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THE TRAVELLING SOLVENT METHOD OF CRYSTAL GROWTH

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I. INTRODUCTION

During this period work has continued on the SiC crystal growth and P-N junction fabrication using chromium as solvent. Some electrical properties of the junctions have been studied.

Work was commenced on the use of Cr/Si alloys as possible solvent materials in applying TSM to SiC.

II. DISCUSSION

A. FABRICATION OF P-N JUNCTIONS

Quarterly Report No. 6 described, in detail, the new technique which led to successful crystal growth of SiC by TSM using Cr as solvent. Single crystals containing large area P-N junctions have subsequently been prepared utilizing that same preparation route.

Since both P and N conductivity type of SiC were available to us, sandwiches were assembled such that one type could be deposited from Cr-rich solution onto the other. Fig. 1 shows a photograph of a "block" cut from one such zone passing run. This piece measured 3 mm x 3 mm x 2 mm and is quite typical. Although not obvious from Fig. 1, the darker colored (P-type) material remained transparent following passage of Cr through it. No unsuccessful zone passing experiments have been encountered with our new technique, and the type of specimen shown in Fig. 1 is now readily obtainable. Supply of raw material is likely to be the greatest problem.

In addition to P-N junction fabrication, using the foregoing method, a few experiments have been performed by doping the travelling zone at some point during its passage. A sample of "rather dirty" P-type material was used for the test during which nitrogen was added to the usual argon blanket gas. Nitrogen is a well known N-type dopant inducing a level at about 0.03 eV below the conduction band. Fig. 2 shows a photomicrograph of a cross-section through a specimen nitrogen-doped during growth. As is readily seen, a quite flat junction resulted, being delineated by electrolytic etching in hydrofluoric acid for 30 secs at room temperature.

B. ELECTRICAL PROPERTIES OF P-N JUNCTIONS

Before electrical property measurements could be made on the P-N junctions, suitable ohmic contacts were required. Platinum was tried with some measure of success, but required a high temperature for alloying, and yielded somewhat high resistance contacts; this led to our rejection of this metal. Pure gold did not wet SiC surfaces adequately, but addition of 1% wt of Ta greatly aided this. Subsequently, small additions of aluminum (dopant) to the Au/Ta alloy were found to yield excellent contacts to P-type SiC. Antimony has been added to Au/Ta alloy for the purpose of contacting to N-type material. Even though the antimony atom is extremely large (relatively) and should not therefore be readily accommodated in the SiC lattice, its addition resulted in ohmic contacts superior to those obtainable with undoped Au/Ta alloy. A gold-rich alloy has the advantages of requiring only relatively low temperatures for alloying into SiC and also, being soft and ductile, it imposes only moderate stress on the semiconductor during thermal transients.

Fig. 3 shows a typical oscilloscope trace for a SiC diode prepared by TSM. While the reverse characteristic leaves much to be desired and is almost certainly a result of inadequate surface treatment, the forward-biased characteristic is unique for SiC diodes. Turnover has been found to occur at about 1.3 volts. Fig. 4 shows the results from point-by-point I-V measurements. It is of interest to compare the forward characteristics exhibited by the TSM prepared diodes with those reported previously in the open scientific literature. While the "forward voltage drop" for a diode is not easy to define, since:

$$I = I_0 \left[\exp (eV/nkT) - 1 \right] \quad (1)$$

where I is the current, I_0 the diffusion current, and V applied voltage, it is expected that "a reasonably large current" should be passed by a SiC P-N junction at an applied potential of the order of 1 - 1-1/2 volts. The measured currents in the forward direction for these diodes are several orders of magnitude greater than for any previously reported. From Fig. 5,

which is a semilog plot of current as a function of voltage, "n" (Eq. 1) is found to be 2.4. The true physical significance of the factor "n" is not understood, but its value, which ideally should be unity, is frequently taken as the criterion for the "quality" of a diode. Work on other semiconductors, e. g. GaAs, revealed that "n" decreased continually towards unity as the purity of the bulk semiconductor was progressively improved. The somewhat high "n" value found for SiC diodes may, therefore, have its root in an undoubtedly high impurity content in presently available material.

The variation of junction capacitance with applied voltage for a typical diode is presented in Fig. 6. As may be readily seen, a $1/c^2 \propto V$ relationship is exhibited, indicating a relatively abrupt junction. The variation would tend towards $1/c^3 \propto V$ for a diffuse junction.

The extrapolated voltage " ϕ " (Fig. 6) corresponding in theory to an infinite capacitance, is identified as that voltage producing a flat band condition across the junction, i. e., zero space charge. ϕ can never possess a value greater than the fundamental energy gap, "Eg." for a non-degenerate semiconductor, and will vary with resistivity. Typically ϕ is found to be 0.6 Eg - 0.8 Eg in practice; our experimentally determined value of ~ 2.1 volts for SiC lies within the anticipated range for the solid.

Since, from the purely technological viewpoint, the principal interest in SiC devices is for elevated temperature applications, we have conducted preliminary investigations into the effect of temperature upon diode I-V characteristics. Fig. 7 shows a series of oscilloscope traces for a typical diode. The forward-biased characteristic improves continuously, while only in excess of 500°C does the reverse characteristic begin to "soften". During these experiments some indication that the relatively poor reverse characteristic may result from surface leakage was found since during heating some "hardening" was observed.

In summary, TSM has been successfully applied to P-N junction fabrication during crystal growth in α -SiC. Ohmic contacts have been made to dice cut from the junction-containing single crystals. Electrical measurements on the resulting diodes reveal unique forward voltage characteristics, the currents passed being several orders of magnitude greater than for previously reported SiC diodes and of the order expected for the solid. Capacitance

measurements indicate that abrupt P-N junctions have been prepared by TSM. The rectifying properties of the P-N junctions remain good to temperatures in excess of 500°C.

III. THE SILICON CARBIDE - SILICON SYSTEM

A study of the available data on the silicon-carbide system indicates that the slope of the liquidus, in this system, is very steep. It was concluded therefore that in order to provide a driving force of sufficient magnitude for zone movement, the gradient across the specimens must be very large. A highly efficient heat sink was, therefore, designed and constructed and is shown in Fig. 8. The length of the tungsten rod and hence the temperature gradient across the sandwich can be altered at will. Thus, optimum conditions for growth can be quickly found. With this heat sink it was observed that a maximum temperature gradient greater than 200°C could be maintained between the top and bottom surfaces of the sandwich. This was sufficient to cause the silicon zone to move. This is shown in Fig. 9.

The rate of zone movement was extremely slow, even with this large temperature gradient. A calculation, using the solubility data of Scace and Slack⁽¹⁾ and assuming a diffusion coefficient of 10^{-4} cm²/sec, shows that only small rates can be expected. The investigation of this system as a practical method of growing silicon carbide single crystals was, therefore, discontinued.

It should be emphasized, however, that two important conclusions can be drawn from this work:

1. Silicon will wet silicon carbide with no surface preparation other than a routine degrease;
2. The rate of zone movement is too slow to be of any practical value.

IV. SILICON CARBIDE - PLATINUM SYSTEM

The apparatus to investigate this system has been illustrated in previous reports. It has also been shown that platinum will react well with silicon carbide, though no attempt has been made to produce any zone movement.

A feature of this system has always been the poor reproducibility of the results. The apparatus was, therefore, modified to permit visual observation of furnace conditions and heat sink similar to the one illustrated in Fig. 8. These improvements have made the experiments easily duplicated, but at the present time the heating unit has not proved capable of maintaining a sufficient temperature gradient for zone movement to take place. Work is still proceeding with a view to optimizing furnace conditions.

V. SILICON CARBIDE - SILICON CHROMIUM SYSTEM

It was reported in Quarterly Report No. 6 that chromium would pass through silicon carbide, providing good wetting was achieved. The only disadvantage of this method is that the surface preparation has to be carried out very carefully and is relatively time-consuming. Silicon is known to wet silicon carbide very easily, but zone movement is very slow. A combination of silicon and chromium together should, therefore, provide good wetting and an acceptable rate of zone movement.

A silicon chromium alloy was, therefore, made up containing 12% by weight of silicon. This alloy melts at 1515°C , and its composition corresponds to the eutectic between Si and Cr_3Si . Zone passing was then attempted using the apparatus designed for the silicon carbide - chromium system. Encouraging results were obtained, although it became obvious that some attempt to optimize growing conditions must be made. The following variables were, therefore, investigated:

1. Zone movement and cleanliness of pass as a function of average temperature of the alloy;
2. Zone movement and cleanliness of junction as a function of zone thickness;
3. Determination of the rate controlling process for the reaction.

Figures 10 and 11 illustrate the results obtained from investigations 1 and 2.

It should be pointed out that the horizontal coordinate of Fig. 10 refers to heating temperature in excess of that required to melt the alloy. If

the actual alloy temperature were recorded, then the experimental dependence would be even more pronounced since radiation losses from the heater will be greater at the higher temperatures. Thus, a 50°C rise in temperature of the heater will not correspond to a 50°C rise in temperature of the sandwich. This effect will increase at the higher temperatures.

Figure 11 can be examined in a calculation similar to the one performed for the silicon - silicon carbide system. If one assumes a liquid diffusion coefficient of 10^{-4} cm²/sec. , which is reasonable for a just molten liquid, then we get a difference in concentration between the hot and cold regions of the alloy of 7.5×10^{-2} molecular %. The process would, therefore, appear to be diffusion controlled. Microscopical observation of the regrown layers indicate that junction cleanliness is independent of temperature. Increasing the zone thickness much above .015 inches, results in partial break-up of the zone, while zones much below .006 inches, tend to give irregular movement. The rate controlling process of the reaction can be investigated quite simply. It has been reported that hexagonal silicon carbide exhibits different etching rates on opposite sides of a single crystal platelet⁽²⁾. This difference in dissolution is similar to that found on the (111) surfaces of III-V intermetallic compounds⁽³⁾. The different faces were, therefore, identified by etching in a molten salt solution and zones were passed through different combinations. Thus the dissolution and deposition rates were varied. However, since no effect on the rate of zone movement was observed, it can be concluded that the process is diffusion controlled.

VI. FUTURE WORK

1. The effect of the temperature of regrowth will be studied using back reflection X-ray techniques;
2. Attempts will be made to grow a large single crystal;
3. P-type material will be grown onto N-type and the electrical properties of the junctions will be studied;
4. The alloy will be doped with various impurities and the effect on the regrown material will be studied.

VII. REFERENCES

1. R. I. Scace and G. A. Slack, Silicon Carbide, Pergamon Press, pg. 24.
2. J. W. Faust, Jr., Silicon Carbide, Pergamon Press, pg. 403.
3. J. W. Faust, Jr., Electrochemical Society Meeting, Cleveland, Ohio, October 1956.



FIG. 1 Photograph of "Block" Cut from SiC Single Crystal Containing P-N Junction



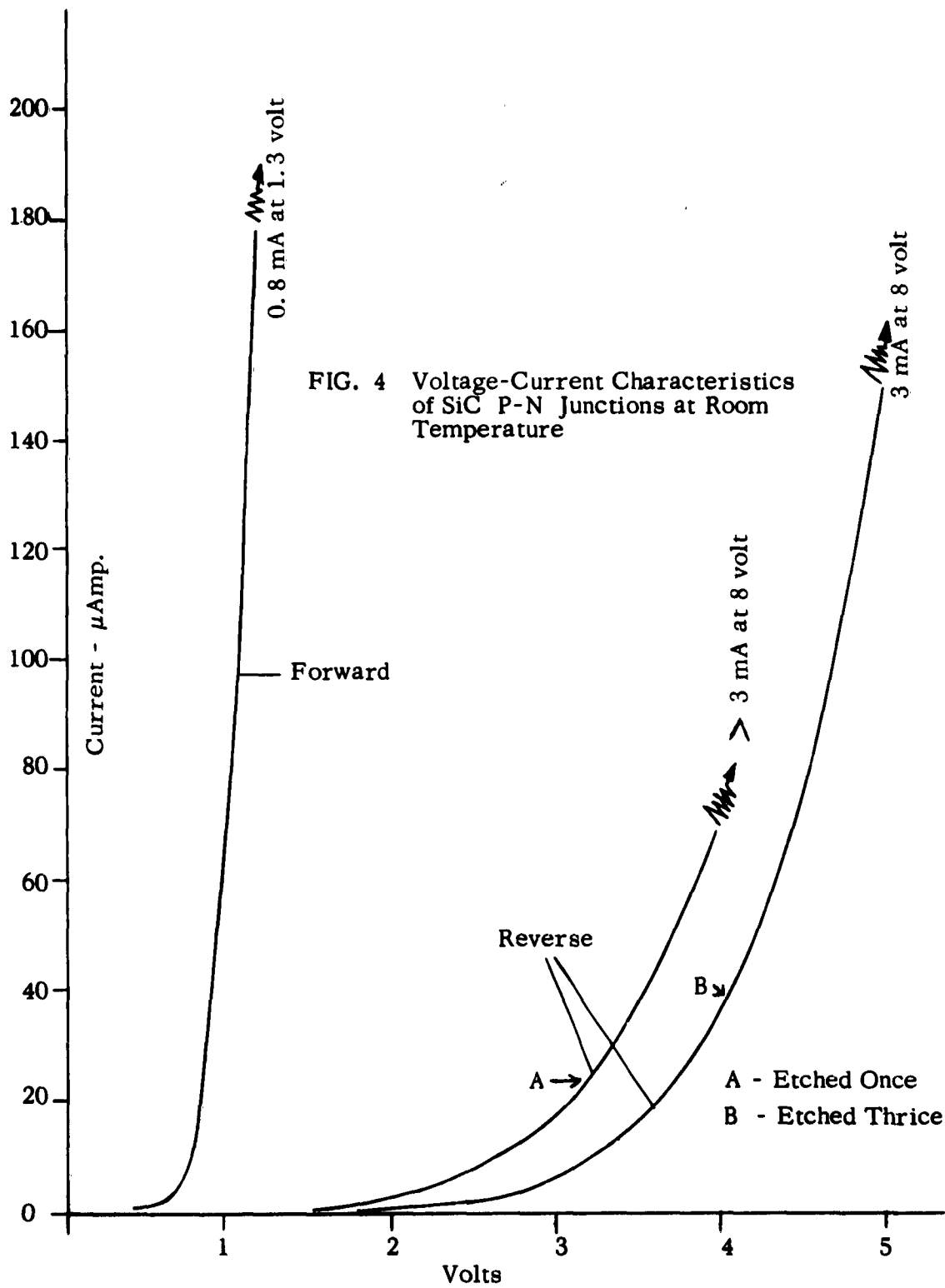
FIG. 2 Cross-Section through SiC Crystal Showing P-N Junction; mag. x 250; etched electrolytically in HF

5 mA/cm



2 volts/cm

FIG. 3 Room Temperature I-V Characteristics of SiC P-N Junction Diode



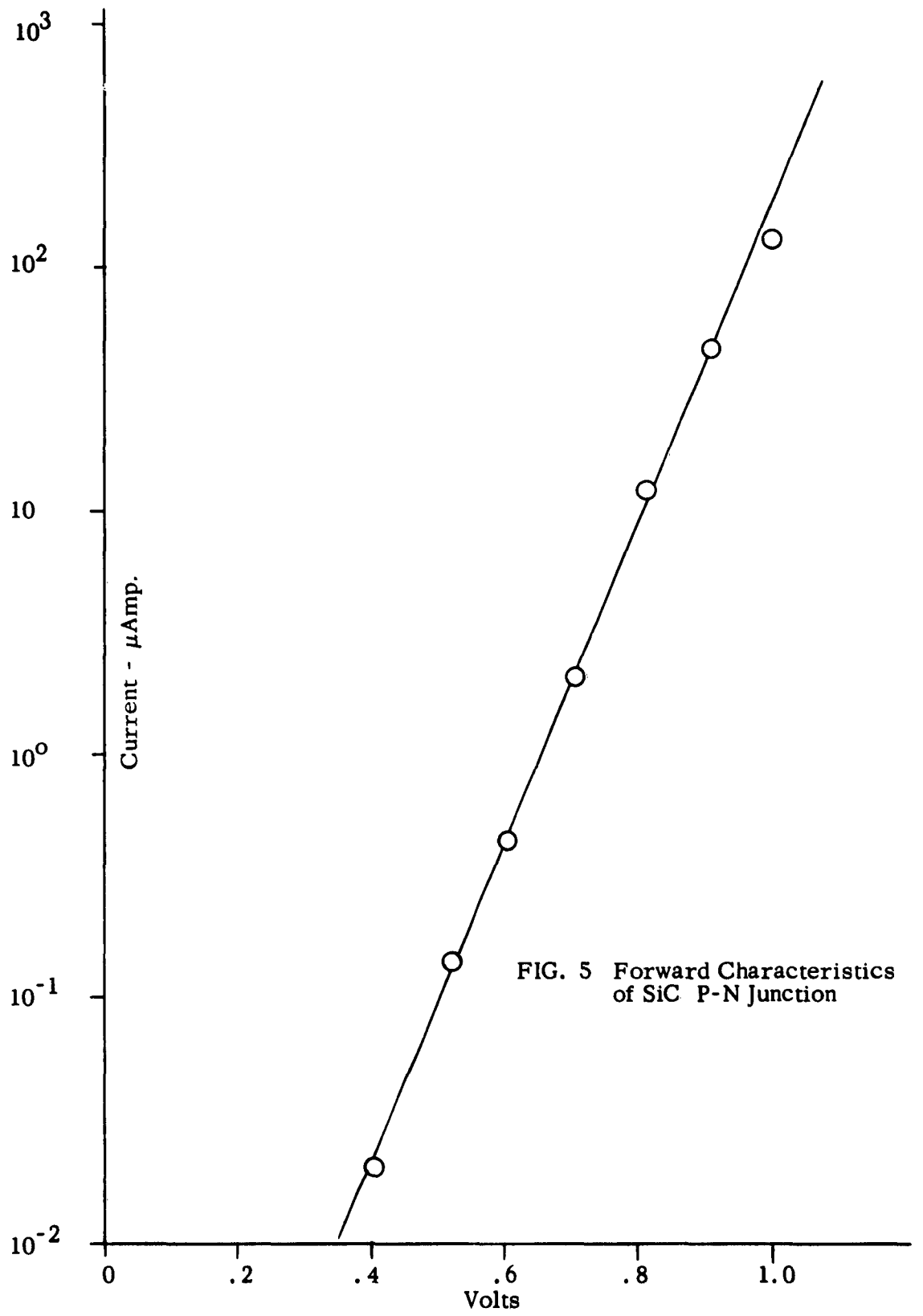
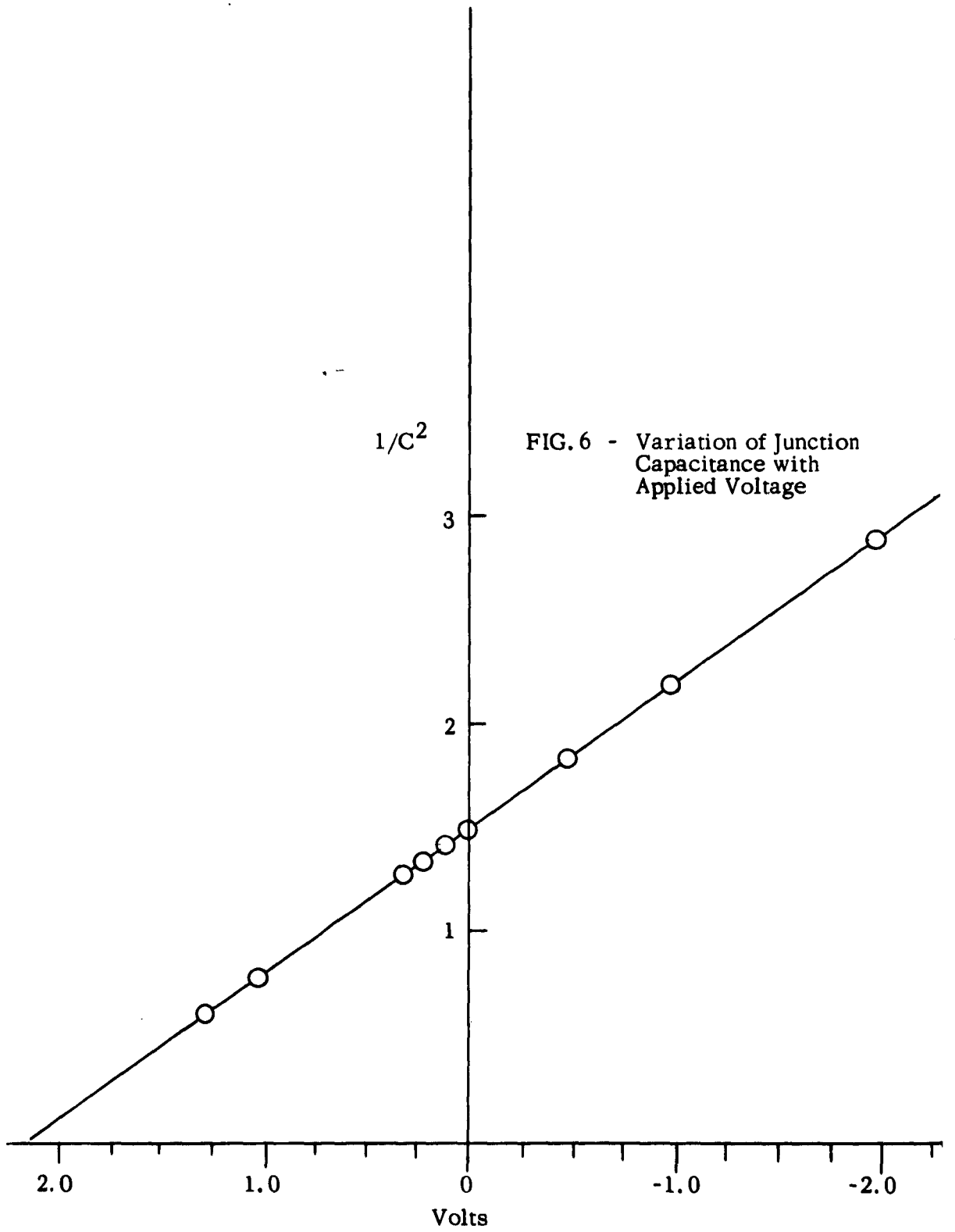
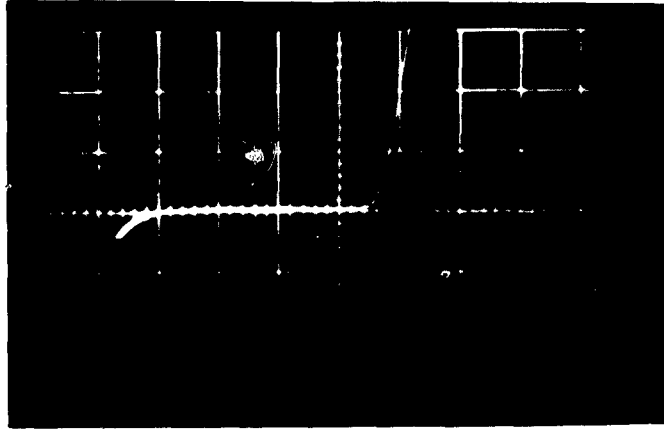
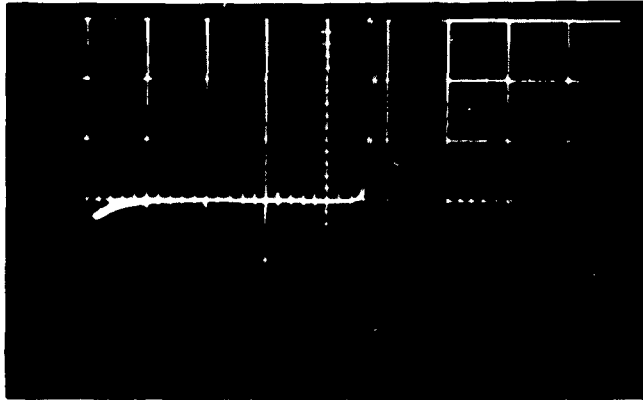


FIG. 5 Forward Characteristics of SiC P-N Junction

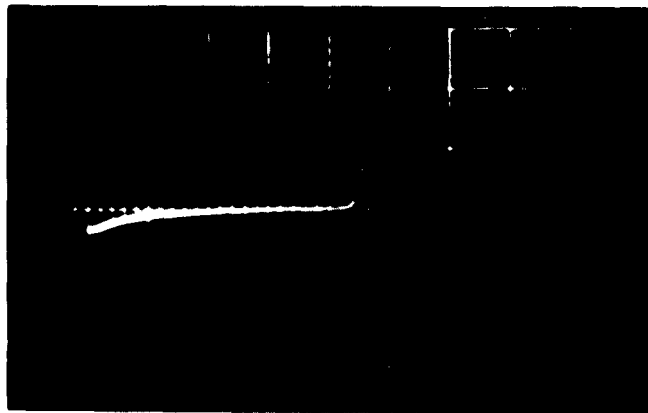




30°C

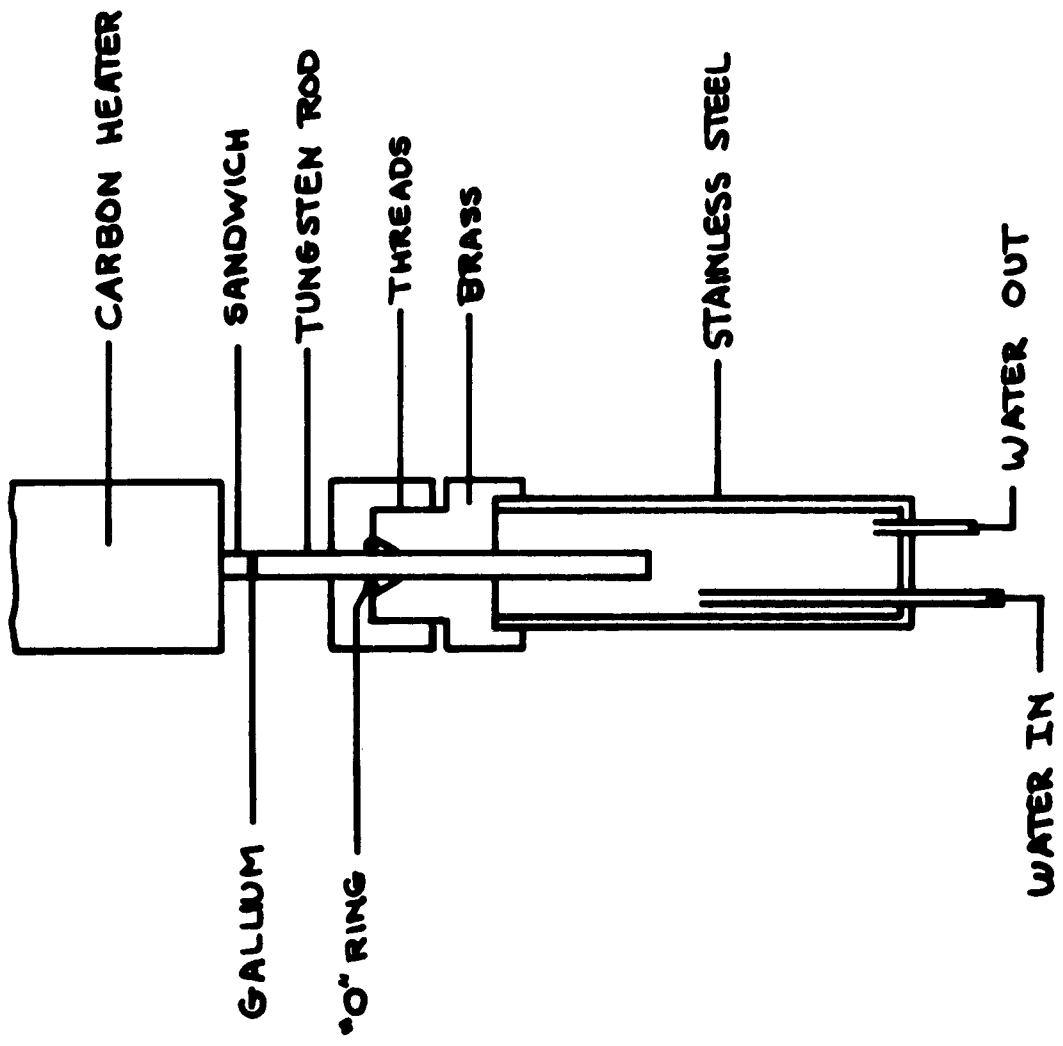


320°C



540°C

FIG. 7 Temperature Dependence of I-V Characteristics of SiC P-N Junction Diode (5ma/cm and at 2 volts/cm)

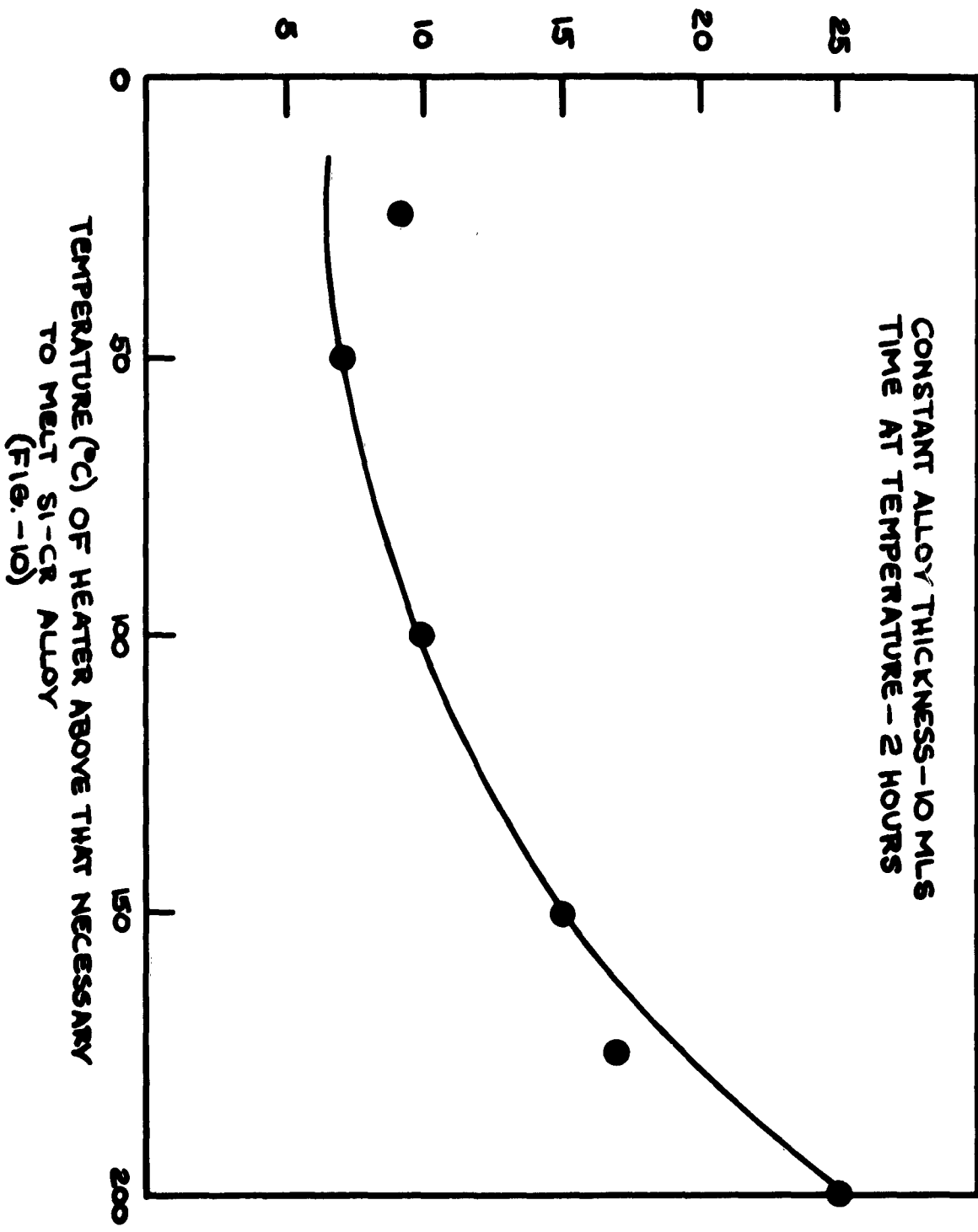


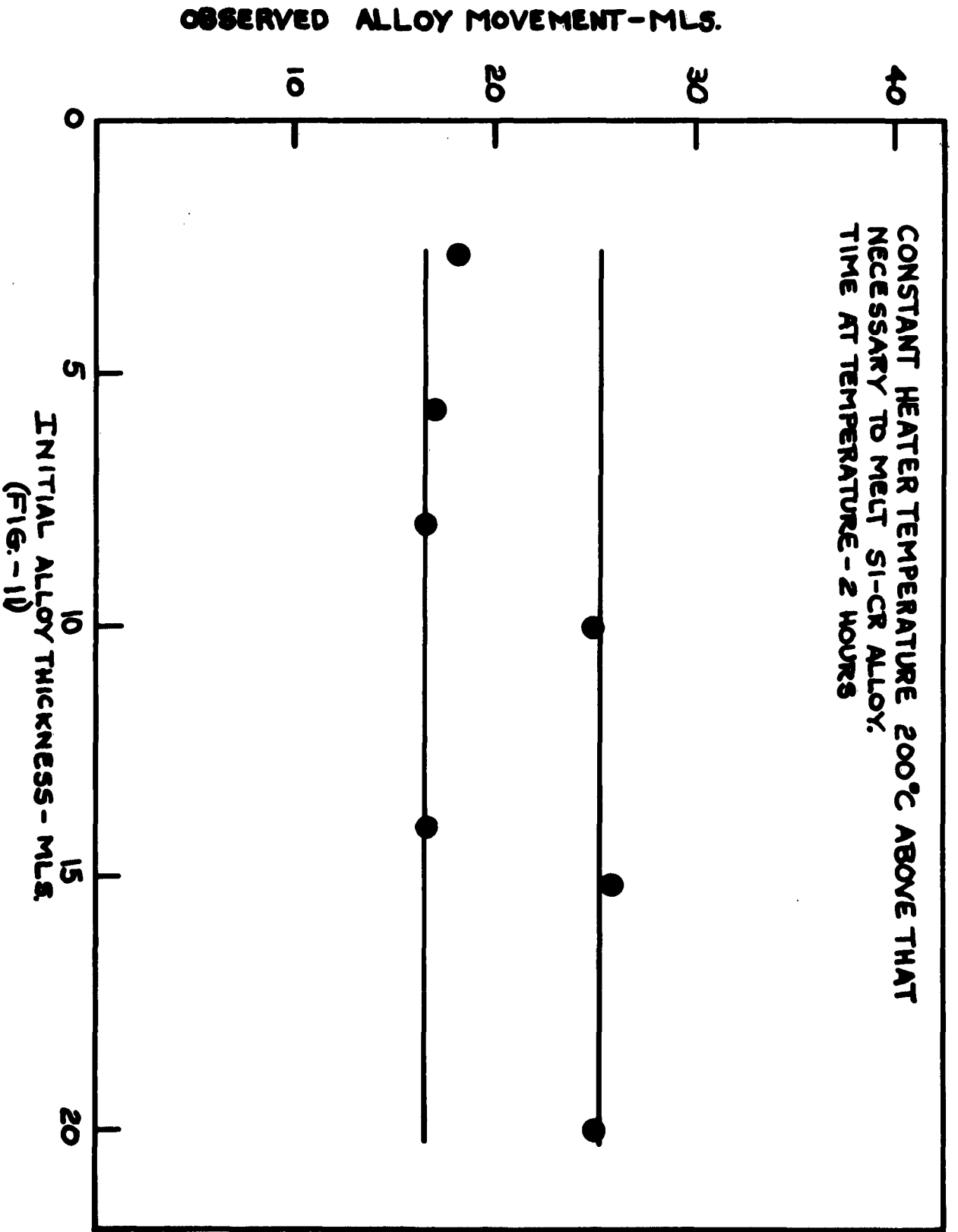
(FIG.-8)



FIG. 9 Zone Movement in Si/SiC Sandwich

OBSERVED ALLOY MOVEMENT - MLS.





AF Cambridge Research Laboratories, L. G. Hanscom Field, Mass. Rpt. No. AFCRL 63-75, THE TRAVELLING SOLVENT METHOD OF CRYSTAL GROWTH, Qtrly rpt No. 7, 12 March 1963, 18p., illus. Unclassified Report tables.

P-N junctions in α - SiC made by TSM exhibit unique forward characteristics, the current density at low voltages being orders of magnitude greater than for SiC diodes made by other techniques.

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