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EXOTIC FORMS of SILICON

P. Craig Taylor

The element's complex free-energy landscape allows such structural motifs as rings, cages, and channel-like holes to emerge in extreme or unusual conditions.

In the early 1980s, University of Sussex chemist Harold Kroto was trying to prove that long-chain molecules of carbon in space are born not in interstellar clouds, where they had been found years earlier, but in the hot stellar atmospheres of red giants. As part of that effort, he persuaded Richard Smalley and Robert Curl Jr to interrupt their molecular-cluster research on metals and semiconductors and examine the forms that molecular C morphs into at stellar temperatures.

On 1 September 1985, the three used high-energy laser pulses in Smalley's lab to vaporize a graphite sample and ionize the reassembled molecular debris in order to analyze it in a nearby mass spectrometer. In addition to finding the long-chain molecules Kroto expected, they discovered C_{60} , the closed-caged macromolecule buckminsterfullerene. Twelve days later the trio published the results, and the race to discover many other closed-cage, sheet, and open-tube allotropes of C was on. In 1996 Kroto, Smalley, and Curl were awarded the Nobel Prize in Chemistry for their achievement. (See *PHYSICS TODAY*, December 1996, page 19.)

The past 30 years have seen many dramatic discoveries of exotic, low-density forms of C, such as nanotubes, nanobuds, nanoribbons, and, most recently, nanothreads,¹ in which all the C atoms are tetrahedrally bonded, just as atoms are in silicon's most common form, diamond cubic. Silicon is the second most abundant element (behind oxygen) in Earth's crust and the

most technologically significant one. The C discoveries prompt one to wonder whether scientists are on the brink of making similar advances with Si, either by exploring and exploiting its little-known existing allotropes or by discovering new ones predicted by theory. Some indications suggest they are.²

Prior to 1985 there were just four known bulk structures of C: graphite, diamond, and their metastable forms—

rhombohedral graphite and metastable hexagonal diamond. By contrast, there are currently 14 known allotropes of Si: 13 high-pressure forms³ outlined in the box on page 36, and the newly discovered Si_{24} . Most of the 13 allotropes discovered at high pressure are not stable at ambient pressure, and those that are stable are available only in extremely small quantities—a diamond-anvil cell will produce them on the scale of a thousandth of a gram. Such small quantities make investigating mechanical, optical, and electrical properties difficult.

Recently developed techniques that substitute chemical reactions for sustained pressure have spurred interest in synthesizing larger quantities of various allotropes of Si. Other progress toward new allotropes is coming from using alternative methods of pressure exposure and applying them not on elemental Si—the precursor that led to the allotropes described in the box—but on novel precursors that contain a mixture of Si and other elements, such as alkali metals. On the theoretical

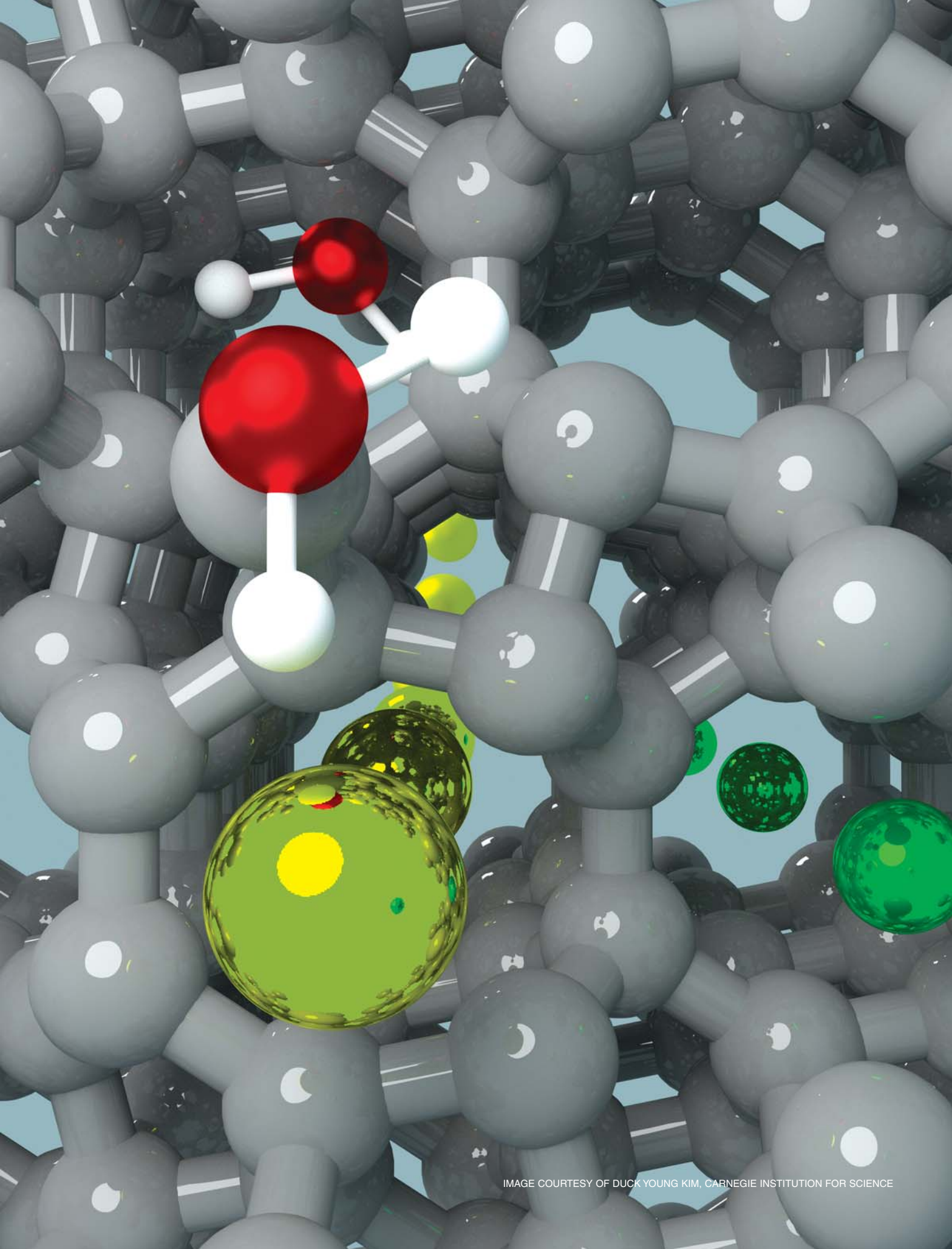


IMAGE COURTESY OF DUCK YOUNG KIM, CARNEGIE INSTITUTION FOR SCIENCE

front, a resurgence of interest in Si over the past couple of decades has resulted from the availability of first-principle approaches, such as density functional theory, for calculating electronic structures and efficiently predicting low-energy crystal structures.⁴

The case for Si

Silicon is abundant, is nontoxic, and forms the basis for the semiconductor devices that abound in most of today's integrated circuits and power electronics. That technological dominance exists because of several advantageous properties of the diamond-cubic lattice structure: its capacity to accept n- and p-type dopants, its ability to grow an oxide surface layer, and its stability at high temperature. Indeed, that form of Si is arguably the most exhaustively studied form of any element in the periodic table, and its various materials properties are understood in minute detail.

Yet little is known about most of the other allotropes of Si. One of the exotic structures could become the basis for the next revolution in electronics. That's partly because the diamond form of Si has an Achilles' heel, at least for photonic applications: The electronic gap between the valence and conduction bands is indirect, meaning that valence electrons can only be photoexcited across the gap when lattice vibrations are simultaneously excited in the crystal. Si devices such as solar cells and lasers, which absorb or emit light, are thus inefficient compared with direct-bandgap semiconductors such as gallium arsenide.

Fortunately, the free-energy landscape of Si is rich in local minima, each of which may correspond to a metastable crystalline phase. One theoretical approach to help determine the structure associated with a minimum considers how to partition three-dimensional space into cells of equal volume with

minimal surface area. That and other recent calculations predict that hundreds of new metastable silicon structures are energetically plausible.^{5,6} And many of those theoretical structures are also predicted to have direct (or nearly direct) bandgaps, which would make them ideal for thin-film photovoltaic cells and other optoelectronic devices.

A historical perspective

Swedish chemist Jöns Jacob Berzelius is generally credited with the discovery of Si in 1824 when he heated a silicate in the presence of potassium to produce K_8Si_{46} and Si, which he subsequently purified by reacting the K_8Si_{46} with water. (Today Si is produced by heating sand [silicon dioxide] and coal to temperatures approaching 2200 °C.) Prior to that discovery, Joseph Gay-Lussac and Louis Jacques Thénard probably produced an impure form of the element by reacting silicon tetrachloride with K. Even before that, French chemist Antoine Lavoisier proposed that the mineral quartz contained a new, as yet undiscovered element, which turned out to be Si. The only other form of Si known in the 19th century was amorphous Si—a material with its own fascinating story.⁷

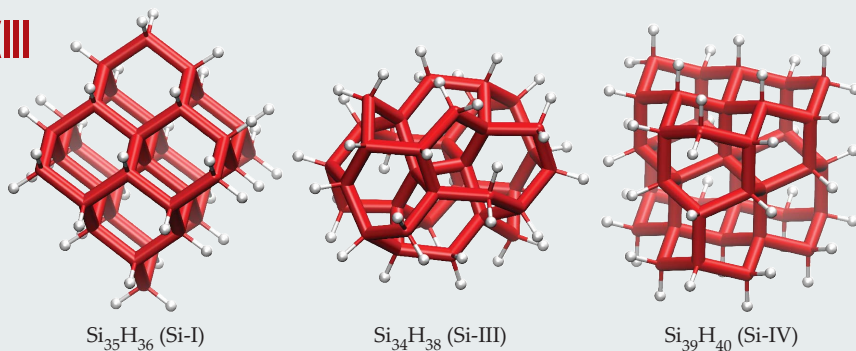
Allotropes of Si beyond its diamond-cubic form have been known since the middle of the 20th century. A major difficulty with finding new ones is that various predicted structures of Si often have small differences in the free energies of formation. Those small differences complicate the synthesis of pure-phase materials far from equilibrium—even ones that are metastable under ambient conditions.⁸ That's the case, for example, for many potential Si clathrates, cage-like structures that form around guest atoms or molecules. The impurity guests turn out to be hard to remove after the cage has formed.

So why should we expect transformative discoveries now? One reason is the development of two relatively new exper-

ALLOTROPES SI-I THROUGH SI-XIII

Metastable silicon phases are conventionally synthesized by applying pressure to the standard semiconducting form of Si (diamond-cubic, denoted Si-I) held in a diamond-anvil cell. The process normally follows a series of discrete loading or unloading steps and occurs on time scales that can vary from minutes to hours. The structures that emerge from progressively harder squeezing are measured using x-ray diffraction or optical spectroscopy.¹⁵

Under compression to 11 GPa, the tetrahedral-bonding structure of Si-I becomes tetragonal (Si-II), which is metallic. Above 13 GPa, the material distorts into an orthorhombic structure and then, with yet more pressure, a simple hexagonal one. Those structures and others repeat themselves, albeit with denser unit cells, as pressure keeps rising. Three allotropes crystallize in tetragonal unit cells, for example, and two crystallize into or-



thorhombic ones. Other allotropes form body-centered and face-centered cubic structures, and yet another (Si-XIII) remains undetermined.^{3,15}

Most of the structures are stable only at high pressures. The three bulk structures that are stable at ambient temperature and pressure are Si-I, Si-III (body-centered cubic), and Si-IV (hexagonal diamond). Those allotropes are shown here in their nanostructured forms,⁶ in which the Si atoms are terminated by hydrogen atoms

(white). Except for Si-I, the allotropes are metals. That's not surprising, because formation under pressure normally creates denser structures and more nearest-neighbor atoms, which tend to favor metallic behavior. The pictured nanostructured forms, however, may be insulators due to the effects of quantum confinement. At the moment, besides their metallic character, little is known about the last six allotropes, Si-VIII through Si-XIII, that have been discovered.

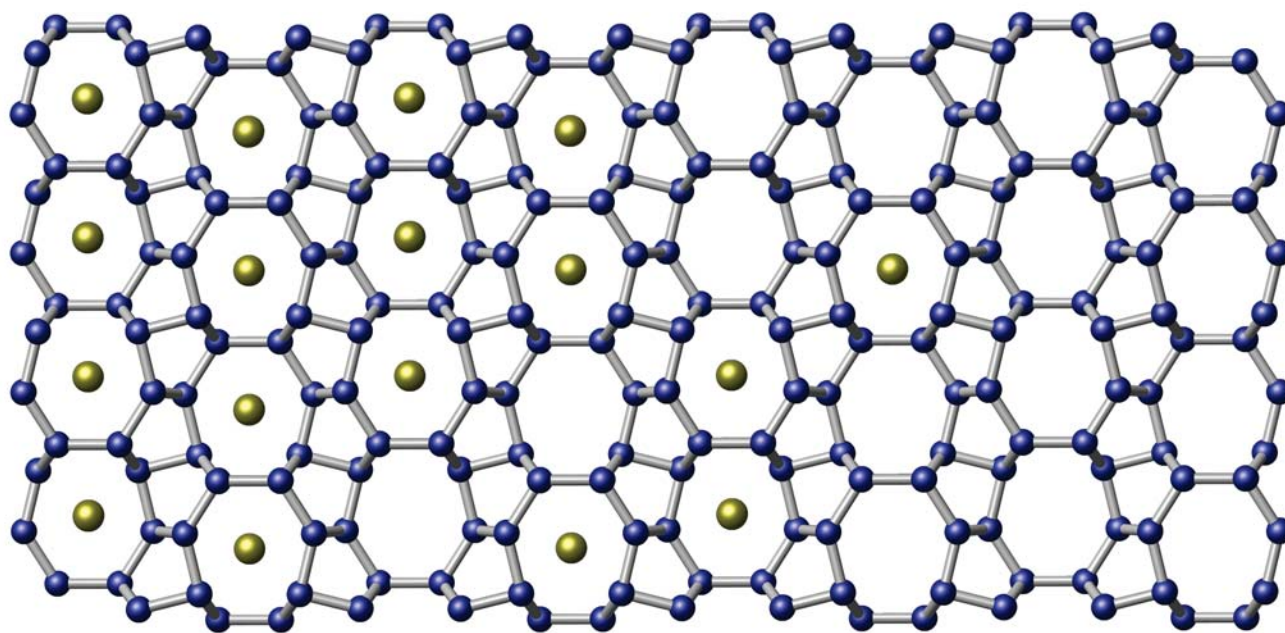


FIGURE 1. THE ORTHORHOMBIC ALLOTROPE SILICON-24

is synthesized by extracting sodium atoms from the precursor macromolecule $\text{Na}_4\text{Si}_{24}$ through thermal diffusion. In this schematic of a two-dimensional slice of the precursor, Si atoms are blue and Na atoms are gold. Na atoms diffuse out of the slice through large channels. This view shows the five- and eight-membered rings but not the six-membered rings that are perpendicular to this plane. (Image courtesy of Timothy Strobel, Carnegie Institution for Science.) A related schematic, with lithium ions diffusing through the lattice along with Na atoms and water molecules, is on page 35.

imental techniques. The application of static pressure from diamond-anvil cells is often insufficient to overcome particularly strong kinetic barriers to breaking or making new bonds. But scientists can now turn to high-power, short-pulse laser irradiation or to nanoindentation from a sharp tip, both of which supply fast and asymmetric pressure loading and unloading. The novel pressure applications rapidly freeze-in target structures.

Another reason to be optimistic is embodied in the 2015 discovery of Si_{24} at high pressures,⁹ made possible by the use of a novel precursor, $\text{Na}_4\text{Si}_{24}$, shown in figure 1; all previous high-pressure phases were made from elemental Si. One can imagine a diverse range of potential precursors to explore. Yet a third reason for optimism is that experimenters have recently found methods to grow much larger quantities of various structures. Those methods include colloidal synthesis—essentially, the use of chemical solutions to control reactions that precipitate solid structures¹⁰—high-temperature processing with novel precursors such as NaSi_x , and thin-film preparation using small seeds obtained under high pressure but stable at ambient pressure. With the larger samples, a structure's optical and electronic properties can be measured and understood. To judge from scientists' experience with C allotropes, we should expect some surprises.

Absent the experimental verification of some of the predicted open-cage structures, researchers are currently exploring several known polymorphs of Si, such as single monolayers, clathrates, dots, and wires. Let's examine each in turn.

Honeycomb silicon

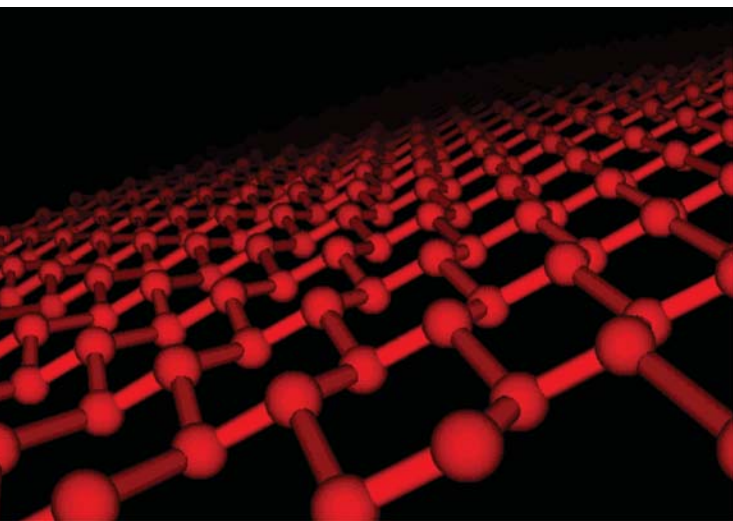
A form of Si whose lattice structure resembles that of graphene is silicene, a structure that is one-atomic-layer thick (figure 2).¹¹ The resemblance is not perfect—silicene is buckled out of the plane and contains no double bonds. But near the so-called Dirac point, where valence and conduction bands meet, the electronic band structure is linear, just as it is in graphene.¹² Because no double bonds exist in the lattice and Si remains tetra-

hedrally coordinated, the Si atoms must be “functionalized,” or bonded to some other molecule or lattice. To date, no one has experimentally synthesized free-standing silicene. The material differs from bulk Si because of quantum size effects and surface functionalization.

Silicene can be fabricated by exfoliating layered Si compounds—such as Si_6H_6 , $\text{Si}_6\text{H}_3(\text{OH})_3$, and CaSi_2 —and then depositing the layers on a metallic substrate in ultrahigh vacuum. But to exfoliate single layers of CaSi_2 , shown in figure 3, researchers must somehow compensate for the compound's highly ionic nature, and the resulting chemically synthesized sheets are oxygen terminated.¹³ According to recent calculations, silicene and its multilayer sibling, silicite, are stable in ambient conditions.¹⁴ But only sheets with lateral dimensions of a few hundred nanometers have ever been produced.

Clathrate silicon and other cages

As previously noted, Si possesses a complex array of structures whose formation energies and ground-state energies are quite similar. High-pressure techniques have historically been the most used to explore that configuration space. One recent discovery using static pressure from a diamond-anvil cell is the synthesis of the open-cage allotrope Si_{24} , an example discussed earlier. When its precursor $\text{Na}_4\text{Si}_{24}$ is heated at high temperature, essentially all of the Na diffuses out of it along open channels,^{9,15} as illustrated on page 35. Such structures may



potentially be practical as membranes for molecular or ionic diffusion between reservoirs.

Si clathrates are also promising for use as battery anodes. (See the article by Héctor D. Abruña, Yasuyuki Kiya, and Jay C. Henderson, *PHYSICS TODAY*, December 2008, page 43.) Although graphite is today's anode material of choice in commercial lithium-ion batteries, Si is more alluring because it exhibits the highest specific energy density among all materials currently considered for the job. The problem is that the volume of Si in cubic-diamond form expands and contracts with the diffusion of Li into and out of the lattice. But with their open cages connected by face-sharing polyhedra, Si clathrates can, by contrast, capture, store, and transport large quantities of ions or molecules with little or no change in volume. Moreover, they can do so, in principle, at higher charging and discharging rates than graphite can and without degrading during multiple cycles.¹⁶

Although Si_{24} was discovered recently, Si clathrates are not new. And although the number of possible open-cage Si structures is theoretically enormous, few have been realized experimentally, probably because of the dearth of effective methods for nonequilibrium synthesis. $\text{Na}_x\text{Si}_{136}$ ($0 < x \leq 24$), shown in figure 4, and $\text{Na}_8\text{Si}_{46}$ were both discovered¹⁷ around 1965. The materials are so-called degenerate semiconductors: They are so heavily doped with Na^+ interstitial donors inside the cages that they act more like metals than semiconductors. Researchers have not yet been able to remove the Na atoms from the $\text{Na}_8\text{Si}_{46}$ structure because its cages, each composed of just 20 Si atoms, are too small.

Likewise, although most Na atoms can be removed from $\text{Na}_x\text{Si}_{136}$, enough dopants remain that the clathrate cannot yet be considered an intrinsic semiconductor. Synthesizing defect-free Si clathrates would likely be a revolutionary achievement, because one could then controllably redope the material from scratch to produce such electronic and optoelectronic devices as FETs, direct-gap lasers, thin-film LEDs, and solar cells.

Heating samples to high temperature can achieve Na concentrations only as low as about 10^{18} cm^{-3} . Researchers have tried improving on that. One approach is to grow structures with an inert guest atom, such as helium or neon, or to use a smaller alkali metal, such as Li, that might diffuse out more easily. Another is to construct a clathrate Si lattice with an

FIGURE 2. SILICENE is a quasi-two-dimensional form of silicon.

The structure gets its name from graphene, the one-atom-thick carbon honeycomb lattice it resembles. But whereas graphene is flat, silicene buckles out of the plane because Si atoms prefer to bond tetrahedrally. Each Si atom bonds with only three other Si atoms, though, so a remaining dangling bond on each must be capped with hydrogen or some other termination atom or molecule (not shown). (Image courtesy of Gian Guzmán-Verri and Lok C. Lew Yan Voon.)

electron-acceptor element, such as boron or aluminum, to perfectly compensate for the interstitial Na electron donors—the compensation is precisely controlled by the chemistry. Theorists have suggested the compound $\text{K}_8\text{Al}_8\text{Si}_{38}$ for that effort.⁶ But to date, none of those dopant-reduction efforts has succeeded experimentally.

Quantum dots and wires

When a structure is made small enough that one or more of its dimensions approach interatomic distances, its electrons feel the effects of the crystal boundaries as well as the periodic potential, and its various physical properties can differ from those of the bulk material because of the quantum size effects (see the article by Michael Tringides, Mieczysław Jałochowski, and Ernst Bauer, *PHYSICS TODAY*, April 2007, page 50). That's the case for tiny, zero-dimensional Si quantum dots and 1D Si quantum wires, whose behaviors differ markedly from that of bulk diamond-cubic Si. Although not strictly allotropes, the confined structures have material properties that can be tuned for specific device applications.

For small enough dots and wires, the electronic bandgap increases and sometimes becomes nearly direct. As discussed earlier, the change makes Si a much more efficient material for

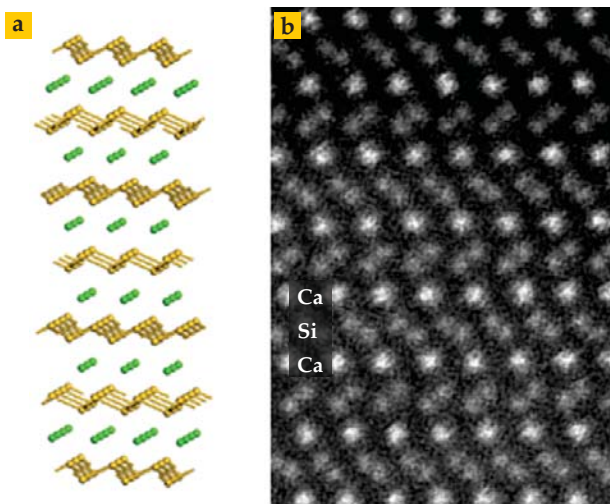


FIGURE 3. CALCIUM SILICIDE is an important precursor for making silicene, a single honeycomb layer of Si. **(a)** In a CaSi_2 crystal, each buckled, hexagonal layer of silicon atoms (yellow) is sandwiched between a layer of calcium atoms (green). **(b)** In this transmission electron microscopy (TEM) image of CaSi_2 , Ca atoms appear brighter because Ca has more electrons than Si. The horizontal scale between Ca atoms is 3.5 Å. (Adapted from ref. 13.)

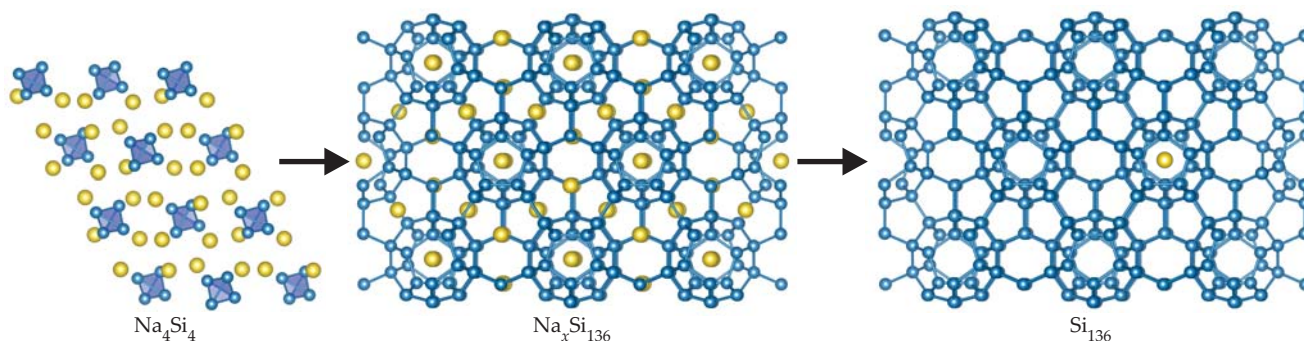


FIGURE 4. THE FORMATION OF THE CLATHRATE SILICON-136 starts with the sodium silicide precursor Na_4Si_4 , which is synthesized from a high-temperature reaction of Na (yellow) and Si (blue). When heated under a partial vacuum, the silicide decomposes. The Na atoms supply internal forces that stabilize the Si_{136} clathrate structure. Through repeated heating under vacuum or by reaction with iodine, the Na content can be reduced—to about 500 ppm—but, at least so far, not completely removed. (Adapted from ref. 17.)

optoelectronic devices that include LEDs and solar cells. Among other device possibilities are novel antennas, such as 1D nanostructured arrays.

One important method for growing Si quantum wires is the so-called metal-assisted vapor-liquid-solid (VLS) technique, used to produce the collection of nanowires shown in figure 5. In that technique, a Si substrate is seeded with an array of nanoscale metal dots that are then exposed to a source of Si atoms, usually silane gas (SiH_4), whose H atoms are ripped away by a strong electric field under vacuum. As the Si atoms impinge on the metal dots, a metal silicide is formed; when the Si concentration reaches saturation, the excess is extruded below the dot to form a Si nanowire. Of the several methods that can produce such single-crystal nanowires, the VLS method has the advantage of allowing chemists to carefully control the wires' shape and dimensions.¹⁸

Gold is the catalyst most often used to grow Si nanowires. But the resulting wires become heavily doped with the Au, a deep electron donor. Recent work has used aluminum, a shallow electron acceptor, instead of Au; the hope is that Al's incorporation into the nanowires can be more easily controlled,

because shallow dopants are easier to charge compensate. One might thus make an intrinsic semiconductor more easily. Even so, the Al-doping concentrations achieved so far remain at about 10^{20} cm^{-3} . At that concentration the wires are still metallic. The other major problem with Al as a catalyst is oxidation, which inhibits the wires' growth; fortunately, a hydrogen environment helps avoid the problem.¹⁸

A good bet

The field of Si synthesis is rich and active. In this article I have limited the discussion to crystalline Si. Porous Si, which has a diamond-cubic structure pervaded by nanopores, was discovered by accident in 1956, when certain etching procedures intended to polish the material instead produced a highly textured surface. It has its own intriguing physical properties and uses—a story for another time. Many of the exotic forms of crystalline Si were also discovered serendipitously. On the one hand, that makes it difficult to predict whether we are on a path to the next technologically important semiconductor. On the other hand, if we do get lucky, that proves yet again the mantra, “Don’t bet against silicon.”

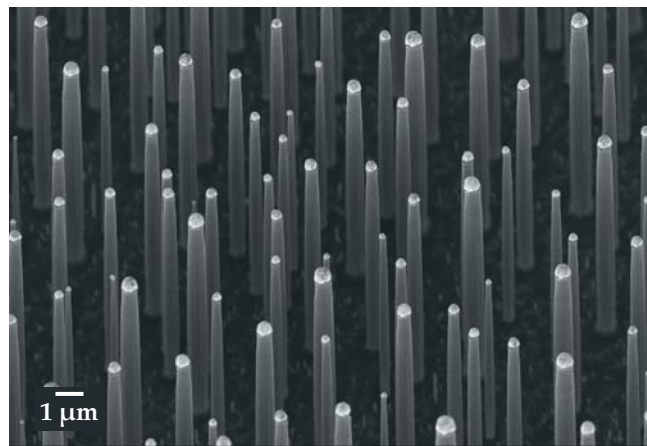


FIGURE 5. THIS COLLECTION OF SINGLE-CRYSTAL SILICON NANOWIRES was grown by seeding a cubic-diamond Si substrate with nanoscale metal dots. After the dots are exposed to a source of Si, dots of aluminum are added to promote the Si's growth into wires up to 100 μm long. (Image courtesy of Sarah Eichfeld and Joan Redwing, the Pennsylvania State University.)

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