Si-6H polytypes. From left to right, for two different patterns are reported: FFT-TEM data; Si-4H simulation superimposed to the data to underline the good agreement between data and simulation; Si-2H and Si-6H simulation of the electron diffraction pattern along the same direction. Comparison evidences that the experimental data are compatible with Si-4H structural model and could not be explained with other hexagonal polytypes.



Figure S6. TEM image and Electron Diffraction pattern of the sample (zone 14). Green dots are simulated Si-4H diffraction pattern along [010] and [100] direction respectively.

3. DFT Calculations Results

Calculations for the NMR chemical shift and for Raman spectra were done using density functional theory (DFT) using periodic boundary conditions, plane-waves and pseudopotential approaches as implemented in the Quantum ESPRESSO package [4-5] (see Sect. 4 for computational details).

The difference between the applied external magnetic field and the effective magnetic field at the nucleus positions is at the origin of the NMR chemical shift. It can be obtained by calculating, for a given crystalline structure, the shielding of the nuclei relative to the electronic current induced by the external magnetic field. This induced current can be calculated by using the GIPAW (Gauge Including Projector Augmented Wave) approach, which allows reconstructing the all-electron magnetic response from the pseudo-wavefunctions. In Table S1 calculated ²⁹Si NMR chemical shifts are reported for Si-2H, Si-4H and Si-4H polytype; d-Si is reported for comparison.

Table S1. 251 NIVIR Chemical Shifts of Hexagonal SI Polytypes		
	Crystallographic position	δ _{iso} (²⁹ Si) [ppm]
Si-I (d-Si), O ⁷ h	Si	-79
Si-2H D ⁴ ch A	Si	-122 7
	51	122.7
Si-4H, <i>D</i> ⁴ _{6h}	Si1	-127.7
	Si2	-96.9
Si-6H, <i>D</i> ⁴ _{6h}	Si1	-90.0
	Si2	-90.4
	Si3	-128.8

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The simulated Raman spectra are obtained within the non-resonant (Plackzek) approximation: the position (Stokes Raman shift) of the peaks is equal to the zero-wavevector phonon vibrations ω_{ν} (ν is the branch index) and the corresponding intensity I_{ν} is given by:

$$I_{\nu} \propto |\boldsymbol{e}_{i} \cdot \boldsymbol{\vec{A}}^{\nu} \cdot \boldsymbol{e}_{s}|^{2} \frac{1}{\omega_{\nu}}(n_{\nu}+1),$$

where e_i (e_s) is the polarization of the incident (scattered) radiation, n_v is the phonon occupation given by the Bose-Einstein statistics (calculated for room temperature), and $\overleftrightarrow{A}^{\nu}$ is the Raman tensor. The Raman tensor can be calculated as the derivative of the dielectric tensor $\overleftarrow{\epsilon_{\infty}}$ with respect to the atomic displacement pattern corresponding to the phonon mode v. In the present work the phonon frequencies were calculated using standard first-order density functional perturbation theory [6] and the Raman tensor was calculated using the second-order approach of Ref. [7]. Both approaches are exact within DFT and the computational details are given in Sect. 4.

Table S2. Frequency of the	Raman active modes of	¹ Hexagonal Si Polytypes
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Mode	Degeneration	Raman Shift [cm ⁻¹]	Relative Intensity	
Si-2H, D ⁴ 6h 4	atoms/unit cell			
A1g (LO)	1	511	1	
<i>E</i> 1g (TO)	2	511	0.11	
<i>E_{2g}</i> (TO)	2	496	0.14	

Si-4H, D ⁴ 6h 8 atoms/unit cell				
<i>E</i> _{1g} (TO)	2	518	0.22	
<i>A</i> _{1g} (LO)	1	513	1	
<i>E_{2g}</i> (TO)	2	501	0.34	
<i>A</i> _{1g} (LO)	1	416	0.05	
Si-6H, D ⁴ _{6h} 12 atoms/unit cell				
<i>E</i> _{1g} (TO)	2	518	0.29	
<i>A</i> 1g (LO)	1	515	1	
<i>E_{2g}</i> (TO)	2	510	0.44	
<i>E_{2g}</i> (TO)	2	491	0.02	
<i>A</i> _{1g} (LO)	1	462	0.05	

It is known that LDA-DFT slightly underestimates the phonon frequencies of the considered Si polymorphs. In order to simplify the discussion of FigureS4 in the main text, we have upshifted the calculated frequencies by +2.6 cm⁻¹ so that the frequency of diamond Si (d-Si) coincides with the experimental value of 521 cm⁻¹. Results are reported in Table S2. Note that, in [8] the Raman active A_{1g} and the E_{1g} modes of Si-2H are split by 9 cm⁻¹. A similar splitting is not observable in the calculations reported by [9] and also according to the present calculation (Table S2) the two modes have the same frequency. We remark that all the present calculations are done by relaxing, through energy minimization, the two cell parameters of the hexagonal cell and the atomic positions. If we compute the Raman spectra of the ideal configuration for the wurtzite structure (with ideal c/a ratio and no relaxation of the internal degrees of freedom), we obtain that the A_{1g} and the E_{1g} modes of Si-2H are split by ~10 cm⁻¹, similar to the value reported by [8]; this split is reduced to ~8 cm⁻¹ if we relax only the atomic position but we keep the ideal cell parameters, and it disappears once we let both relax. We argue that this is the origin of the mentioned discrepancy.

In order to compare with previous literature [10-11] in Figure S7 we show the electronic band structures of the polytypes described in the text. There is a good agreement with the LDA-DFT results previously published. All hexagonal polytypes of Si are indirect bandgap semiconductor, with the maximum of the valence band at the Γ point and the minimum of the conduction band at the M point for Si-2H and moving along the M- Γ line for Si-4H and Si-6H. Indirect bandgap values are smaller than that of d-Si [10-11], with a clear trend of approaching d-Si value with decreasing "hexagonality" (i.e. from Si-2H, 100% hexagonal, to Si-4H, 50%, and Si-6H, 33%). Since LDA-DFT systematically underestimates the bandgap value, another useful reference for understanding hexagonal Si optoelectronic properties is given by [12]. In this study, manybody perturbation theory was used to compute quasiparticle band gaps and optical absorption spectra for Si-2H. With this approach, more reliable value for the electronic bandgaps can be obtained. While the computed value of the indirect bandgap (0.95 eV) is not substantially smaller than d-Si one (1.14 eV), a larger difference is found for the direct transition at the Γ point, i.e. 1.63 eV for Si-2H compared to 3.20 eV for d-Si. This reduction of the transition energy is due to the backfolding of d-Si electronic bands when the symmetry changes from cubic to hexagonal in Si-2H and has the effect on increasing the absorption in the whole visible spectral range compared to d-Si [12]. Even though this study addresses Si-2H and this approach has not yet been applied to Si-4H, it seems reasonable to expect that all hexagonal polytypes would exceed d-Si absorption in the visible range. Indeed, this absorption increase is primarily caused by the change in the symmetry and by the reduction of the transition energy at the Γ point, which has been reported by LDA-DFT calculations for both Si-4H and Si-6H [10]. Another factor that could play a fundamental role for increasing hexagonal Si polytypes absorption is crystal size. Indeed, the transition at the Γ point is optically forbidden in Si-2H [12], but we could expect a relaxation of dipole transition selection rules in strongly confined system which could tremendously raise the absorption around the direct bandgap energy.



Figure S7. Electronic band structures of different polytypes as calculated by LDA-DFT. 3C polytype (i.e. cubic d-Si) is reported for comparison. Our results are in good agreement with previous calculations [10-11].

4. Experimental and Calculation Procedures

In-situ X-Ray Diffraction

During HP-HT synthesis at the ESRF, angle-dispersive PXRD patterns were collected continuously. The data write-rate was typically maintained at 32s/pattern during compression and decompression, while during the heating rate was increased up to 0.1s/pattern and 32X rebin. A constant wavelength ($\lambda = 0.3757$ Å) was selected by a Si111 double-crystal monochromator from the emission of a U18 cryogenic insertion device at ~6 mm magnetic gap. Data acquisition was performed in the 2 θ range of 6.27–14.64° using a Detection Technology X-Scan series1 linear pixelated detector. Sample-to-detector distance and the detector offset were calibrated using LaB6-SRM660a (NIST). Data were integrated and manipulated using Fit2D software [13-14].



Figure S8. Comparison of XRD diffraction measured pattern and computed profiles for different hexagonal polytypes. Data are reported with a black line and were collected using a Mo radiation source ($\lambda_{K\alpha 1} = 0.709319$ Å, $\lambda_{K\alpha 2} = 0.713609$ Å). Structural models for hexagonal polytypes are taken from [10] and thus do not correspond with the ideal polytypic structure, but with a relaxed one obtained by DFT calculations.

X-Ray Diffraction at IMPMC

X-Ray powder diffraction measurements were carried out at the XRD platform of the IMPMC on a Rigaku MM007HF diffractometer equipped with a Mo rotating anode source ($\lambda_{K\alpha 1} = 0.709319$ Å, $\lambda_{K\alpha 2} = 0.713609$ Å), Varimax focusing optics and a RAXIS4++ image plate detector. X-ray data were collected at 25°C between 0° and 30° 20 with a 0.028° 20 step. Cell parameters, crystallite sizes and microstrain were refined using Rietveld method as implemented in the Fullprof [15-16].



Figure S9. 2D diffractogram of Si-4H sample. Since there is no evidence of texture in the sample, such effects have not been taken into account when performing Rietveld refinement.

A Rietveld refinement was performed starting from the known model for Si-4H [10]. The unit cell and Si atomic positions were refined first. Then, since the peak width was larger than the instrumental one, isotropic size (Y) and isotropic strain (X) parameters were refined. The two effects can be decoupled on the diagram because the first induces a peak broadening as Y/cos θ whereas the second as Xtan θ . Then, anisotropic refinements of size parameters allowed to improve the fit and the corresponding spherical harmonic coefficients are given in the following tables. To perform anisotropic size refinement, Y (isotropic Lorentzian size parameter) was reset to zero. Fractional atomic coordinates along the *c* axis were then refined independently for both Si atoms (4e and 4f), while a constrain maintained the isotropic displacement B equal for both atomic site. The result of Rietveld refinement are reported, together with the corresponding errors, in the following tables.

Table S3. Results of the	Rietveld refinement	on the X-Ray	powder pa	attern of Si4H
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Si4H , X-ray Diffractometer, λ_{Mo}				
P 6₃/mmc			R _{Bragg} = 18.1 %	
<i>a</i> = 3.7948(7) Å	b = 3.7948(7) Å	<i>c</i> = 12.7099(60) Å		
<i>V</i> = 158.51(8) Å ³				
Size Parameters				
Y00 = 14.5(1.3), Y20	= 11.6(1.3)			
Strain Parameters				
X = 2.2(2)				

Atom	x	У	Z	B(eq)
Si1 (4e)	0	0	0. 0906(5)	1.94(6)
Si2 (4f)	1/3	2/3	0. 1646(8)	1.94(6)

Table S4. Fractional atomic coordinates and equivalent isotropic displacement parameters

Photoluminescence

PL measurements have been performed at ambient temperature using the blue excitation laser beam (λ = 460 nm, 10 µm beam spot) of an Ar laser. The PL & Raman spectra were collected using a high-resolution confocal Horiba Jobin Yvon HR800 µRaman system with Peltier-chilled Si detector. The spectrometer was calibrated at room temperature using Ne lines for absolute energy values (for PL spectra) and a single crystal of cubic Si for relative inverse wavenumber (for Raman spectra). A laser power at the sample was estimated to be less than 30 mW. No effect due to laser heating of the sample was observed. Raman spectra have been performed prior to PL in order to assure the good signal from the sample.

Nuclear Magnetic Resonance + DFT Calculations

²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) experiments were performed at LCMCP on a 700 MHz AVANCE III Bruker spectrometer operating at 139.15 MHz, using a 2.5 mm Bruker probe spinning at 20 kHz. A single-pulse excitation with a flip angle of 90° and a recycle delay of 200 s were used. ²⁹Si chemical shifts were referenced to TMS.

The theoretical ²⁹Si NMR properties of various Si polytypes were investigated within the DFT framework, using periodic boundary conditions and the generalized gradient approximation (GGA) to the exchange-correlation functional as proposed by Perdew, Burke and Ernzerhof [17]. The NMR chemical shift describes the difference between the applied external magnetic field and the magnetic field at the nucleus positions. It can be obtained on the structural model by calculating the shielding of the nuclei relative to the electronic current induced by the external magnetic field. This current was calculated by using the GIPAW approach, which allows reconstructing the all-electron magnetic response from the pseudo-wave-functions [18-19]. The calculations were performed using the PWscf and GIPAW codes of the Quantum ESPRESSO package [4-5]. Norm-conserving pseudo-potentials were used and the wave functions kinetic energy cutoff was increased to 80 Ry. The integral over the Brillouin zone was done using Monkhorst-Pack 13×13×8, 16×16×5, 15×15×3, *k*-point grids for Si-2H, Si-4H and Si-6H structures respectively. A 10×10×10 *k*-point grid was used for Si-1, calculated as a reference. The isotropic chemical shift δ_{iso} is defined as $\delta_{iso} = -(\sigma - \sigma^{ref})$, where σ is the isotropic shielding (one-third of the trace of the NMR shielding tensor) and σ^{ref} is the isotropic shielding of the same nucleus in a reference system. In our calculations, absolute shielding tensors are obtained. To fix the scales, σ^{ref} was chosen by comparing experimental (79 ppm) and calculated δ_{iso} values of Si-1.

Raman Spectroscopy + DFT Calculations

The Raman spectra were recorded at the IMPMC spectroscopy platform on a HR460 (Jobin-Yvon/Horiba) spectrometer using as excitation source an Ar⁺ laser under 514.5 nm excitation wavelength. The light was dispersed in a grating of 1500 lines and centered in 532 nm. The power of the laser was kept lower than 15 mW over the sample to avoid overheating and the typical recording parameters for the spectra were 5 accumulations of 30s each.

Density functional theory calculations were done with the quantum-espresso package [4-5], by using the local density approximation [20-21], norm-conserving pseudopotential and plane-waves (80 Ry energy cut-off) approaches. The Brillouin zone integration is performed by using k-points sampling with a grid equivalent to the 10x10x4 for the Si bulk in the hexagonal 3C structure (6 atoms per cell). Atomic positions and cell parameters were always relaxed by energy minimization. Phonon modes and Raman tensor were calculated with the approaches of [6] and [7]. The Raman spectra shown in the text simulate a non-polarized experiment done on powder and are obtained by averaging over different polarizations and orientations. The 521 cm⁻¹ mode of d-Si has been taken as a reference to evaluate systematic errors. Therefore, in order to make DFT

and experimental d-Si phonon coincide at 521 cm^{-1} , all computed Raman frequencies have been shifted of $+2.6 \text{ cm}^{-1}$.

Transmission Electron Microscopy and Diffraction

TEM observations (High Resolution TEM and Selecting Area Electron Diffraction) were carried out at IMPMC on a Jeol 2100F TEM operating at 200 kV, equipped with a high-resolution UHR pole piece and a Gatan US4000 CCD camera.

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