
# INTERNATIONAL CONFERENCE ON SILICON CARBIDE BOSTON, MASS. APRIL 2-3, 1959

*A Conference Report by* ***J. R. O'Connor***

THERE exists a need, especially in the cases of some military applications, for a stable, high-temperature semiconductor material. Active and passive devices fabricated from such a material could operate in a high-temperature ambient and simultaneously resist radiation damage. The most useful semiconductor materials, to date, have been the Group IV elements, germanium and silicon. Devices made from silicon, however, cannot be efficiently operated at temperatures in excess of 200°C. Logically, one should next consider diamond, the cubic modification of carbon. At this time, however, the technological problems that one would encounter with diamond are formidable.

We know that silicon and germanium form continuous solid solutions. We also know that the addition of a small amount of silicon in a germanium matrix raises the band gap of the resultant alloy appreciably. Unfortunately, silicon cannot dissolve even small amounts of carbon. However, a compound silicon carbide exists in two modifications: cubic and hexagonal. Both modifications are semiconductors with relatively large band gaps. By 1958 it seemed that the time was opportune for an international conference in which the various technological difficulties concerning the use of silicon carbide as a semiconductor could be discussed.

An International Conference on Silicon Carbide was accordingly held April 2–3, 1959, at Boston, Massachusetts, after having been initiated by C. E. Ryan of the Air Force Cambridge Research Center during the summer of 1958. The need for such a meeting was amply demonstrated by the attendance of more than five hundred scientists, representing ten nations.

The conference was organized and sponsored by personnel of the Electronic Material Sciences Laboratory at the Air Force Cambridge Research Center, and the program was arranged by a committee consisting of C. E. Ryan, J. Smiltens, and J. R. O'Connor (chairman). The committee benefited greatly from the help and cooperation of R. J. Young and his associates at Wentworth Institute. This Institute coordinated many aspects of the conference and was especially helpful in extending aid to overseas participants.

Initially, only a small conference was contemplated. However, the purpose of the meeting was to further the exchange of information among all scientists interested in research and development of silicon carbide, and announcements concerning the conference were widely disseminated by several scientific journals and periodicals. The subsequent response to these notices soon indicated a widespread interest in this new semiconductor and also the likelihood of a rather large attendance. The setting of the conference was transferred from the Air Force Cambridge Research Center to John Hancock Hall in Boston, and plans were made to accommodate the large number of scientists who had already indicated a desire to participate. In retrospect, the large attendance did not increase the formalism of conference procedures and obviously dispensed with the difficult, if not impossible, task of selecting a small number of qualified conferees.

In outline, the conference program and session chairmen were as follows: I. *The Silicon-Carbon Binary System* (F. N. Rhines, University of Florida); II. *The Growth of Silicon Carbide Single Crystals* (R. E. Davis, Westinghouse Electric Corporation); III. *Silicon Carbide as a Solid* (M. J. Buerger, Massachusetts Institute of Technology); IV. *Silicon Carbide as a Semiconductor* (K. Lehovec, Sprague Electric Co.); and V. *Silicon Carbide Devices* (I. A. Lesk, General Electric Co.).

Following the above technical program, a summary

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Some of the more than 500 persons who took part in the conference as seen during session on crystal structure characteristics of silicon carbide. The speaker is H. Arnold of the Max-Planck Institut für Silikatforschung.

session presided over by W. Shockley (Shockley Transistor Corporation) was held. Reviews of the sessions were (respectively) presented by: (I) J. Chipman (Massachusetts Institute of Technology), (II) P. H. Keck (Sylvania Research Laboratory) and M. Tanenbaum (Bell Telephone Laboratories), (III) G. A. Busch (Eidgenössiche Technische Hochschule) and H. A. Farnsworth (Brown University), (IV) G. A. Slack (General Electric Research Laboratory) and R. W. Keyes (Westinghouse Research Laboratory), and (V) R. N. Hall (General Electric Research Laboratory) and H. K. Henisch (University of Reading). In addition to these reviews, there were many lively and stimulating discussion periods throughout the conference.

The following is a brief summary of the impressions that were gained from the papers and discussions concerning the status of silicon carbide as a high-temperature semiconductor.

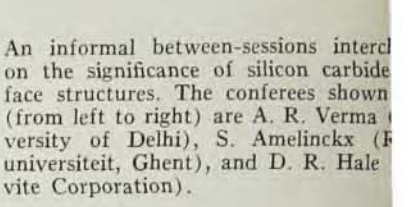

W. Shockley discussed use of proton scattering process to examine surface structure of binary compounds.

SESSION I considered the silicon-carbon binary system. To synthesize a compound, the pressure, temperature, and composition relationships must be determined. Although silicon carbide is one of the older of man-made materials, the exact nature of its binary phase diagram has proved to be quite elusive.

The first paper, by J. Smiltens (Air Force Cambridge Research Center), presented the necessary thermodynamics to compute theoretically the pressure and composition of the vapor phase in the silicon-carbon binary system. For numerical calculations, the following quantities are necessary: partition functions of the various molecular species $C_i$ $Si_j$, vapor pressures of both graphite and liquid silicon, and the Gibbs free energy increments for formation of silicon carbide from graphite and liquid silicon. The next paper, by J. Drowart (University of Chicago), fortunately provided mass spectroscopic information concerning the gaseous species in equilibrium with (1) silicon carbide and graphite and (2) silicon carbide and liquid silicon. The predominant species are Si, $SiC_2$, and $Si_2C$. Less important species are C, $C_2$, $C_3$, $Si_2$, $Si_3$, and finally SiC. Data was next presented on the solubility of carbon in liquid silicon by R. I. Scace (General Electric Research Laboratory). Over a wide temperature range,

Questions concerning the solubility of SiC in liquid Si were posed by J. Chipman of MIT.

he found that the enthalpy of solution is substantially a constant, and equals 59 ± 3kcal/mol. A peritectic transformation was found at 2830± 40°C. In the last paper of this session, W. V. Wright (Electro-Optical Systems) considered the ternary system, carbon-silicon-germanium. If germanium can substitute for silicon in silicon carbide, then a series of semiconductors with energy gap less than that of the binary compound is likely to result.



An informal between-sessions interch on the significance of silicon carbide face structures. The conferees shown (from left to right) are A. R. Verma ( versity of Delhi), S. Amelinckx (R universiteit, Ghent), and D. R. Hale vite Corporation).

GROWTH of silicon-carbide single crystals was discussed in Session II. The first group of papers in this session dealt with the growth of silicon carbide by sublimation in Lely-type furnaces. The growth mechanisms leading to high-purity crystals have been examined in some detail by D. R. Hamilton (Westinghouse Research Laboratory). The crystal habit, growth rate, and nitrogen solubility were found to be strongly dependent on temperature. In a later paper, A. H. Smith (Raytheon Research Laboratory) reported on the use of pyrolytic graphite, which is impervious to silicon vapor. A crucible made of this material can contain and funnel vapor minimizing the contamination problem inherent in massive furnaces with carbon black insulation. The conditions required for epitaxial growth onto silicon carbide were described by K. M. Hergenrother (Transistron Electronic Corporation). Single-crystal films can be grown onto hexagonal seeds at temperatures in excess of 2000°C and at a pressure of 20mm of Hg.

The next part of this session contained five papers on the growth of silicon carbide by gaseous cracking. The first, by J. T. Kendall (Texas Instruments, Ltd.), reviewed possible methods for growing silicon carbide. Suggestions were made of procedures whereby the usual gaseous cracking experiment can be modified to permit growing large cubic crystals. In the next paper, K. M. Merz (Carborundum Company) reported on the discovery of the long-looked-for wurtzite-type modification of silicon carbide. This modification was found among the products formed by cracking methyl trichlorosilane at 1400–1500°C. The following three papers, by V. E. Straughan (Horizons, Inc.), S. Susman (Armour Research Foundation), and W. Brenner (New York University), also reported on various techniques for preparing silicon carbide crystals by gaseous cracking. F. A. Halden (Stanford Research Institute) reported on his attempts to pull silicon carbide crystals from silicon melts by the Czochralski technique. Also, R. C. Ellis told us about the various techniques which he has used in order to increase the size of the crystals from the melt. Perhaps there is still an unknown solvent which would bring better results. Nobody has yet attempted hydrothermal growing. However, there are indications that experiments of this type will be performed.

THE third session was concerned with the properties of silicon carbide as a solid. The chief characteristic of the crystal structure of silicon carbide, in all of its many variants, is a tetrahedral arrangement of four carbon atoms around each silicon atom and, conversely, a tetrahedral arrangement of silicon atoms around each carbon atom.

There are a large number of possible tetrahedral structures. For silicon carbide, however, only periodic layer arrangements have been found. These problems were discussed more fully in the paper by H. Arnold (Max-Planck-Institut für Silikatforschung). A. Taylor (Westinghouse Research Laboratories) reported on his investigations on the thermal expansion of silicon carbide, and F. Euler (Air Force Cambridge Research Center) discussed the structure of a carbon residue obtained from the decomposition of silicon carbide. S. Amelinckx (Rijksuniversiteit Gent) and A. R. Verma (University of Delhi) described studies of the growth mechanisms of various silicon carbide crystals and correlated these mechanisms with polytypism. R. W. Keyes (Westinghouse Research Laboratories) presented goniometric data on some silicon carbide crystals.

L. F. Lowe (Air Force Cambridge Research Center) reported on the technique of neutron activation analysis for the detection of extremely low levels of impurities in silicon carbide. R. L. Rupp (Sylvania Research Laboratory) presented an emission spectrographic method of enhanced sensitivity. J. A. Dillon (Brown University) studied the interaction of oxygen with silicon carbide surfaces, and P. J. Jorgensen (University of Utah) investigated the kinetics of oxidation; they found that the rate of oxidation is diffusion controlled.

PROPERTIES of silicon carbide as a semiconductor were covered in Session IV. The first group of papers dealt with the band structure of silicon carbide. The tight binding method of comparing energy bands was applied to zinc blende and wurtzite structures by J. L. Birman (Sylvania Research Laboratory). This method is helpful in understanding the energy states in twinned crystals, as well as those having stacking faults. The next paper by L. Patrick (Westinghouse Research Laboratory) considered impurity bands and electroluminescence from silicon carbide *p-n* junctions. Measurements have been made on junctions of the type *p-n*-n*. The last paper of this group by W. J. Choyke (Westinghouse Research Laboratory) reported on the absorption of light in hexagonal silicon carbide

near the band edge. This paper shows that the interband transitions are indirect, requiring the absorption or emission of a 0.09 ev phonon.

The three papers that followed considered the electrical properties of silicon carbide. In the first, R. G. Pohl (Armour Research Foundation), reported values of electron mobility, energy gap, and thermoelectric power of very small cubic silicon carbide crystals. Next, E. A. Fagen (Armour Research Foundation) presented a method he has used to study both the isothermal and excess conductivity of black silicon carbide aggregates. The last paper of this group, by P. Carroll (The Carborundum Co.), reported on the resistivity of granular silicon carbide. The diffusion of III and V impurities into colorless silicon carbide was also discussed.

Several papers considered the optical properties of silicon carbide. Infrared transmission and reflectivity data on green hexagonal silicon carbide was reported by W. G. Spitzer (Bell Telephone Laboratories). A method of growing films of cubic silicon carbide on high-purity silicon surfaces was also described. The optical constants of cubic and hexagonal silicon carbide for the region of 1–10 ev were given by H. R. Philipp (General Electric Research Laboratory) and the effects of impurity absorption in silicon carbide were measured by H. G. Lipson (Air Force Cambridge Research Center). In the last paper of this group, W. T. Eriksen (Raytheon Research Laboratory), told of having utilized carrier injection electroluminescence to measure the minority carrier lifetime in silicon carbide.

The remaining material of the session dealt with the important problem of structural changes in silicon carbide caused by nuclear radiation. Aeolotropy of the radiation-induced expansions was studied by W. Primak (Argonne National Laboratory) and the paper by L. W. Aukerman (Battelle Memorial Institute) considered the effects of fast neutrons on silicon carbide. Both papers indicate that radiation damage effects in silicon carbide are small, which is primarily because of its tightly bound structure.

PAPERS describing process techniques and silicon carbide devices were presented in Session V. Several methods of etching silicon carbide were enumerated by J. W. Faust (Westinghouse Research Laboratory), the most promising etchants being mixtures of molten salts. The use of phosphoric acid as an etchant was discussed by R. C. Ellis (Raytheon Research Laboratory).

The next group of papers dealt with the preparation of contacts on silicon carbide. Shear seizure contacts were discussed by J. J. Bowe (Air Force Cambridge Research Center). Ohmic and rectifying contacts can be formed depending on the work function of the sheared metal. Rectifying contacts on *n*-type SiC have been investigated by T. C. Taylor (Raytheon Research Laboratory); these contacts are made by an alloy fusion process using aluminum. A high-temperature furnace utilizing a graphite-silicon carbide thermocouple was described by M. T. Minamoto (Air Force Cambridge Research Center). The papers that followed described two-terminal silicon carbide devices. The analysis of capacitance-voltage curves of *p-n* junctions in silicon carbide enabled H. G. Rudenberg (Transitron Electronic Corp.) to study several device parameters. C. Goldberg (Westinghouse Electric Corp.) described the fabrication of a silicon carbide rectifier capable of operation at 500°C. The rectifier was made from a silicon carbide crystal containing a grown *p-n* junction. The physics of semiconducting surfaces was employed by R. Goffaux (Ateliers de Constructions Electrique de Charleroi) to help explain the problem of conduction in silicon carbide varistors. The use of a point contact silicon carbide diode in switching circuits was described by A. L. Hopkins (Harvard University). These diodes have the advantage of being relatively insensitive to environmental changes.

The use of silicon carbide for the fabrication of transistors operating at 500°C was discussed by H. Chang (Westinghouse Electric Corp.). Unipolar and bipolar device designs were analyzed and the fundamental fabrication techniques were discussed in detail.

The contents of all papers, review material, and informal discussions presented at the conference have been edited by J. Smiltens and the writer. This material has been assembled into a book entitled *Silicon Carbide—A High Temperature Semiconductor*, published by Pergamon Press, Inc.