Silicon beyond the valley

Mietek Jaroniec reflects on how silicon, whether bonded with other elements in a variety of materials, in high purity for electronic devices, or in its newer 'black silicon' form, continues to be invaluable in many aspects of our lives.

Silicon is, after oxygen, the most abundant element of the Earth's crust. But although about 75% of the Earth is made from silica — or silicon dioxide (SiO_2), the main constituent of silicate minerals such as sand, quartzite or granite — elemental silicon itself is only occasionally found in nature and was unknown until the nineteenth century. In 1811 Gay-Lussac and Thenard probably obtained impure amorphous silicon by heating potassium with silicon tetrafluoride; however, the discovery of this element is usually credited to Berzelius, who in 1824 added extra washings to isolate pure silicon. It is now produced on a large scale by heating silica with carbon in an electric furnace, at high temperatures (1,900–2,350 °C) far exceeding its melting point (1,414 °C).

According to the US Geological Survey, the world's reserves of pure silicon (including that synthesized) exceeded five million tons in 2007 — the best indicator of its importance in today's technology. Over 90% is consumed for the production of silicon-containing chemicals and alloys. Aluminium-rich alloys, for example, are commonly used in the automobile industry; silicones (which feature silicon–oxygen and silicon–carbon bonds) have found extensive applications as greases, resins, rubbers and sealants; silica, in the form of sand, is also a basic ingredient of glass and concrete, some of the most widely used materials; and aerogel, an extremely light form of silica because 90% of its volume is occupied by pores, is a very efficient insulating material.

Without diminishing the enormous importance of these applications, the greatest impact of silicon on today's technology and lifestyle is accounted for by only a small fraction of the world's reserves (about 5%) — the high-purity silicon used in a variety of electronic devices, ranging from computer microchips and power transistors

Silicon valley: Scanning electron microscopy image of the laser-irradiated silicon surface (inset), which resembles a fragment of Bryce Canyon National Park in Utah, USA.

to solar cells, liquid-crystal displays, and semiconductor-based detectors. Remarkable advances in microelectronics have been made possible by the miniaturization of silicon integrated circuits, and this field is now heading towards nanoelectronics. The use of porous silicon, for instance, for the development of a range of sensors arose from its luminescence properties and large surface areas. The high-purity silicon required for such microelectronic devices is obtained by a complex multi-step process, usually involving the transformation of a crude metallic silicon to chlorosilanes (compounds containing silicon–chlorine bonds). After separation and purification these are reduced with hydrogen to the polycrystalline silicon used to make silicon wafers (smooth thin discs).

The richness of silicon chemistry is amazing; new discoveries arise continuously in this field. And although the surface area of 1 g of sand particles is extremely small, the internal surface area of the same amount of silica particles with accessible nanoscale pores (about 3 nm) can easily exceed 1,000 m² (approximately the area of an Olympic-size swimming pool). Such particles with ordered nanopores are

synthesized in the presence of surfactant templates — a synthesis strategy that has created almost unlimited opportunities for the development of nanomaterials, such as nanoporous silica-based particles, for catalysis, separations, environmental cleanup, drug delivery and nanotechnology.

While discussing silica, it would be remiss to neglect the large-scale formation of silica structures with nanoscale precision by various marine organisms. Understanding this 'biosilification' process occurring in nature offers tremendous opportunities for the development of environmentally benign syntheses of novel silicon-based materials, and could eventually lead to advances in biosensors, biocatalysis and the engineering of biomolecules — a field now known as 'silicon biotechnology'.

Another amazing and technologically promising discovery shows the importance of unveiling microstructure and nanostructure. In 1998, Mazur and his team at Harvard University showed that the irradiation of a silicon wafer with femtosecond laser pulses in the presence of a sulfur-containing gas transforms its shiny surface into a forest of microscopic spikes, which resembles Bryce Canyon in Utah, USA (pictured). Normally, the surface of silicon reflects a substantial amount of light — but this 'black silicon' strongly absorbs visible light by trapping it between its spikes, which makes it very promising for solar cells. It also absorbs infrared radiations with wavelengths as long as 2,500 nm and, surely, novel optical and electronic applications of black silicon can be expected in the future. This example shows that silicon, although known for almost 200 years, can still amaze us. □

MIETEK JARONIEC is in the Department of Chemistry, Kent State University, Kent, Ohio 44242, USA. e-mail: jaroniec@kent.edu

Si