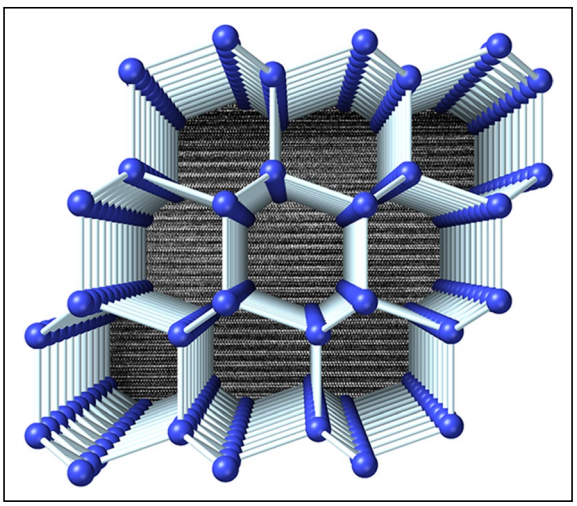
Slow and steady heating wins the race for a new crystalline silicon allotrope

Nearly every piece of silicon in existing transistors and modern electronics exhibits a diamond-cubic (DC) crystalline structure with an indirect bandgap. The bonding arrangement of this ubiquitous semiconductor finitely bounds its electronic properties and caps the capabilities of processors and devices that rely on this material. However, theoretical calculations have long predicted the existence of a thermodynamically metastable hexagonal silicon phase, which is more akin to the layered stacking of silicon carbide than to the covalent network structure of diamond. Moreover, while these predictions calculated similar bandgaps for both the diamond and hexagonal Si phases, elemental substitutions or mechanical strain may convert the latter into a direct-bandgap semiconductor. In turn, this behavior could unlock the use of hexagonal silicon for a much broader range of applications, such as photovoltaics and optoelectronics. Previous synthesis attempts have produced only minute and/or disordered quantities of this material. Resulting bulk hexagonal silicon has, to date, exhibited far too much heterogeneity to enable meaningful characterization of its physical properties.

Researchers from the Earth & Planets Laboratory of the Carnegie Institution for Science in Washington, DC, along with collaborators from RMIT University in Melbourne and The Australian National University in Canberra, have now developed a novel route to obtain this untapped hexagonal silicon phase. Their approach uses another metastable silicon allotrope with an orthorombic structure, Si_{24}, as the starting material. The research team annealed this material under vacuum for three days at 300°C. This slow heating process transitioned the bonding in the solid into a hexagonal metastable phase with sixfold symmetry. Researchers used x-ray diffraction, Raman spectroscopy, and electron microscopy to confirm its structure. Their findings appeared in a recent issue of *Physical Review Letters* (https://doi.org/10.1103/PhysRevLett.126.215701).



Visualization of the crystalline hexagonal structure of *4H*-Si overlaying a transmission electron microscope image of the synthesized material. Credit: Thomas B. Shiell and Timothy A. Strobel.

"There is a current worldwide push to advance semiconductor technology for both renewable energy conversion and next-generation electronics. Novel forms of pure silicon have been predicted to exhibit improved optoelectronic properties that compliment and/or exceed those of the currently used diamond-cubic (DC)-Si," Thomas B. Shiell and Timothy A. Strobel, the Carnegie Institution scientists who led this effort, told *MRS Bulletin*, "Our unique high-pressure/temperature synthesis method has unlocked the discovery of this new, bulk, crystalline allotrope *4H*-Si, offering new technological opportunities for semiconductor devices, including energy conversion, advanced computing, and microelectromechanical systems. We hope our work will encourage further research to scale up and produce usable devices."

During the annealing process, the silicon atoms in the Si_{24} phase transitioned from an orthorhombic arrangement into a hexagonal one with sixfold symmetry (*4H*-Si). The research team demonstrated exceptional microcrystallinity of their newly synthesized silicon material and confirmed its $P6_3/mmc$ space group. Electron microscope imaging revealed an average grain diameter of 0.5 µm. Unlike previously reported hexagonal silicon phases, the material that had been synthesized through this slow-annealing process was free of amorphous material. Optical and electronic structural measurements determined a bandgap of ~1.2 eV, which supports theoretical predictions.

The researchers used computations to assess the thermodynamic stability of the hexagonal silicon phase and the kinetics of its formation. *4H*-Si is a metastable phase of silicon and is more stable than the *2H*-Si allotrope by ~12 meV per atom. Silicon atoms in the Si_{24} structure overcame a 170 meV/atom transition barrier and assembled into hexagonal rings of *4H*-Si. Notably, this pathway is kinetically favored over one that transitions the Si_{24} precuror to diamond-like silicon and possesses a 289 meV/atom transition barrier.

The new approach developed by Shiell, Strobel, and their colleagues unlocks a reliable and repeatable method to synthesize this new crystalline silicon phase. It is the first and essential step toward modifying its structure and tuning its band structure to optimize it for solar energy harvesting and computer memory applications.

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