

RESEARCH ON SILICON AND GERMANIUM IN WORLD WAR II

The dawn of the age of silicon electronics occurred during the war when point-contact silicon rectifiers became standard nonlinear elements in microwave radar circuits.

Frederick Seitz

A relatively large and well-funded group of investigators did intense research on the electrical properties of silicon and germanium during World War II. Their work completely transformed attitudes toward the physical properties of the pure crystalline forms of the semiconductors: No longer regarded merely as exotic materials, these elements became components of flexibly useful circuit elements that could be manipulated to show various properties by the addition of small amounts of other elements. In this sense, the wartime research laid the groundwork for the invention of the transistor shortly after the war and ultimately the development of the integrated circuit. The work opened up a new age of electronics.

Before the war

Public acceptance of AM radio broadcasts in the kilocycle range during the 1920s, as well as interest in broadening other forms of communications, spurred engineers to explore possibilities in the megahertz range in the 1930s. This effort was expected to open more communication channels and improve fidelity through increased bandwidth. The development of FM radio, which currently operates in the range between 88 and 108 megahertz, was one of many consequences of this work. The frequencies allotted initially for what was then experimental television in the United States were below the current FM range. Vacuum-tube technology proved adequate to meet the needs of this phase of advance.

In the meantime, scientists and engineers were ex-

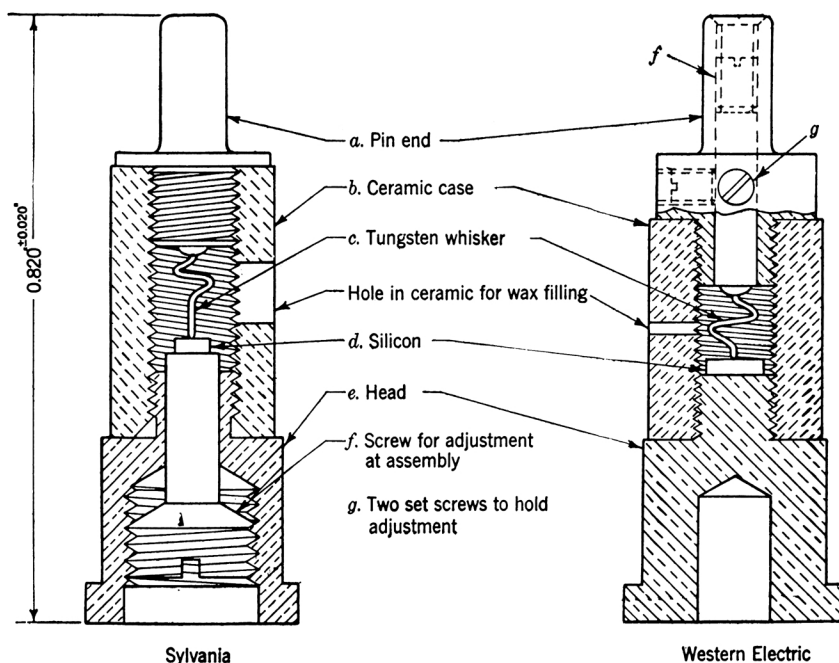
ploring higher frequencies, in the gigahertz range and above, for their own purposes. This led to the invention of such devices as the klystron, traveling-wave tubes and the cavity magnetron. The klystron was developed by William W. Hansen (my mentor when I was a student at Stanford University) with the intention of using it to accelerate particles to high energies in a linear system—a linac. Other inventors, such as the Varian brothers and individuals in the communications industry, were also interested in microwaves.

Radar

The discovery in the 1930s that electromagnetic waves could be used to track aircraft—that is, the development of radar—greatly enhanced interest in producing radiation having shorter wavelengths. Such radiation could be expected to improve beam focusing and enhance the definition of the return signal. That interest became particularly acute once World War II began, and research in the field was soon proceeding as fast as resources permitted. These developments led to systems that eventually operated at wavelengths of a few centimeters, with experiments reaching farther out in the electromagnetic spectrum.

One of the important problems in radar is converting the high-frequency return signal to a more useful observational range. This can be accomplished by the heterodyne principle—that is, by combining, or “mixing,” the incoming signal with a fixed, intermediate-frequency signal produced by a local oscillator in a nonlinear device; this yields a much-lower-frequency version of the envelope of the returning signal. This beat-frequency signal can then be amplified with relatively standard equipment to permit the viewing of the return signal in a standard oscilloscope. While thermionic vacuum tubes served very well as mixers in the range up to several hundred megahertz, those designed to be used in the centimeter-wave-

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State-of-the-art semiconductor units, 1942. This diagram, from Henry Torrey and Charles Whitmer's *Crystal Rectifiers* (McGraw-Hill, New York, 1948), shows typical silicon diodes used in World War II radar.

length range proved to be much less suitable, being noisy as well as unstable.

The British, who had pushed this area of development very hard before World War II as part of their investigations of cavity-magnetron microwave generators, found a rectifying metal-semiconductor diode to be very effective as a mixer. They used a so-called cat whisker system in which the tip of a tungsten wire is placed in firm contact with a piece of aluminum-doped, commercially available silicon. Rectifiers of this type, using various kinds of wire whiskers and semiconductors such as lead sulfide, selenium, silicon carbide and zinc oxide, had been widely employed by amateurs in the early days of radio—the so-called crystal-set era, which began in the early 1920s, when commercial radio broadcasting was in its infancy. Such systems derived energy from the antenna; one listened with sensitive earphones. I engaged in this form of instructive technology while still in grade school; in those days the amateur listener spent much time finding a hot spot on the crystal for which the rectification was good and the signal strength strong.

Although vacuum tubes rapidly replaced semiconductor mixers for AM radio, rectifiers soon found other uses. For example, Lars Grondahl discovered in the 1920s that a surface of cuprous oxide on metallic copper, coated with a layer of silver, formed a practical, relatively high-current rectifier. This technology found many uses at low frequencies. A selenium-cadmium system was employed for similar purposes. Both Walter Schottky and Nevill Mott developed interpretations of the operation of such rectifiers in the 1930s.

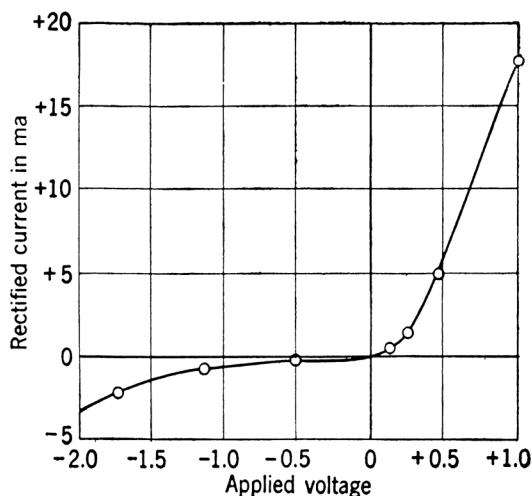
The Radiation Laboratory

As mentioned, the United Kingdom had carried out research on radar, particularly that in the centimeter range, in secrecy before World War II and until the fall of France in the late spring of 1940. The creation of the Radiation

Laboratory at the Massachusetts Institute of Technology came soon after, in November 1940, and was encouraged by a high-level decision of the United Kingdom to share its secret knowledge with the United States. The British were well ahead in their research, but the US began a very rapid catch-up in all phases of the technology and soon became the major coordinator of most radar research. While some individuals in the Radiation Lab hoped for the development of a vacuum-tube mixer that might replace the cat whisker diodes, experience soon showed that the semiconducting systems could perform their task well. Unfortunately, the units initially employed tended to differ radically from one another and, on occasion, to behave erratically. It was common in the early stages of radar for an operator to carry a number of diode units and search for one that worked, replacing it with another if and when it stopped functioning or became erratic.

In late 1940 or early 1941, while at the University of Pennsylvania, I received a call from Lee A. DuBridge, director of the Radiation Laboratory, who asked me to visit there to discuss the state of the available diodes. Soon our group at Penn was busy at work under contracts arranged by the Radiation Laboratory. We assembled test equipment and visited other groups, including those at Bell Telephone Laboratories and the General Electric Research Laboratory, to learn of related activities.

One of our first actions was to construct the means for producing our own special samples of aluminum-doped silicon, both to replicate the action of the diodes being used and to measure the electrical conductivity and the Hall effect as functions of temperature to characterize the semiconductor more completely. A member of our group, Andrew W. Lawson, developed a set of miniature beryllium oxide crucibles in which to produce ingots. It soon became evident that silicon is an intrinsic semiconductor at sufficiently high temperatures, with an activation energy of about 1.1 eV, and that the aluminum additions



Typical current-voltage curve for a silicon rectifier, from Torrey and Whitmer's *Crystal Rectifiers*.

produced an extrinsic hole conductivity with a much lower activation energy, on the order of 0.1 eV or less. We determined the mobility of electrons at room temperature by adding elements such as phosphorus, which rendered the materials n-type. The electron mobility turned out to be about 300 cm/sec per volt/cm; that of the holes was about 100 cm/sec per volt/cm.

Later work with germanium by other researchers gave an intrinsic activation energy of about 0.76 eV and mobilities of about 2600 for electrons and 1700 for holes (at room temperature and in the same units). This work held us enthralled, because we realized we were dealing with two remarkable semiconductors that showed great flexibility.

During early visits to Bell Laboratories, we found a group working under Jack Hall Scaff, who was much concerned about the eccentric behavior of the diodes. He recognized, as we did, that a substantial part of the erratic behavior lay in the use of crude, inhomogeneous, metallurgical-grade silicon. Such impure silicon was commonly used as an additive to ladles of molten steel; the element combines with the oxygen in solution in the liquid metal, preventing the latter from "boiling" as the molten steel cools and releases gaseous oxygen. Scaff had started purification of the commercial silicon by fractional crystallization, with the hope that he would obtain substantial segregation of the impurities. This process was greatly refined in the postwar era by William Gardner Pfann in the procedure known as zone refining. (See the figure on page 31 in Henry Ehrenreich's article in this issue.)

The Du Pont work

Fortunately our group at Penn had a more direct route toward purification—one that indeed solved the problem for the silicon diodes for the time being. Soon after I joined the university in 1939, the pigments department of the Du Pont Company near Wilmington, Delaware, asked me to consult regarding a problem it was facing. Prior to 1930 the standard white pigments used in paints were compounds of lead that were known to be poisonous, such as lead carbonate. They caused a wasting disease, commonly known as painter's colic, which incapacitated and eventually killed many housepainters in their 30s and 40s. Such pigments were being replaced by nontoxic titanium oxide, preferably in the cubic, high-index-of-refraction form, rutile. At the time of my initial meeting at Du Pont, the company was using a wet batch process

invented in Europe to produce rutile. There were two interrelated questions: Was there a better, simpler white pigment? If not, was there a simpler way of producing rutile of satisfactory quality?

I became deeply involved in this fascinating program, because the imaginative, well-funded group was prepared to try any reasonable approach that involved physics and chemistry. In brief, we discovered that rutile pigment of excellent quality could be produced continuously by reacting titanium tetrachloride with oxygen in an appropriately designed furnace—a process that is still widely used. The only conceivable competitor appeared to be strictly stoichiometric silicon carbide, a combination of elements very difficult to produce in practical, commercial quantities because of the high solubility of carbon in silicon carbide at high temperatures.

The problem of producing purer elementary silicon emerged just as the research at Du Pont was nearing its peak, and so it was taken on as a parallel program. We soon found that silicon that was pure to about 1 part in 100 000 with respect to significant impurities (so-called five-nine material) could be produced in powder and granular form at reasonable cost by reacting silicon tetrachloride with zinc in a vapor-phase reaction. The level of carbon in the product may have been relatively high, but it apparently had no significant influence on the diode properties. Our group at Penn was in the fortunate position of receiving samples from the first batches of the Du Pont material, and we promptly carried out a variety of experiments. Lawson tested the effect of various additional agents on the properties, while the other members produced test units and examined their behavior. We soon discovered that boron was an excellent agent for enhancing silicon's extrinsic semiconductivity.

Centralization of planning

During this period, Harper Q. North at the General Electric Laboratories was hoping to resolve the purity problem through another channel. He had decided that germanium might be a better material than silicon and developed interesting semiconducting devices with it. Silicon, however, became the preferred material once the purer form was available, because units made from it were less temperature sensitive and more stable than germanium devices.

By 1942 it had become clear to the leaders at the



Lee DuBridge, director of the Radiation Laboratory at MIT, shortly after World War II.

Radiation Laboratory that for the foreseeable future they would have to depend upon semiconducting diodes as mixers. As a result, they expanded the research program as broadly as possible, including work with other groups at industrial, governmental and academic laboratories. The most important effort was to develop a strong guiding program at the Radiation Laboratory itself, led by Henry C. Torrey and Marvin Fox, who were soon joined by Charles A. Whitmer, Hillard B. Huntington (who had earlier worked with me at Penn), C. S. Pearls and Virginia Powell; they all did an excellent job of guiding the program. (Lawson also left Penn to join the Radiation Laboratory, but he joined a different part of the organization.) During this period Torrey focused much of his personal research on studies of the high-voltage breakdown, or "burn-out," of units; he was dubbed the "crystal crackin' papa," inspired by a then-popular song, "Pistol Packin' Mama."

The semiconductor group at the Radiation Laboratory received much help, particularly in the early stages of the program, from leading theoretical scientists at the laboratory, particularly Hans Bethe. The group was also aided by some members of Edward Purcell's fundamental radar group.

Karl Lark-Horovitz, then head of the physics department at Purdue University, soon learned of the program and developed a major research effort that focused on germanium, which was supplied by the Eagle Picher Company, of Joplin, Missouri. He visited our group at Penn, and we gave him plans for our basic equipment. Hubert M. James helped guide the Purdue group, which included Seymour Benzer, now a distinguished molecular biologist, Ralph Bray, Esther M. Conwell, Vivian A. Johnson, Robert Sachs, R. N. Smith and Hubert J. Yearian. Karl F. Hertzfeld of Catholic University, in Washington DC, and Victor F. Weisskopf, then of the University of Rochester, acted as consultants.

The group at Purdue University deserves special mention because its contributions were formidable in spite of the fact that it focused its activities on germanium, which was of secondary interest for the immediately applied work at the Radiation Laboratory. The research at Purdue was thorough and focused as much on fundamental studies of germanium's characteristics as on rectification. Lark-Horovitz obviously believed that silicon and germanium held great promise for the future of science and technology;



Torrey was a research physicist and coordinator of the diode program at the Radiation Laboratory. This photograph dates from about the time he joined the laboratory. (Courtesy of Torrey.)



Karl Lark-Horovitz, shown here with physicists attending a general physics meeting at Purdue University in 1942, led a research effort on germanium at Purdue. Front, left to right: Wolfgang Pauli, Julian Schwinger, Edward Condon, Joseph Becker. Back: Lark-Horovitz, William Hansen, Donald Kerst. Schwinger, Condon, Becker, Lark-Horovitz and Hansen would have been familiar with the work on diodes. (Courtesy of Purdue.)

he wanted to lay down as firm a foundation of understanding as possible under wartime circumstances while still serving the requirements of the radar workers. The work of the group had practical consequences. While doing more basic studies, it developed some remarkable germanium diodes that could withstand potentials on the order of 100 volts in the back, low-conducting direction. Such diodes were useful in auxiliary radar circuitry and as such were never quite matched in performance by silicon rectifiers during the war.

Regarding the industrial groups, Bell Laboratories continued to work on semiconductors at all levels, including production. Stephen J. Angello, a former Penn student who had become involved with copper oxide rectifiers at Westinghouse, soon shifted his interest to silicon diodes. Similarly, J. R. Woodyard of Sperry Rand became involved in semiconductor research. In addition, the Sylvania Electric Company agreed to become a major producer of units for the Radiation Laboratory and others. At the Sperry Gyroscope Company, Edward Ginzton and Edwin M. Sherwood became participants in semiconductor activity.

The review conferences

One of the notable features of the semiconductor endeavor was the series of regular meetings among participants in the Radiation Laboratory program. At the meetings research programs were reviewed and discussed freely. The meetings, held at various places about every six weeks or so under secure conditions, were by no means restricted to the leaders of the groups; eventually they involved a hundred or more individuals. Almost all discussion was

free and open, although Bell Laboratories, which had a very large internal program with its own long-range interests in communications in mind, understandably limited its representation to matters most directly concerned with its work for the Radiation Laboratory.

It would be hard to overstate the importance of these regular review meetings for the rational development of the program. Although we maintained friendly, open relations with individuals at government laboratories, such as the Naval Research Laboratory, the Signal Corps Laboratory at Fort Monmouth and the National Bureau of Standards, I cannot recall any substantial contribution from them, probably a failing on my part. It must be remembered, however, that most scientists in those organizations were deeply involved in field operations at the time. By 1944 Whitmer and Huntington had moved to other activities, and Torrey and the crystal program had joined a group led by Robert Pound.

Postwar work and the transistor

The Purdue group continued its efforts after the war as a major activity of the physics department. Because a great deal of the work was ultimately cleared for publication, it occupied a prominent place in the open literature. Ernest Braun made good use of these publications in preparing a chapter titled "Selected Topics from the History of Semiconductor Physics and Its Applications" in the historical survey book *Out of the Crystal Maze*, edited by Braun, Lillian Hoddeson, Jürgen Teichmann and Spencer Weart (Oxford University Press, 1992).

One anecdote I heard from John Bardeen deserves

CRYSTAL RECTIFIERS

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mention here. In 1947, after Bardeen and Walter Brattain had discovered transistor action at Bell Laboratories using a point-contact electrode with germanium, and while their success was being kept confidential during the filing of patents, they visited Purdue as guests of the physics department there. Lark-Horovitz, still deeply involved in the study of germanium, said to them in effect: "There must be some way in which we can make a triode from these semiconductors. Do you have any suggestions?"

As a result of immersion in the work on diodes, I was not taken by surprise by the invention of the discrete transistor. The invention of the integrated circuit by Jack Kilby and Robert Noyce, and its subsequent evolution, was a different matter, however, granting that the practical development of such chips took about ten years and much Federal funding. I once asked Bardeen if he had envisioned the development of integrated circuit systems. He said the scale of the development took him by surprise; he had thought of the transistor mainly as an efficient, long-lived complement or substitute for the vacuum tube.

There is little doubt that our collective wartime research work on silicon and germanium made it possible to use semiconducting diodes in radar systems in a completely practical and systematic way—the main objective of the research. I am proud that our small, dedicated group at the University of Pennsylvania was able to contribute to the forefront of this endeavor rapidly at a

Title page of Torrey and Whitmer's book, which was volume 15 of the Radiation Laboratory Series on radar.

critical time. We owed much, of course, to the special events that were taking place at the time in one branch of the Du Pont Company. Du Pont did not become a major supplier of silicon to the transistor manufacturers in the long run. The material it produced for diodes had too short a minority-carrier lifetime to be acceptable as the technology advanced. Du Pont decided not to divert effort from its other commercial activities to achieve greater refinement.

I left the University of Pennsylvania at the end of 1942 to become head of the physics department at the Carnegie Institute of Technology. Leonard Schiff, who was much involved in the diode program, took over from me and carried on until he was called to Los Alamos in the spring of 1945. I continued to participate in the regular review sessions at Penn until 1944, when other wartime activities made this impractical.

As an individual who had followed the advances in solid-state physics almost from the time when the field was opened up by new developments in quantum mechanics, I was thrilled by the wartime revelations concerning silicon and germanium. They stood prominently as links between the metals and the well-recognized insulators with large bandgaps. Understanding their properties required just the type of theory that we had been developing for over a decade. The work and the discoveries provided a very special sense of fulfillment as the revelations emerged. In a relatively minor way I experienced the thrill Isaac Newton must have had when the apple fell on his head.

I'll conclude with the highly prescient comment made by the great Wolfgang Pauli in 1931, and unearthed by Hoddeson: "One shouldn't work on semiconductors, that is a filthy mess; who knows if they really exist!"

* * *

It is a pleasure to acknowledge the constructive advice I received from Henry Torrey in preparing this article. To Lee DuBridge, who died in January 1994 as I was writing the article, I owe a debt that goes much beyond the opportunity to work with the semiconductors mentioned here. ■