

## Growth and Properties of $\beta$ -SiC Single Crystals

W. E. Nelson, F. A. Halden, and A. Rosengreen

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Evaluation of the constants of integration yields:

$$r < r_h \quad T_0 - T_b = (T_0 - T_b) \frac{r_N}{r_h} + \frac{\lambda j^2}{\sigma k} r_N^2 \times \left[ \frac{1}{2} - \frac{1}{3} \frac{r_N}{r_h} - \frac{1}{6} \left( \frac{r_h}{r_N} \right)^2 \right] + \frac{(r_h^2 - r^2)}{6k} \left( \frac{\lambda j^2}{\sigma} + W_i \right), \quad (A26)$$

$$r_h < r < r_N \quad T - T_b = (T_0 - T_b) \frac{r_N}{r} + \frac{\lambda j^2}{\sigma k} r_N^2 \times \left[ \frac{1}{2} - \frac{1}{3} \frac{r_N}{r} - \frac{1}{6} \left( \frac{r}{r_N} \right)^2 \right], \quad (A27)$$

$r > r_N$

$$T - T_b = (T_0 - T_b) (r_N/r). \quad (A28)$$

The value of  $r_N$  is obtained from

$$\frac{W_i r_h^3}{3k r_N (T_0 - T_b)} + \frac{\lambda j^2 r_N^2}{3\sigma k (T_0 - T_b)} = 1. \quad (A29)$$

In terms of the total heater power  $q_h$ , and the total Joule heating in the normal region  $q_N$ , Eq. (A29) reduces to

$$q_h/q_0 + q_N/q_0 = (q_N/q_0)^{1/3}, \quad (A30)$$

where  $q_0$  has already been defined in Eq. (A22).

## Growth and Properties of $\beta$ -SiC Single Crystals\*

W. E. NELSON, F. A. HALDEN, AND A. ROSENGREEN

Stanford Research Institute, Menlo Park, California

(Received 8 September 1965)

Chemical, electrical, and optical measurements were performed on  $n$ - and  $p$ -type  $\beta$ -silicon carbide crystals grown from pure or doped carbon-saturated silicon melts. Pure, transparent yellow crystals showed no detectable impurities and had carrier concentrations in the range of  $10^{16} \text{ cm}^{-3}$ . Extensive twinning was observed. Uncorrected electron mobilities of 700–1000  $\text{cm}^2/\text{V}\cdot\text{sec}$  were measured at room temperature. Intense injection electroluminescence, peaking at 2.28 eV and 2.0 eV, was observed in many diodes. Strong photoluminescence was observed in aluminum-doped crystals at 77°K and at room temperature when irradiated with uv light.

### INTRODUCTION

SILICON carbide has received considerable attention over the last ten years as a potential new compound semiconductor. Many of its properties, such as its high band gap, chemical stability, and resistance to radiation damage, indicate that it could become a valuable addition to the family of semiconducting materials. In addition, its electro-optical properties as well as its existence in numerous structural modifications suggest that it may find some particularly unique applications.

Unfortunately the "material" problem, that of preparing pure single crystals, has proven to be extremely difficult to overcome. In fact, following a swell of activity in the late 1950's, active research on the electronic properties of high-purity silicon carbide decreased considerably. The early surge of activity was stimulated largely by Lely's development of a technique for preparing reasonably large  $\alpha$ -silicon carbide crystals (hexagonal structure) of quite high purity.<sup>1</sup> As work on this

technique progressed to yield crystals of improved purity, however, measured electronic properties did not appear to be improving accordingly. Electron and hole mobilities in particular showed relatively little improvement. Lely measured electron mobilities of about 120  $\text{cm}^2/\text{V}\cdot\text{sec}$  on "pure" transparent crystals. The highest values reported in the literature for high-purity  $\alpha$ -crystals<sup>2,3</sup> are approximately 400–500  $\text{cm}^2/\text{V}\cdot\text{sec}$ .

Work described in this paper was directed toward the growth and electrical evaluation of  $\beta$ -silicon carbide, the crystallographic modification normally obtained when crystal growth is accomplished at temperatures well below 2000°C. This modification has the zinc blende structure found in III-V compounds and is closely related to the diamond structure of silicon and germanium.

### CRYSTAL GROWTH

$\beta$ -silicon carbide crystals are grown from solution in a molten silicon solvent. The Czochralski furnace em-

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<sup>1</sup> J. A. Lely, *Ber. Deut. Keram. Ges.* **32**, 229 (1955).

<sup>2</sup> H. Chang, L. F. Wallace, and C. Z. LeMay, "Study, Development, and Application of Techniques Necessary to Fabricate Active Silicon Carbide Devices," Final Report, Air Force Contract AF 19(604)-5997, Westinghouse Electric Corporation (December 1960).

<sup>3</sup> H. J. van Daal, *Mobility of Charge Carriers in Silicon Carbide*, Philips Res. Rep. Suppl. **3**, (1965).

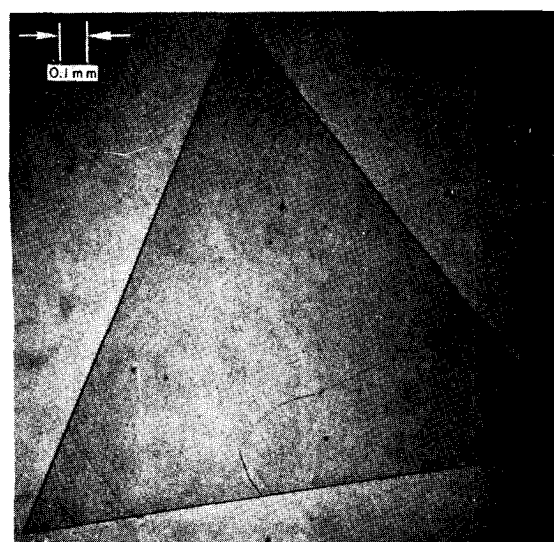
ployed for these studies was described previously.<sup>4</sup> One procedure found suitable for the growth of these crystals involves melting a 100-g charge of silicon in a graphite crucible approximately 1½ in. in diameter and 4 in. tall. The melt is formed in a nearly isothermal region of the furnace with the base of the crucible very slightly hotter than the top of the melt. The base is normally held at 1500°C for one hour to allow complete equilibration. A limited growth of silicon carbide is observed in the meniscus of the melt as carbon is transferred from the hot base of the crucible.

After equilibration, the temperature at the top of the crucible is slowly increased, maintaining the base at exactly 1500°C, until a vertical temperature gradient of 20°C/in. of melt is obtained. The crucible is held at this position for 12–24 h while crystals nucleate and grow at the base of the melt. The furnace is then either cooled slowly or quenched, and the silicon is dissolved out of the crucible by soaking it for several hours in a 3 HF · 5 HNO<sub>3</sub> solution. Subsequently, the β-SiC crystals, which are unaffected by the acid, are rinsed and sorted.

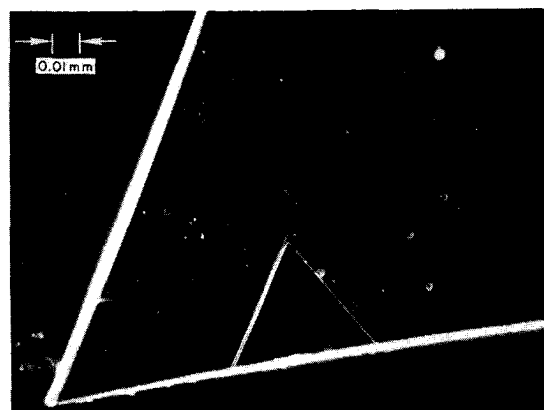
A normal yield consists of up to 1 g of transparent, yellow needles, plates, and dendrites. Needles frequently reach 1 cm in length. Triangular or trapazoidal plates, showing [111] faces, normally are quite thin (5–50 μ) and up to several millimeters on an edge. Figure 1 shows the optical perfection and nature of growth fronts observed in a typical crystal. These plates are selected for electrical measurements.

### CRYSTAL PURITY

In high-purity form, β-silicon carbide has a light canary-yellow color. Presence of any metallic impurities or nitrogen introduces a green cast, and as the impurity concentration increases the coloration rapidly approaches black. Emission spectroscopy can be employed to detect metallic impurities down to a few parts per million.<sup>5</sup> Direct measurement of nitrogen levels is more difficult, however, and requires the use of vacuum fusion procedures.<sup>1,6</sup> The amount of nitrogen incorporated in a growing crystal has been found to be a strong function of the growth temperature over the temperature range from 2300°–2800°C.<sup>7</sup> At the lower growth temperatures employed in this study it soon became apparent that



(a) BRIGHT FIELD



(b) DARK FIELD

FIG. 1. Typical silicon carbide crystal used for electrical measurements.

complete nitrogen elimination from the environment is even more critical.

By careful purity control during processing, including the use of purified graphite heaters and crucibles and semiconductor-grade silicon, it is possible to obtain crystals that show no metallic impurities when examined by emission spectrography. Early in 1961, such crystals were found to retain a greenish cast, to be low-resistivity *n*-type, and to have electron mobilities of about 10 cm<sup>2</sup>/V·sec (run 58, Table I). This corresponds closely with results obtained by Pohl<sup>8</sup> and van Daal.<sup>3</sup> Carrier concentrations in these crystals were approximately 2×10<sup>19</sup>. Subsequent nitrogen analyses indicated doping levels of ~5×10<sup>18</sup> atoms/cm<sup>3</sup>, in agreement with the results of electrical measurements.

<sup>4</sup> F. A. Halden, "Growth of Silicon Carbide Crystals from Solution in Molten Metal Alloys," *Silicon Carbide: A High Temperature Semiconductor*, edited by J. R. O'Connor and J. Smiltens (Pergamon Press, Inc., New York, 1960), p. 115.

<sup>5</sup> F. A. Halden, W. P. Meuli, and W. J. Fredericks, "Growth of Silicon Carbide Single Crystals," Final Report, Bureau of Ships Contract NObsr 72772, Stanford Research Institute (15 June 1961).

<sup>6</sup> W. E. Nelson, F. A. Halden, and A. Rosengreen, "Beta-Silicon Carbide and Its Potential for Devices," Final Report, Bureau of Ships Contract NObsr 87235, Stanford Research Institute, December 1963 (unpublished).

<sup>7</sup> D. R. Hamilton, *Silicon Carbide: A High Temperature Semiconductor*, edited by J. R. O'Connor and J. Smiltens (Pergamon Press, Inc., New York, 1960), p. 50.

<sup>8</sup> R. G. Pohl, "Electrical Properties of β-Silicon Carbide," *Silicon Carbide: A High Temperature Semiconductor*, edited by J. R. O'Connor and J. Smiltens (Pergamon Press, Inc., New York, 1960), p. 312.

TABLE I. Results of Hall measurements on  $\beta$ -SiC crystals at room temperature.

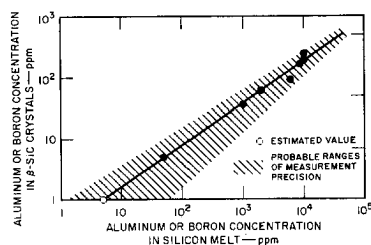
Crystal number	Resistivity <sup>a</sup> ( $\Omega \cdot \text{cm}$ )	Mobility <sup>a</sup> ( $\text{cm}^2/\text{V} \cdot \text{sec}$ )	Carrier concentration ( $\text{cm}^{-3}$ )
H1 <sup>b</sup>	0.16	980	$4.0 \times 10^{16}$
70	0.70	890	$1.0 \times 10^{16}$
73	0.11	760	$7.5 \times 10^{16}$
84	0.32	680	$2.9 \times 10^{16}$
85	0.12	410	$1.2 \times 10^{17}$
90	0.19	310	$1.1 \times 10^{17}$
87	0.54	14.4	$8.1 \times 10^{17}$
58 <sup>b</sup>	0.03	9.6	$21. \times 10^{19}$

<sup>a</sup> Uncorrected values.<sup>b</sup> Measured by conventional method.

To minimize nitrogen and other remaining impurities in the crystals, several process modifications were introduced: (1) graphite crucibles were acid-leached for several days before each run; (2) all graphite elements in the furnace were outgassed at 2200°C and  $10^{-6}$  mm prior to each run; (3) low-nitrogen float-zone-melted silicon was obtained; and (4) premium, low-nitrogen helium was purchased and passed through an activated-charcoal trap held at liquid-nitrogen temperature. The result of these modifications was brilliant-yellow crystals containing no detectable impurities.

Crystals remain *n*-type when grown under conditions obtaining highest purity. By adding aluminum or boron to the silicon melt *p*-type crystals can also be grown. The extent of doping obtained in the crystals appears to be a sensitive function of the dopant concentration in the melt. This is illustrated in Fig. 2, which shows the results of emission spectrographic analyses on the solvent and crystals obtained from several runs. At doping levels higher than 10 ppm in the solvent, all crystals grown were *p* type. The region over which the crystal type changes corresponds to doping levels of  $10^{15}$  to  $10^{17}$  atoms/cm<sup>3</sup> in the crystals, depending on the extent of nitrogen elimination from the system prior to crystal growth.

X-ray studies of the structure of large solution-grown  $\beta$ -SiC crystals show that predominant faces are [111]. All large crystals checked to date indicate some degree of twinning, showing rotation around the (110) axis with the twin pair having the [111] face in common. This is in agreement with earlier studies performed on less pure crystals, where all but two crystals showed various degrees of twinning.<sup>9</sup> Second-order twinning was

FIG. 2. Dopant concentration in silicon melts and  $\beta$ -silicon carbide crystals.

also reported. In addition, boundaries such as those evident in Fig. 3 are sometimes observed. Since these crystals are still being grown under conditions favoring dendritic and dislocation-induced modes of growth, rather than under conditions providing a stable growth front, the presence of such features is not surprising.

### ELECTRICAL MEASUREMENTS

Hall measurements were made at room temperature using both the conventional method and the method described by Van der Pauw.<sup>10</sup> Crystals of uniform thickness were selected for these measurements. Ohmic contacts were made by alloying a gold-tantalum alloy into the crystal at 1200°–1400°C in vacuum ( $10^{-5}$  Torr).<sup>11</sup> To provide the desired wetting characteristics for the size of contacts desired, an alloy containing 10 at.% tantalum was applied. Two-mil gold wires were bonded to the contacts by thermocompression. For crystals of low resistivity ( $0.01$ – $0.1 \Omega \cdot \text{cm}$ ) reasonably good contacts could also be made by using indium solder. In this case, solder-coated gold wires were joined directly to the crystals using a heated wedge on a thermocompression bonder. Figure 3 shows a crystal mounted for measurements.

Some typical results from the Hall measurements are tabulated in Table I. Since the energy band structure for  $\beta$ -silicon carbide is not well determined, the simplified relation for the carrier concentration  $n = 1/e\mu\rho$  has been used, where  $e$  is electron charge,  $\mu$  is mobility, and  $\rho$  is resistivity.

For all the crystals listed, no metallic impurities were detectable by emission spectrography, the principal dopant being nitrogen. The given values of resistivity and electron mobility are not corrected for size of contacts. Even though the contacts were kept to a size of a circle with a diameter of approximately 0.05 mm, they were in many cases of significant size compared to some of the crystal dimensions, most crystals being long lath approximately 0.25–0.5 mm wide and 20–40  $\mu$  thick. Judging from results reported by van Daal<sup>8</sup> on correction factors to be applied to Hall measurements on small crystals, many of the quoted values of mobility should be increased by at least 30%–40%. The increase in resistivity is somewhat smaller.

Some measurements were made on crystals with dimensions even smaller than mentioned above, among them crystal H1 in Table I. For these crystals the corrections were estimated to be up to 300%–400%, resulting in electron mobilities on the order of several thousand. However, such values are of doubtful significance, since it is not known whether these differences may result from a higher degree of crystal perfection in the smaller crystals or from inexact correction procedures.

The effect of crystal imperfections on the mobility values has been underlined by recently initiated meas-

<sup>9</sup> J. A. Kohn and D. W. Eckart, Am. Mineral. 47, 1005 (1962).<sup>10</sup> L. J. Van der Pauw, Philips Res. Repts. 13, 1 (1958).<sup>11</sup> H. J. van Daal *et al.*, Silicon Carbide Semiconductor Device, U. S. Patent 3,047,439 (July 1962).

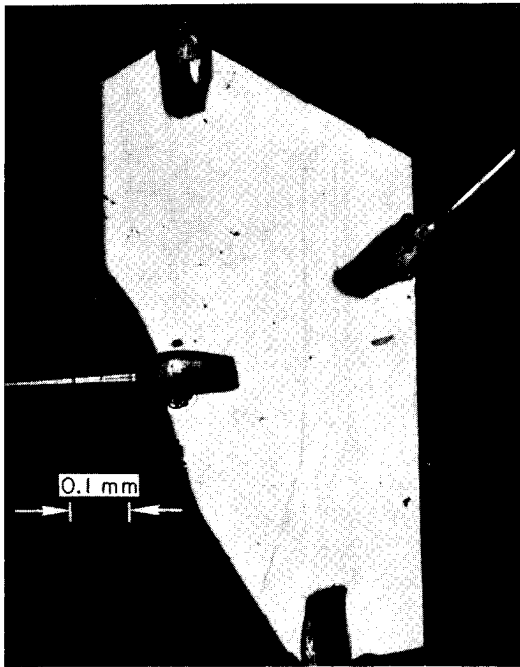


FIG. 3. Hall measurement crystal with Au-Ta contacts and 2-mil gold wires: Van der Pauw method, crystal 85.

measurements of electron mobility at low temperatures. The results for crystals 84 and 85 are shown in Fig. 4, where  $R_1$  and  $R_2$  are the resistances measured to determine the resistivity using Van der Pauw's method.<sup>10</sup> As pointed out by van Daal,<sup>3</sup> the ratio  $R_1/R_2$  depends, for a homogeneous material, on crystal dimensions only and should remain constant with temperature. The fact that  $R_1/R_2$  varies rapidly with temperature indicates the presence of macroscopic inhomogeneities in the crystals such as clusters of impurities and/or crystal imperfections. These create space charges that are effective scattering centers. Weisberg<sup>12</sup> showed that such scattering leads to a  $T^{-3}$  temperature dependence of the mobility  $\mu_{sp.ch.}$ .

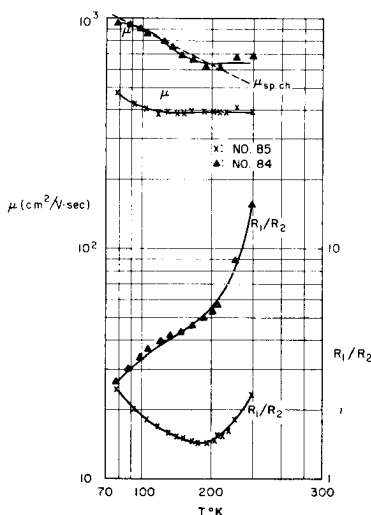


FIG. 4. Electron mobility  $\mu$  and  $R_1/R_2$  as a function of temperature  $T$ . Theoretical temperature dependence of mobility limited by space charge  $\mu_{sp.ch.}$  is indicated by dashed line.

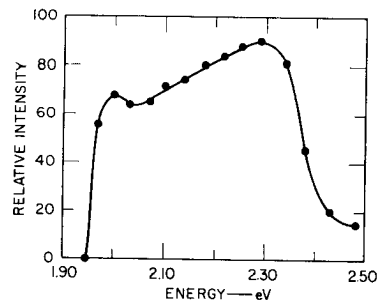


FIG. 5. Spectrum of electroluminescence from alloyed  $p$ - $n$  junction at room temperature.

The variation of the mobility  $\mu$  with temperature (Fig. 4) fits this dependence fairly well for crystal 85 while the mobility for crystal 84 is almost constant. Considering the variation of  $R_1/R_2$  with temperature and the fact that x-ray analysis has shown existence of twinning in these crystals, it is believed that the mobility in samples investigated is limited by crystal inhomogeneities similar to those observed in  $\alpha$ -SiC.<sup>3</sup> The values of electron mobilities should therefore be considered only as effective values. For perfect  $\beta$ -SiC crystals van Daal<sup>3</sup> estimates a value of  $1300 \text{ cm}^2/\text{V}\cdot\text{sec}$  at  $300^\circ\text{K}$  assuming polar scattering to be the dominant lattice-scattering mechanism.

## OPTICAL MEASUREMENTS

Fabrication of  $p$ - $n$  junctions was done by alloying silicon heavily doped with arsenic into  $p$ -type crystals doped with aluminum. Most of the diodes emitted light when biased in the forward direction. At a current density of  $20 \text{ A/cm}^2$  the light was red-orange, the junction area having a brightness of approximately 10 ft-L. With increasing current the visible radiation changed to green and at  $170 \text{ A/cm}^2$  had a brightness of 100 ft-L. The spectral distribution of the emitted light for the latter case was as shown in Fig. 5. A simple efficiency measurement using silicon solar cells indicated an efficiency in the range  $10^{-5}$ – $10^{-4}$  at room temperature.

Many  $\beta$ -silicon carbide crystals show strong photoluminescence at  $77^\circ\text{K}$  when irradiated by ultraviolet light. Some are also photoluminescent at room temperature. Varying intensities of colors are observed in the range from red to green. Crystals from very pure runs, boron-doped crystals, and impurity-laden crystals do not show photoluminescence. Crystals slightly doped with aluminum, but free of any other detectable impurities, display the strongest photoluminescence, emitting intense orange or pink light at  $77^\circ\text{K}$ .

## ACKNOWLEDGMENT

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<sup>12</sup> L. R. Weisberg, J. Appl. Phys. 33, 1817 (1962).