

Silicon and Germanium

In the late 1940s, two elements—silicon and germanium—suddenly received a surge in interest due to the discovery of their ability to act as “semiconductors,” i.e., to conduct electricity more efficiently than an insulator (such as rubber) but less efficiently than a conductor (such as copper). The invention of the semiconductor device called the transistor in 1947 by John Bardeen, Walter H. Brattain, and William B. Shockley at the Bell Telephone Labora-

tories ushered in a revolution in electronics that continues today in the rapid advances in solid-state devices, integrated circuits, and miniaturized electronic components.

Both silicon and germanium were recognized as elements long before their uses as semiconductors were even imagined. Silicon is the second most abundant element in the earth's crust (second only to oxygen), and is found in almost every rock, all natural water, plants, and animal skele-

tons, as well as body tissues and fluids. It is never found in the free state, however, but most often as a compound with oxygen (SiO_2) called silica; 95% of the earth's rocks contain silica as their principal component.

Germanium, on the other hand, is a very rare element, comprising only about 0.0005% of the earth's crust; making recovery difficult, too, is the fact that germanium is not found in natural concentrations or deposits, but rather is evenly distributed in trace quantities in many rocks. Like silicon, germanium is never found in the free state, but always in various uncommon minerals and sulfide ores, especially those of silver, lead, tin, zinc, and antimony.

Until the late 18th century, chemists were not able to separate elemental silicon from its silica compound; some chemists even considered silica itself to be a pure element. In 1787, A. Lavoisier in France speculated that silica was probably the oxide of an as-yet-undiscovered element. Various chemists attempted to isolate the element, including Sir Humphry Davy in England in 1800, and Louis Thenard and Joseph Gay-Lussac in 1811, but their results were not conclusive. In 1817, a chemist in Sweden, Jöns Jakob Berzelius, discovered that the element was present without oxygen inside cast iron; in 1823 Berzelius finally succeeded in establishing the existence of silicon as an element, though he could prepare only an impure form.

Silicon was finally created in reproducible crystalline form in 1854—nearly 70 years after its existence had first been proposed—when Henri Saint-Claire Deville crystallized it out of an alloy he produced by mixing melts of chlorides and then electrolyzing them. He named the element silicon (loosely) after the Latin word for flint, “silex.”

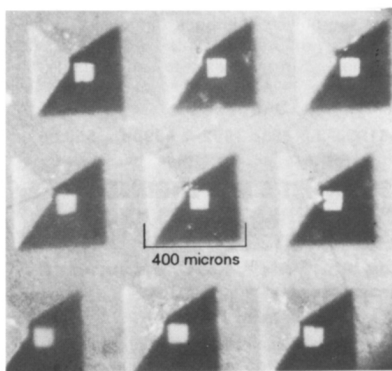
In 1871, a chemist in Russia, Dmitri Ivanovich Mendeleev, predicted a hypothetical element in group IVA of the Periodic Table between silicon and tin, describing its expected physical properties and naming it tentatively “eka-silicon.” Fifteen years later, in 1886, Clemens Winkler analyzed argyrodite, a sulfide mineral, and found a previously unknown constituent; he isolated it and named it “germanium” after his native country of Germany. Further investigation by other chemists confirmed its position between silicon and tin in group IVA in the periodic table, just as Mendeleev had predicted.

Germanium is a hard, silvery-gray solid with a metallic appearance. It is brittle rather than ductile, with the arrangement of atoms in its crystalline structure similar to the diamond lattice of carbon. Before its

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HISTORICAL NOTE

use in the semiconductor industry, germanium had little commercial importance. It was used only in an alloy (with gold) for dental work, and in glass, for infrared optical devices such as lenses, prisms, and windows.

Like germanium, crystalline silicon is also a brittle solid, and is black to dark gray in appearance, with a high metallic luster. Elemental silicon is dark brown in its amorphous form. Unlike germanium, elemental silicon had found many commercial applications by the turn of the century. Silicon is used as an alloying ingredient to strengthen magnesium, aluminum, and copper. Mixing silicon with tin and copper makes silicon bronze, which found wide use in telephone and telegraph wires. Ferrosilicon is used in making very resistant silicon steels.

Silicon carbide (also known by the trade name Carborundum) is an exceedingly hard, clear, green-tinged crystalline compound first created in 1891 in the United

States by Edward G. Achison. Until the creation of boron carbide in 1929, silicon carbide was the hardest synthetic material known.

Silicon is also the starting material for the organic-compound silicones used as plastics, oils, greases, and synthetic rubbers. Inorganic silicon compounds are used in the manufacture of glass and ceramics, piezoelectric crystals, and insulating materials.

Toward the end of World War II, new processing methods made available large quantities of extraordinarily pure germanium, opening the door to its use in the electronics industry. Highly pure germanium ingots are remelted and doped with specific impurities (such as arsenic or gallium) to produce desired electronic characteristics. After about 1945, germanium's properties as a semiconductor became widely known. The first transistor was announced in 1947, and a year later the germanium triode was put on the market.

Germanium semiconductor devices replaced many of the vacuum tubes, diodes, and rectifiers normally used in common electronic devices, and also performed new functions that vacuum tubes could not handle. Since 1948, there have been many developments in the industry, for example, the diffused-junction transistor.

During the 1960s, elemental silicon supplanted germanium as the most common semiconductor material. Heating silica with coke in an electric furnace yields elemental silicon of ordinary purity, but "zone refining" yields silicon of a much higher purity, suitable for electronics. Silicon has several advantages over germanium, in that it is vastly more common than germanium and is thus intrinsically less expensive; silicon also retains its semiconducting properties at higher temperatures. Silicon forms an oxide film with excellent electrical insulating properties; the film can be used as a mask to permit the introduction of specific impurities needed for doping the

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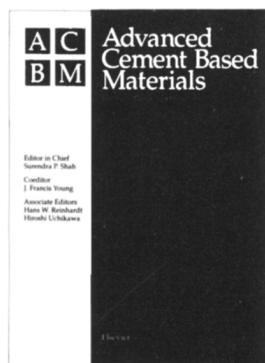
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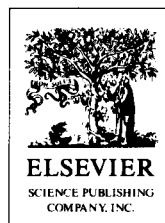
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semiconductor (such as boron, gallium, arsenic, and phosphorus).

Since the 1970s, materials other than silicon and germanium have been investigated for application as semiconductors in transistors, rectifiers, photocells, and tunnel diodes. Most notable among these are compounds made of aluminum, gallium,

or indium, mixed with phosphorus, arsenic, or antimony. These compound semiconductors are particularly useful in devices that emit light efficiently or operate at exceptionally high frequencies, such as semiconductor lasers, light-emitting diodes, or solar cells.

KEVIN J. ANDERSON

BOOK REVIEWS

Photoelectronic Properties of Semiconductors

Richard H. Bube
(Cambridge University Press, 1992, 318 pages).
ISBN: 0-521-404916 (hardback);
0-521-406811 (paperback)

In my formative years as a physicist I read this author's book on *Photoconductivity of Solids* (Wiley, 1960), and I was influenced by his clear, authoritative style. The present volume updates much of the previous material, while retaining the style. The author's broad experience is apparent, and this book will be a useful reference.

After an introductory chapter, which could have been longer and more "introductory," the second chapter gives a general treatment of photoconductivity parameters, setting the nomenclature for subsequent chapters and dealing specifi-

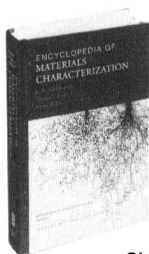
cally with intrinsic recombination.

Chapters 3 and 4 deal with one-center recombination models, the latter chapter being devoted in detail to the Shockley-Read model. Chapter 5 deals with models in which two recombination centers having markedly different capture coefficients are present, and includes a liberal set of examples drawn largely from the author's own work.

Chapter 6 discusses the various recombination processes that can occur, such as luminescence, phonon emission, and Auger emission; however, I would have placed this chapter earlier in the book. Chapters 7 and 8 are devoted to the most useful experimental methods for photoelectronic measurements on solids. The first of these chapters covers steady-state methods, such as Hall, thermoelectric, capacitive, and luminescence techniques; the second deals with transient measurements and looks at the rates of decay and how these are related to trapping mechanisms. Deep-level transient spectroscopy is covered, but I would have welcomed a clearer exposition and more examples of this technique. Many illustrations of the main points are made in these chapters, again drawn almost exclusively from the author's work.

The effects at grain boundaries, a subject often neglected, are covered in Chapter 9. Chapter 10 provides a good introduction to photoeffects in amorphous semiconductors, a subject worthy of a book by itself. Chapter 11 deals with photovoltaic effects and considers heterojunctions and practical solar cell junctions. However, the subject of the band energy line-up problem, which should be very important, is not discussed. The final chapter covering quantum wells and superlattices is rather superficial and descriptive—a pity, given the examples abounding in the literature. Although I am somewhat disappointed overall, I am sure that the book will be useful in both my research and teaching.

Reviewer: Peter J. Dobson is in the Department of Engineering Science at the University of Oxford, England. His main interests are in the optoelectronic properties of materials.



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