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Negative Resistance Tunnel Diodes in Silicon Carbide

Although rectifying p - n junctions in silicon carbide have been known for a long time, great difficulties have been encountered in constructing useful active devices in this material. This communication describes an active device operable at temperatures as high as 500°C and consisting of a tunnel diode p - n junction¹ formed by alloying Si to crystals of very heavily doped p -type hexagonal SiC. The diode is made by using a very fast alloying cycle similar to those used to produce tunnel diodes in such materials as Ge or GaAs. The I - V characteristics have been generally similar to those of tunnel diodes produced in these materials, but the peak-to-valley current ratios achieved so far have been much lower, the highest value being 1.37.

Figure 1 shows the I - V characteristics for a diode taken at different ambient temperatures. The characteristics at liquid helium temperature (-269°C), which are not shown in the Figure, almost coincide with those shown for liquid nitrogen temperature (-196°C). For this unit the room temperature peak-to-valley ratio is 1.1. The series resistance is not accurately known, but a measurement of the slope of the I - V characteristic at a negative current of 100 mA, where it is not yet linear, gives a value of $3.3\ \Omega$, which represents an upper limit. The curves of Fig. 1 show certain distinctive features not generally observed for tunnel diodes made from the well-studied materials such as Ge and GaAs. First, at room temperature and below they indicate a high impedance at the origin. Second, the peak voltage is unusually high, approximately 0.9 V at 24°C , the reason for which has not yet been established. Unusually high tunnelling currents at high forward biases are known to occur in tunnel diodes in other materials such as Si, Ge, and GaAs, and are generally attributed to such mechanisms as tunnelling via defect states or deep impurity levels operating in the excess current region of the forward bias I - V characteristics.² In the present case, band-to-band tunnelling cannot

be excluded since the doping levels, and especially the level on the n -side of the junction, are not accurately known. It will be observed from the curves of Fig. 1 that a negative resistance still persists at 400°C . In a few units,

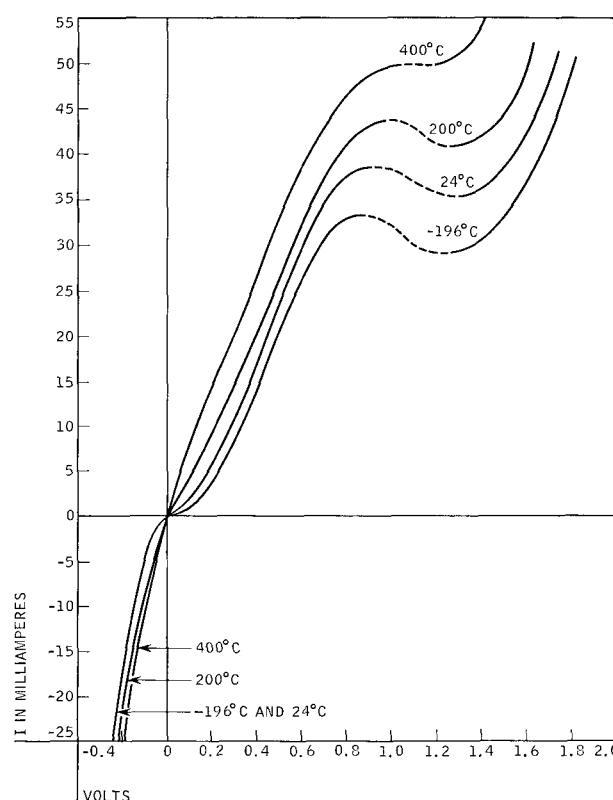


Figure 1 I - V characteristics for a SiC tunnel diode at different ambient temperatures. These curves were taken on a unit in which the Si dot had been etched away and a pressure contact made to the n -region in the SiC.

negative resistance was observed at temperatures as high as 500°C. The peak current densities of diodes showing a negative resistance at room temperature varied from 10 to 150 A/cm². The capacitance per unit area at 1.1 V forward bias was measured to be 2 μF/cm² for a particular diode which had a peak current density of 120 A/cm².

The SiC diodes were fabricated from a group of very heavily Al-doped hexagonal crystals, with well defined (0001) faces, obtained from The Carborundum Company. Separate electrical measurements on two representative crystals from this group showed the doping levels to be 4.5×10^{20} and 9×10^{20} uncompensated carriers. Solid-state mass spectroscopy measurements on another of the crystals indicated a slightly higher total Al content with evidence of inhomogeneity throughout the crystal and, possibly, localized accumulations of Al.

The SiC crystals in various thicknesses from 10 to 40 mils were cleaved into sections having areas of approximately 3000 mil². These were fused to tungsten tabs at a temperature of approximately 1900°C after a method first described by Hall.³ This formed the ohmic contact to the *p*-type SiC. Small fragments of Si were then alloyed to the exposed (0001) face of the SiC chip. The alloying was carried out in a hot-stage furnace allowing visual observations. The heater element was tungsten, and a forming gas atmosphere (10% H₂, 90% N₂) was generally used. The heating cycle lasted 10 to 15 sec and the units were quenched to room temperature. The maximum temperatures reached were in the range of 2000° to 2200°C. The temperatures were determined by measuring the current into the heater strip and comparing it to calibration charts made by using an optical pyrometer to measure the brightest region of the heater strip for different steady-state currents.

Experiments were performed in which some Si dots were doped to concentrations approaching 1% with P or As, which are commonly used *n*-type impurities for Group IV elemental semiconductors, and others were doped with Ga or B, which are *p*-type impurities. There was no discernible difference between the resulting *I-V* characteristics and those obtained using very pure Si (<10¹³ total impurities). This suggests that if the *n*-type layer formed in the SiC is due to a chemical impurity other than Si itself (which is difficult to account for), then that impurity must be already present in the SiC or be introduced from the ambient gas. It is believed that N₂ is introduced from the forming gas, this belief being based on experiments in which the same alloying temperature cycle was used but the ambient gas was varied. When one used He, which is not expected to be a chemical dopant, no tunnelling characteristics were produced. However, the same SiC chips which had been tried unsuccessfully in the He ambient did show tunnelling characteristics when alloyed in forming gas or pure nitrogen.

Further, a chip with a Si dot alloyed in forming gas so as to produce a tunnelling characteristic lost it when cycled through the same temperature range in He, but regained it on recycling in forming gas.

A considerable fluctuation of peak tunnelling current densities occurred when several fragments of Si were alloyed simultaneously to the same SiC chip. Also, characteristics varied from chip to chip. While almost all diodes showed a tunnelling hump, only a relatively few showed a negative resistance at room temperature. This nonuniformity in the forward characteristics is believed to be due to inhomogeneities in the SiC itself in the group of crystals tested, and to variations in the maximum local temperature reached at the particular positions of the Si dots on the chips.

The negative resistance was initially observed by making ohmic contacts to the Si dot and the tungsten tab. Aluminum was sometimes alloyed to the Si dot at 600°C after the tunnel diode had been formed; this was done to facilitate good contact. To insure that the tunnelling effect was not due to a junction formed in the Si itself, the Si dot was etched off of several units either in CP₄ or in a mixture of HF and HNO₃. A pressure contact was then made to the area that had been wetted by the Si. Figure 2 shows these two methods of mounting. The *I-V* characteristics for the units with pressure contacts were substantially the same as they had been for these units with the Si dot intact, although series resistances tended to be slightly higher with the pressure contacts. On some units with pressure contacts, the peak and valley currents varied depending upon the position of the pressure contact in the wetted region. This is believed to be due to the fact that the resistivity in the *n*-type region in the SiC produced by the alloying cycle was not uniform everywhere over the wetted area.

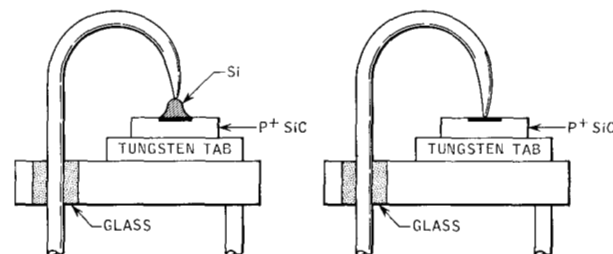


Figure 2 SiC tunnel diode mounting schemes showing arrangements with and without the Si alloy present. (a) The arrangement with the Si alloy dot present; (b) the arrangement with the Si dot etched away and a pressure contact applied.



Figure 3 Two SiC tunnel diodes on the same $p+$ SiC chip. The two circular regions are slightly depressed areas wet by the Si dots; that on the left has a diameter of 0.014 inch. The peripheral ridge is a tungsten, silicon, and carbon residue produced when the SiC melted into a tungsten tab during violent heat treatment at 2200°C.

Figure 3 is a photograph of the top of a SiC crystal on which two Si dots had been alloyed simultaneously and the Si subsequently etched off. Both alloyed regions produced diodes with peak-to-valley ratios greater than 1.1. The photograph includes the tungsten tab and also shows a ridge of tungsten, carbon, and silicon residue material which formed around the Si chip during the heating cycle. Shallow depressions about 2 microns deep with very flat and shiny bottom surfaces appear where the Si dots have been etched away. The smaller depression on the left is 14 mils in diameter. The depressions, which represent the maximum wetted areas, showed n -type under thermoelectric probing and the remaining areas gave a strong p -type indication. The two depressions show the results of two types of alloying action. That on the left is produced when the surface tension is such that the Si freezes over almost the entire wetted area; the Si in this case has a rough surface and has a flat pancake-like appearance. The depression on the right, which is more typical, is the result when the Si contracts, due to evaporation and to different surface tension conditions, and migrates so that it freezes over only a portion of the total wetted area; this is represented by the darker area at the top of the depression. The Si dot in this case freezes in a conical shape with an altitude approximately equal to base diameter and has a very shiny appearance.

To help establish the effect of the tungsten-SiC contact on the shape of the I - V characteristics, a pressure contact

was made to the p -type upper surface of the SiC chip, away from the n -type depression. Only slight nonlinearities were observed in the I - V characteristic between this contact and the tungsten tab, but no tunnelling humps or negative resistance regions such as are shown in Fig. 1. These appeared only when the top contact was made to the n -type regions in the wetted areas. This indicates that these features are due to a junction in the SiC formed under the Si dots. Further evidence for a junction here was the appearance of orange light from the shiny wetted area under very high forward bias currents (currents several times the peak tunnelling current). Such light emission is typical of rectifying p - n junctions made by alloying Si in a nitrogen atmosphere into SiC of lower Al concentrations ($<10^{19}$ atoms/cm³). No light was observed under reverse bias, even at currents of several amperes. Nontunnelling rectifying p - n junctions made in more lightly doped SiC normally show localized bluish emission when reverse biased into a breakdown condition.³

A second characteristic of some of these diodes, one not normally observed in tunnel diodes made from other semiconductor materials, is the appearance at liquid He temperatures of another negative resistance of the voltage controlled variety. An example is presented in Fig. 4, which shows characteristics taken on a Tektronix 575 Curve Tracer. It will be observed that, in addition to the

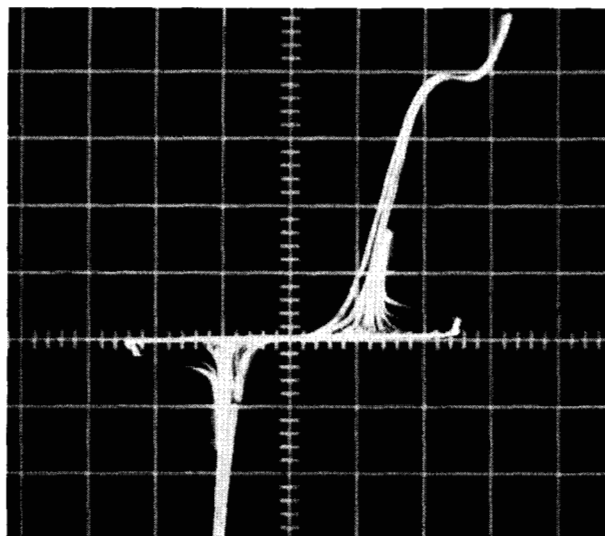


Figure 4 I - V characteristics of a SiC tunnel diode at 4°K. Major horizontal divisions are 0.5 V; vertical divisions are 10 mA. Several successive traces not completely swept out on the curve tracer are included which show the highly temperature-dependent, current-stable negative resistance regions at both forward and reverse biases. Self-heating due to the current through the device removes the negative resistance for the fully swept out traces which include the tunnel diode characteristics.

tunnel diode characteristic in the forward direction, there are two negative resistances at low currents, approximately symmetrical with respect to the origin, for both forward and negative voltage biases. These are extremely temperature dependent and do not repeat themselves from trace to trace. Several traces are shown only partially swept out. The self-heating due to current through the device removes the low-current negative resistances for the fully swept out traces, which include the tunnel diode characteristic. A possible explanation⁴ is a thermal breakdown in an extremely thin layer of lower doped *n*-type material in the SiC, which at low temperatures has a very high resistivity due to freeze out of carriers. Why such a layer should exist is not known, but possibly it might be produced in the highly nonequilibrium alloying process. On diodes which show this effect, the results are the same whether contact is made to the Si dot or is made by pressure contact after the Si has been etched away.

One of the devices having a tunnel diode negative resistance region at 500°C was incorporated in a simple self-exciting oscillator circuit. It was operated at 330 kc/sec at 500°C in an air ambient for 20 minutes, delivering 20 μ W into a 10-ohm load. Afterwards, the *I-V* characteristics at room temperature showed the same peak and valley currents as before, but the peak and valley voltages were slightly higher, indicating an increase in series re-

sistance probably due to oxidation at the contact between the header and tungsten tab (a pressure contact, in this case). Other units were operated as oscillators at room temperature with the highest frequency obtained being 8Mc/sec. These results demonstrate the possibility of making useful active elements in the form of tunnel diodes from the very stable high temperature material, SiC, and suggest that the temperature range of operation for all-solid-state circuit applications may be greatly extended.

Acknowledgments

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