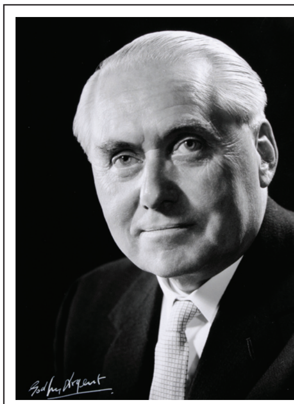
Historical Background

Silicon: A Child of Revolution

by Robert W. Cahn

Antoine Lavoisier, the pioneering French chemist who (together with Joseph Priestley in England) identified oxygen as an element and gave it its name, in 1789 suggested that quartz was probably a compound of oxygen with an as-yet undiscovered but presumably very common element. That was the year in which the French Revolution broke out. Five years later, the Jacobins, despite Lavoisier's extensive services to the state, cut off his head. It was not until 1824 that Jöns Berzelius in Sweden succeeded in confirming Lavoisier's speculation by isolating silicon. Argument at once broke out among the scientific elite as to whether the newly found element was a metal or an insulator. It took more than a century to settle that disagreement decisively... as so often, when all-or-nothing alternatives are fiercely argued, the truth turned out to be neither all, nor nothing.

In the nineteenth century, silicon found a growing role as an alloying element for iron. In the 1880s, the great British metallurgist Robert Hadfield discovered some interesting properties in iron-silicon alloys with a few percent by weight of silicon. Systematic experiments at the end of the century by William Barrett, an Irishman, culminated in the single-phase silicon-iron alloys that for more than a century have been used for transformer laminations, saving significant money because transformers made with this alloy had very low core losses. By 1920, an electrical engineer in America claimed that in the preceding 20 years, the savings resulting from the use of silicon-iron would have sufficed to finance the building of the Panama Canal.



Sir Alan Herries Wilson, 1905-1995. Photograph by Godfrey Argent, collection of the National Portrait Gallery (UK); reproduced with permission of the artist.

The electrical uses of silicon began hesitatingly. Crystal rectification, making use of cat's-whisker counter electrodes developed into early detectors for wireless telegraphy, and coarse-grained silicon of metallurgical-grade purity (99%) was used until World War I, when vacuum tubes began to take over the role of detector. During World War II, silicon-tungsten diodes were developed, against resistance from devotees of vacuum tubes, as effective detectors for ultrahigh frequency (MHz) electromagnetic waves used for radar. Each advance was fiercely resisted by the exponents of the previous orthodoxy.

Understanding of the electrical properties of silicon was slow in coming. Following some early, tentative work by Alexander Volta, the existence of semiconductors was confirmed by Michael Faraday in the middle of the nineteenth century, and various sulfides were studied soon after. It was impossible to get good reproducibility, however, and it became the orthodoxy that semiconductors must be impure to function as such and, ipso facto, were not respectable materials, because impurities necessarily varied from one sample to another. Until the end of the 1930s, most physicists looked down their noses at semiconductors and kept clear of them. The man who changed all this was Alan Herries Wilson, a theoretical physicist in Cambridge, who as a young man spent a sabbatical with Heisenberg in Leipzig and applied the brand new field of quantum mechanics

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to issues of electrical conduction, first in metals and then in semiconductors, as reported in two Royal Society papers in 1930 and 1931. When he returned to Cambridge, Wilson urged that attention be paid to germanium but, as he expressed it long afterward, "the silence was deafening" in response. He was told that devoting attention to semiconductors, those messy entities, was likely to blight his career among physicists. He ignored these warnings and in 1939 brought out his famous book, *Semiconductors and Metals*, which explained semiconductor properties, including the much-doubted phenomenon of intrinsic semiconductivity, in terms of electronic energy bands. His academic career seems indeed to have been blighted, because despite his great intellectual distinction, he was not promoted in Cambridge (he remained an assistant professor year after year). At the end of World War II, he abandoned his university functions and embarked on a notably successful career as a captain of industry, culminating in his post of chief executive of a leading British pharmaceutical company; he kept clear of electronics! In due course he became Sir Alan Wilson.

It was only in the 1940s that n and p conductivity type domains were observed and their nature identified, and only in the early 1950s that it was at last accepted that the way forward for transistor technology lay in the use of single crystals of semiconductors. Gordon Teal at Bell Labs was the visionary who pushed through this recognition against fierce opposition. Teal, incidentally, was a convinced admirer of Wilson's great book as were numerous subsequent students of solid-state physics. The process of crystal growth was enhanced by Dash in such a way as to get rid of almost all crystal defects such as dislocations. Additionally, the other recognition which came at this time was the imperative need for extreme purity, in germanium and in silicon. True, transistors had to be doped to create controlled n- and p-type domains, but such doping only worked if it was applied to ultrapure starting material. In those early days, the essential approach was zone-refining, invented at Bell Labs. For a decade at least, zone-refining was the inescapable technique for achieving ultrapure germanium. However, this technique was not applicable for silicon owing to its reactivity with the walls of the zone re-refining chamber material at silicon's melting point of 1414°C. For silicon, thereafter, chemical purification using silicon halides and silane was utilized (zone-refining could not be applied in any case to the huge crystals grown nowadays, although it still seems to be used with germanium for radiation detectors). Students of electronics today may not sufficiently appreciate the importance of zone-refining, without which the age of solid-state electronics, including microcircuits and nanocircuits, would have been substantially delayed.

After the long years during which semiconductors, including silicon, were held in contempt, silicon has now become the most-studied element in the periodic table; its physics, chemistry, and processing captivate a ceaseless procession of highly skilled scientists and engineers.

The methods developed for shaping silicon crystals on an ultrafine scale, making use of controlled etching, oxidation, and vacuum deposition, have recently led to some unexpected applications. The whole field of microelectromechanical systems (MEMS) is based on this technology. The most recent exemplification of this approach is the construction of microscale gas turbines, made from silicon and producing a mere few grams of thrust; these improbable engines can be used to propel diminutive robot aircraft. *Silicon is used here not because, in mechanical engineering terms, it is the ideal material (it clearly is not), but because it can be shaped with the extreme precision needed, using techniques developed in the microelectronics industry.*

The latest projected use of electronic-grade silicon, perhaps the most unexpected of all, is as a tool in one of the last great unsolved problems in metrology. The standard units of length and of time are based on spectroscopy, and the old standard meter, made of precious metal, has been abandoned. But the standard unit of mass is still a lump made of platinum-iridium alloy and deposited in a well-guarded vault in the outskirts of Paris. There are all sorts of drawbacks to having mass defined in this old-fashioned way. One way proposed to replace the standard kilogram by a reproducible natural quantity is by counting the number of atoms in a silicon crystal that has a nominal mass of 1 kg. Silicon has been chosen because of the great expertise available in the growth of pure, virtually defect-free crystals, although point defects such as vacancies and self-interstitials are thermodynamically permitted at any non-zero absolute temperature. The crystal is machined into a sphere of extreme perfection: a sphere recently machined in Australia is so accurate that if it were magnified to the size of the earth, its valleys and hills would not differ in altitude by more than 7 m. Atoms in the sphere are counted by measuring the lattice parameter and the diameter of the sphere is measured by optical interferometry. (A spherical shape is chosen because the only distance which must be measured is the diameter.) It is now being proposed that a further increase of precision may be attained by using a mass-separated isotope to grow the crystal. If this works as well as is hoped for, the approach will permit an uncertainty of only about 100 μg in the measurement of the standard kilogram. This whole project could be conceived only because of the labors of generations of microelectronics specialists.

Silicon, the child of revolution, has spawned a whole series of revolutions of its own. No end is yet in sight. ■

About the Author

Robert Cahn, F.R.S. is emeritus professor of materials science of the University of Sussex and now, at the age of 80, distinguished research fellow in the Department of Materials Science and Metallurgy at the University of Cambridge. He remains active in the writing and editing of books and encyclopedias. He can be reached at rwc12@cam.ac.uk.