OHMIC CONTACT TO SILICON CARBIDE

by

James Albert Frick

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Reginald L. Call
Reginald L. Call
Professor of Electrical Engineering

21 April 1972
Date

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ABSTRACT

The purpose of this work is to fabricate ohmic contacts on silicon carbide utilizing plentiful, low cost contacting materials. In conjunction with these constraints on the contacting materials, a simple laboratory process for forming the desired ohmic contacts is developed.

The experimental data for application of contacting solutions and for fusion of contacting materials and the conclusions drawn from these data are presented.

Ohmic contacts were formed on heavily doped silicon carbide by fusing phosphorus doped silicon in a horizontal tube furnace at 1432°C. A similar fusion to lightly doped silicon carbide resulted in blocking contacts. The fusion of platinum to heavily and lightly doped silicon carbide in an evaporation system at a pressure of 5×10^{-5} mm of mercury and a heating strip temperature of 1340 ± 10°C resulted in ohmic contacts.

CHAPTER 1

INTRODUCTION

The formation of ohmic contacts on silicon carbide utilizing contact materials which are both inexpensive and plentiful, is important and desirable in the continuing investigative efforts on silicon carbide as a semiconductor. Until this time, ohmic contacts have been made on silicon carbide utilizing processes that require very high temperatures, in excess of 2700°C, or exotic contact materials, such as a gold-tantulum alloy.

The semiconducting properties of electronic grade crystals of silicon carbide make this material potentially useful in the field of semiconductors, particularly for some military and space applications. Devices fabricated from such a material can be expected to operate successfully and reliably in a high temperature and high radiation environment.

Considerable research [Henisch and Ray, 1969] has been conducted in an effort to obtain silicon carbide crystals of the proper size and purity for semiconductor applications. Silicon carbide is difficult to grow, shape, and etch, and although the technological understanding of other semiconductors has contributed to the development of silicon carbide, new techniques of crystal growth may need to be developed before silicon carbide devices requiring the use of single crystals can be reliably produced.

Device fabrication utilizing silicon carbide, however, can proceed only when formation of contacts, both ohmic and rectifying, is clearly understood and economically feasible. Since a clear understanding of contacts is essential to silicon carbide device fabrication, this thesis shall first consider the theory of contacts. After the theory of contacts is reviewed, procedures developed, equipment, and materials used in silicon carbide contact experiments will be explained. Then the experimental results of the various contacting procedures are presented.

The ultimate goal of the experiments is to find a process for forming ohmic contacts on silicon carbide that is reliable, simple, and requires neither high temperatures nor exotic materials.

CHAPTER 2

THEORY OF CONTACTS

Although many different interfaces are of interest in the study of semiconductor physics, the particular interface of interest in the study of the ohmic contact is that between a metal and a semiconductor. In 1874, K. F. Braun discovered that such an interface carried current more easily in one direction than another [Braun, 1874]. Braun properly identified the current as electronic in nature and also properly identified the origin of the rectification as the interface itself. Figure 2.1 shows a current-voltage characteristic taken by Braun in 1877 [Braun, 1877] for a contact between a metal wire and a lead sulfide crystal. The direction of the rectification was such that current flowed easily when the metal was positive with respect to the semiconductor; very little current flowed if the metal was negative.

Since it was understood at the time that the current was carried by negative charges in the metal and that there were many more charge carriers in the metal than in the semiconductor, this was a very puzzling result. One would think at first glance that if rectification occurred at all, the current would flow more easily from the material with larger carrier concentration into the material with lower concentration. This situation is illustrated in Fig. 2.2 where electrons in the metal have been pulled away from the interface in the forward direction - the direction of easy current flow, and are pushed up

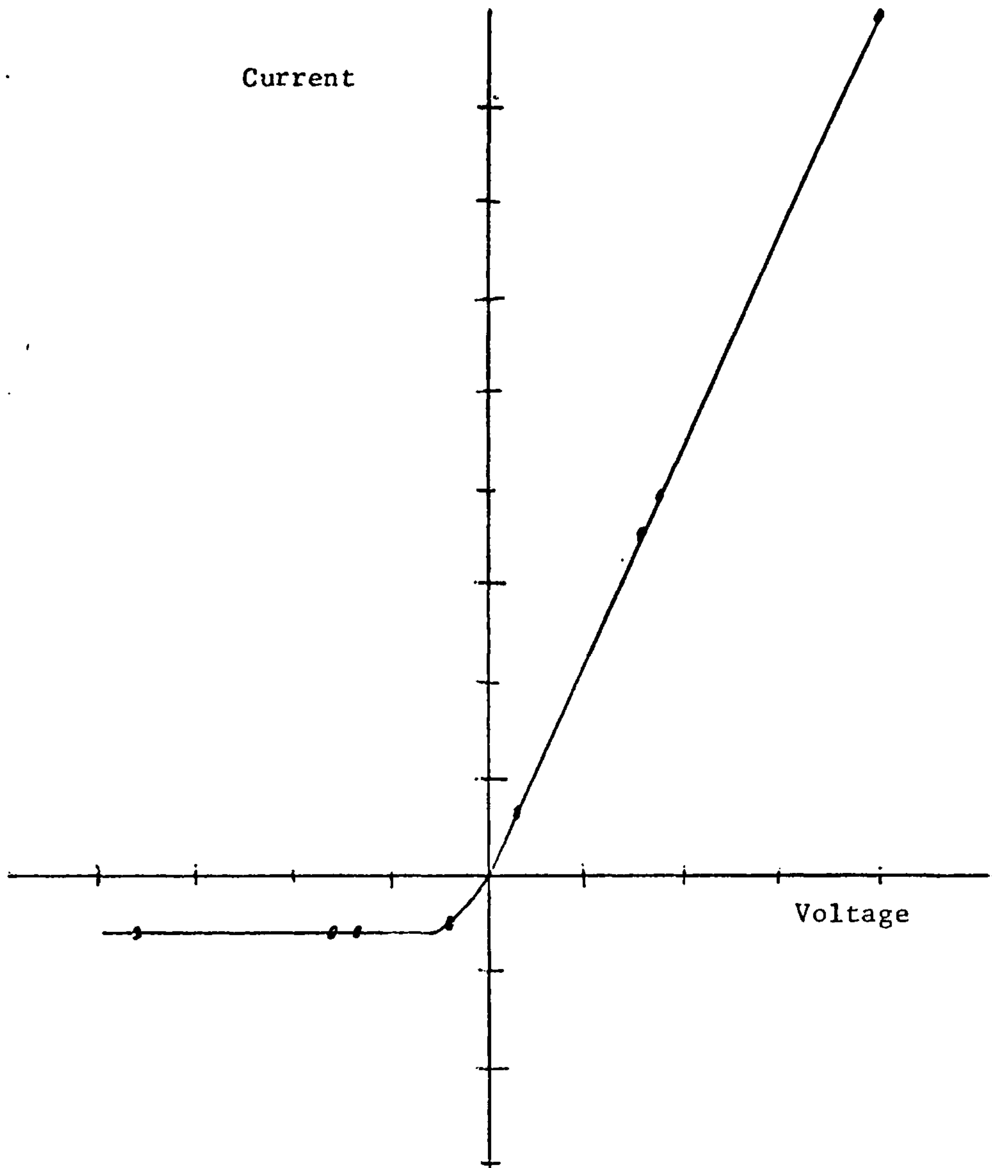

Fig. 2.1 A Typical Current Voltage Characteristic of Metal Wire Contact to Lead Sulfide Crystal Taken From K. F. Braun [1877]

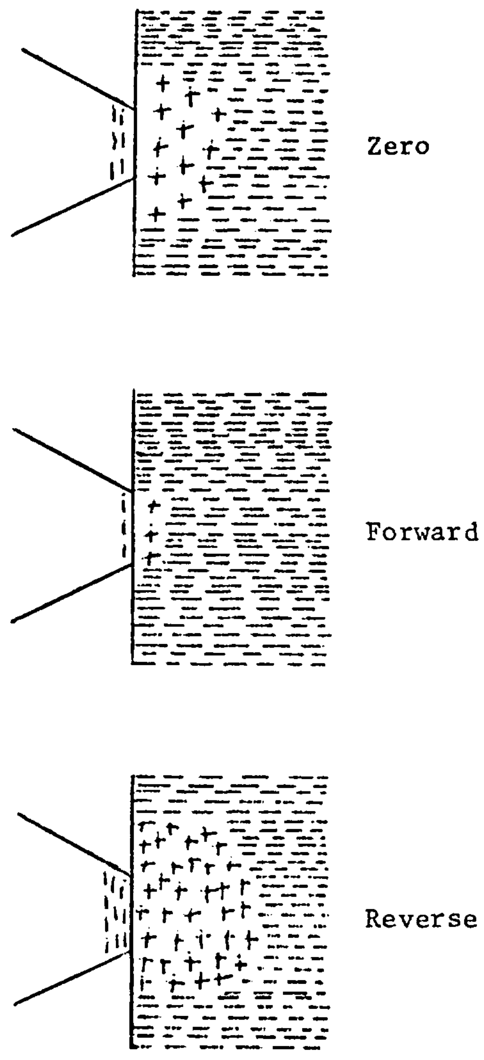

Fig. 2.2 Drawing of the Metal-Semiconductor Interface Indicating the Difficulty of Injecting Electrons From the Metal Into the Semiconductor

against the interface in the reverse direction - the direction where very little current flows.

Many theories were proposed giving a direction of rectification opposite to that observed experimentally. The question, of course, is not why current flows in the forward direction; there are charged carriers in both the metal and the semiconductor and it is clear that, in the absence of some other phenomenon, current should flow. The real puzzling result is that very little current flows in the reverse direction. Many electrons in the metal are crowded against the interface and somehow cannot get across into the semiconductor.

The metal-semiconductor interface is not the only interface in which such a phenomenon is known. A vacuum is commonly known to be a good insulator. This means that when two metal plates are placed in a vacuum and a voltage is applied between them, very little current flows. The reason, of course, is not that there are no electrons in the metal, nor is it that if the electrons were free, they could not cross the vacuum from one metal plate to the other. The reason is that the electrons experience great difficulty in leaving the metal and going into the vacuum. There is an energy barrier between the highest energy electron in the metal and the lowest energy in the vacuum where an electron can exist. This energy difference is illustrated in Fig. 2.3 and is called the work function of the metal. A similar energy barrier is developed when a metal and a semiconductor are brought into contact. Electrons in the metal are distributed over a range of energies, the highest energy at which appreciable electron density exists being the

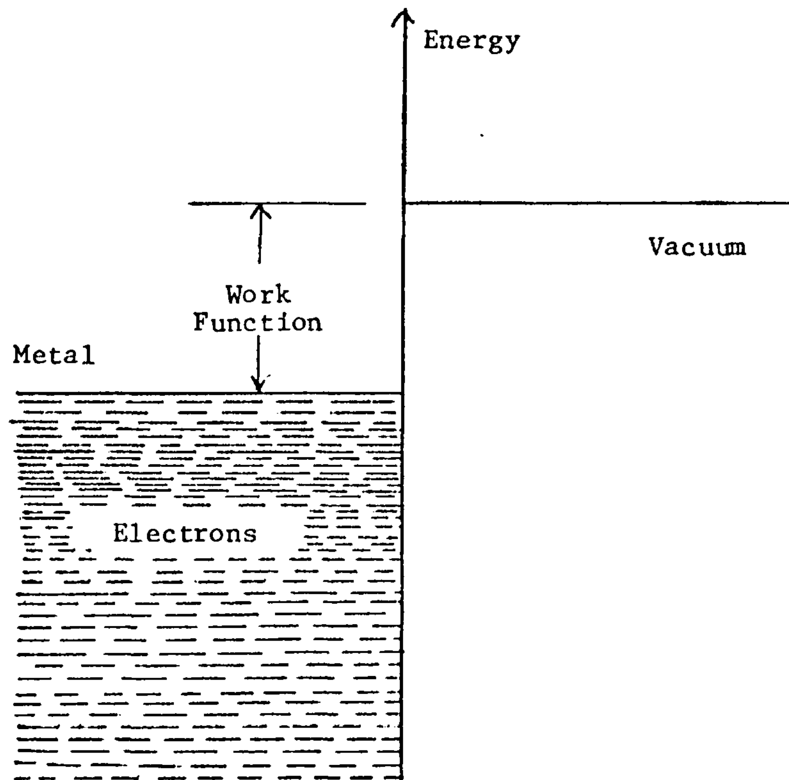

Fig. 2.3 Diagram of Electron Energy Versus Distance Through a Metal-Vacuum Interface Showing the Work Function Barrier

Fermi level. By contrast, electrons in the semiconductor are all crowded into a very narrow energy range near the edge of the conduction band. When the metal and the semiconductor are brought into contact, in most cases the bottom of the conduction band of the semiconductor is at a higher energy than the Fermi level of the metal. Electrons then flow momentarily from the conduction band of the semiconductor into the Fermi sea in the metal until, at distances far from the interface, the two energies, that is the Fermi level in the metal and the bottom of the conduction band in the semiconductor become nearly equal, as shown in Fig. 2.4. The energy difference at the interface between the Fermi level of the metal and the conduction band edge of the semiconductor is known as the barrier energy of the particular metal semiconductor interface.

At present, how to calculate the barrier energy of any given metal semiconductor interface from first principles is not known exactly. By using approximations such as thermionic field, etc., a calculation can be done. Also, considerable experimental information is known about a wide variety of such interfaces.

Basically, barrier energies can be grouped into two broad classes:

1. On the covalent semiconductors, such as silicon, germanium, and gallium arsenide, the barrier energies do not depend very strongly upon which metal is placed on the semiconductor surface and are thus largely a property of the semiconductor itself.

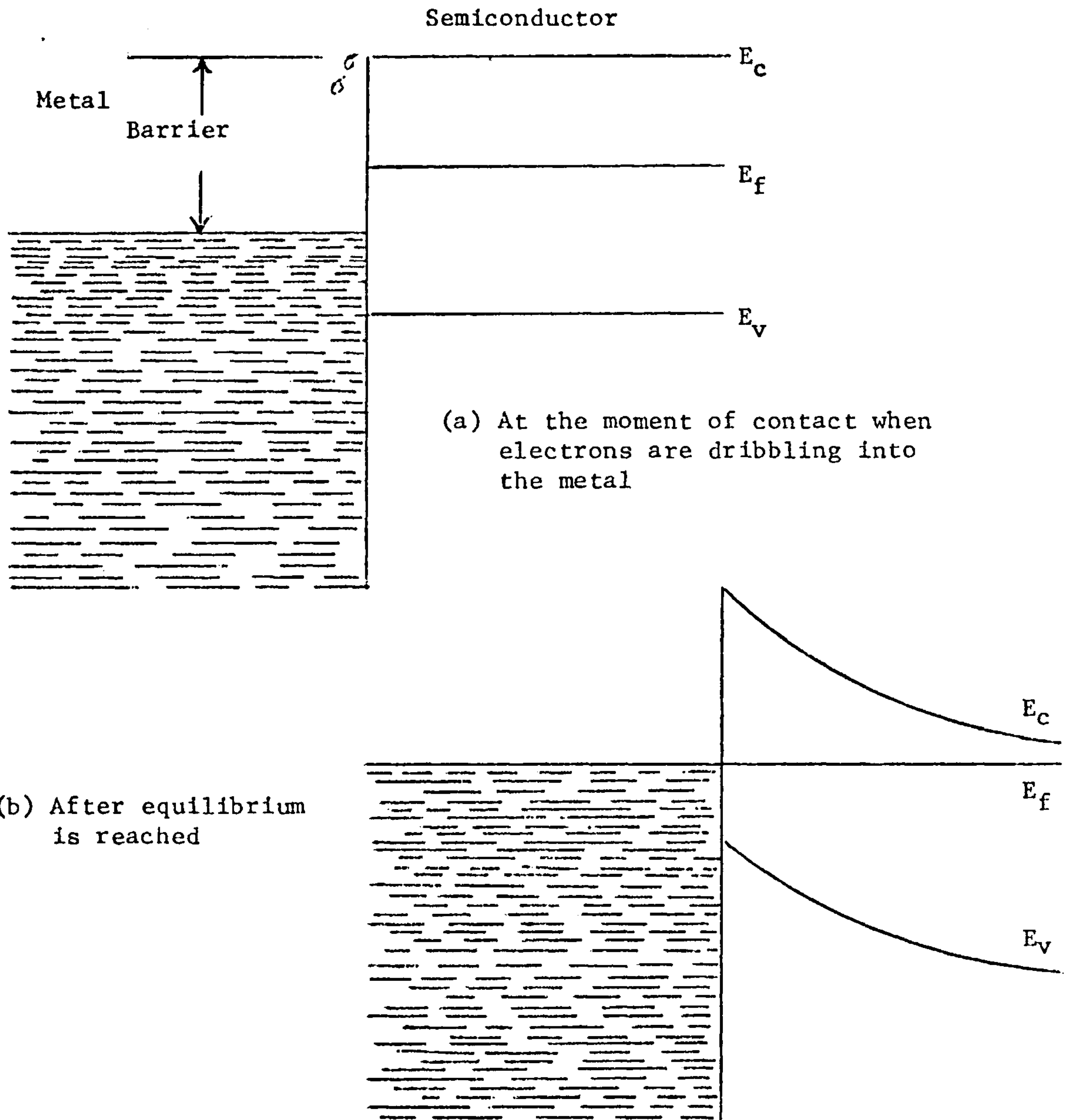

Fig. 2.4 Energy Diagram of a Metal-Semiconductor Contact

2. By contrast, on the more ionic semiconductors such as cadmium sulfide, zinc sulfide, and zinc oxide, barrier energies are a function of both the work function, or electronegativity, of the metal and of the particular semiconductor [Mead, 1966].

The situation is illustrated in Fig. 2.5 where the barrier energies for different metals on a typical covalent material, gallium arsenide, and a typical ionic material, zinc sulfide, are shown as a function of the electronegativity of the metal [Archer and Yep, 1969].

Over the range of metals involved here, the electronegativity given in electron volts is equivalent to the work function with a shift in zero, and is used because a more well-defined scale is available. The straight line through the zinc sulfide points has a slope of unity, whereas in the gallium arsenide case the slope is approximately 0.1. As can be seen, the barriers on the ionic materials can be characterized by giving the intercept of a plot such as Fig. 2.5, whereas, to a first approximation, the barriers on the covalent materials are nearly independent of the metal and can be specified by knowing the barrier energy of any one particular metal. Figure 2.6 shows the barrier energies for gold on the various covalent semiconductors as a function of their band gap. It is interesting to note that, except for one or two materials, the barriers can be given quite well by the expression

$$\phi_B \approx \frac{2\ Eg}{3} \tag{2.1}$$

which is the straight line in Fig. 2.6.

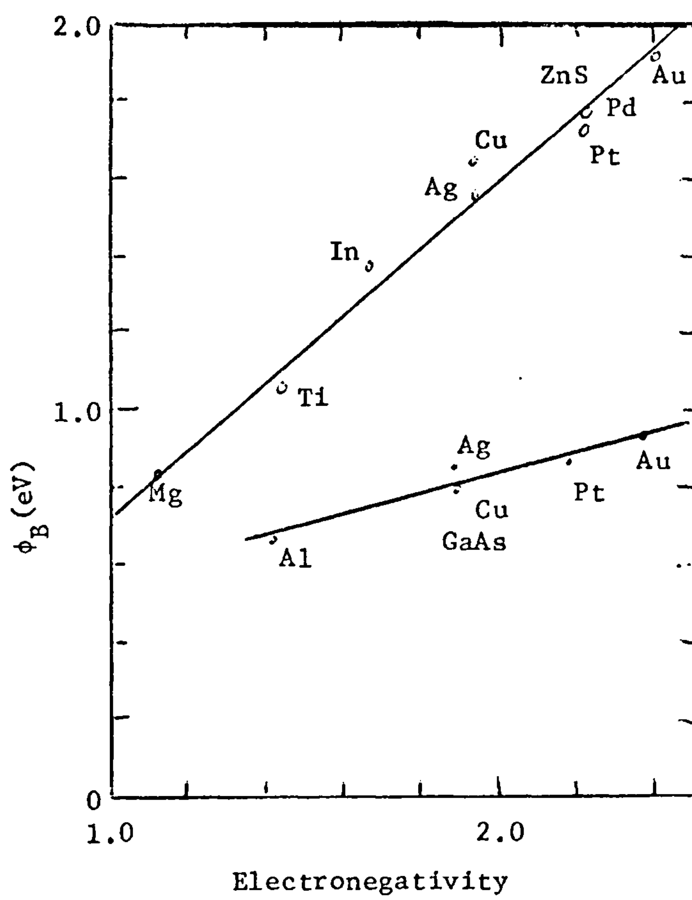

Fig. 2.5 Measured Barrier Energies for Several Metals on an Ionic Semiconductor (Zinc Sulfide) and a Covalent Semiconductor (Gallium Arsenide)

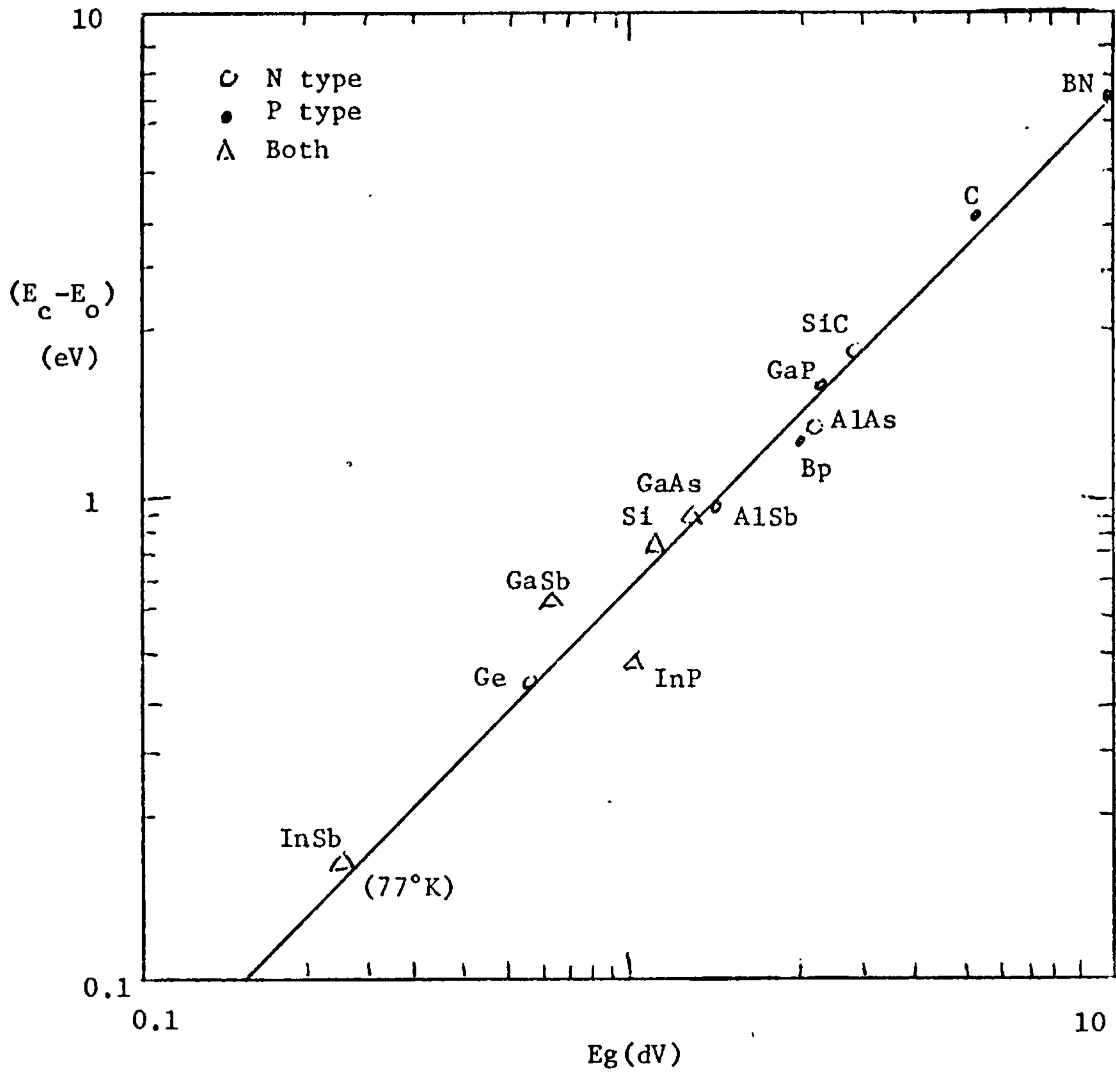

Fig. 2.6 Barrier Energies for Gold on Several N-Type Covalent Semiconductors; the Straight Line Is Where the Barrier Energy is 2/3 of the Band Gap

We will now discuss the nature of the current flow in a typical metal semiconductor interface. It was mentioned earlier that electrons in the semiconductor are confined to a very narrow energy range near the conduction band edge while the highest energy electrons in the metal are at the Fermi level. This is not strictly true, of course, because there are thermally excited electrons at higher energies, although their number decreases rapidly with energy according to the well-known Boltzmann distribution. The situation is illustrated schematically in Fig. 2.7(a) for the case where no bias voltage is applied between the metal and the semiconductor. When a negative voltage is applied to the semiconductor, as shown in Fig. 2.7(b), the electron energy distribution in the semiconductor is raised in relation to that in the metal and there are now more electrons in the semiconductor with energies higher than the peak of the barrier which flow by diffusion into the metal. However, with the opposite bias applied, as shown in Fig. 2.7(c), the energy distribution in the semiconductor is lowered in relation to that of the metal. A net current flow from the metal into the semiconductor now results, because of those few electrons with energies higher than the barrier energy. However, this current is very small and does not increase appreciably with reverse bias. This situation leads to the familiar diode current-voltage characteristic shown in Fig. 2.8. If the logarithm of the current is plotted as a function of the applied voltage in the forward direction, a straight line is obtained as shown in Fig. 2.9. If the current at a given forward bias voltage is measured as a function of temperature, an Arrhenius plot can be constructed as

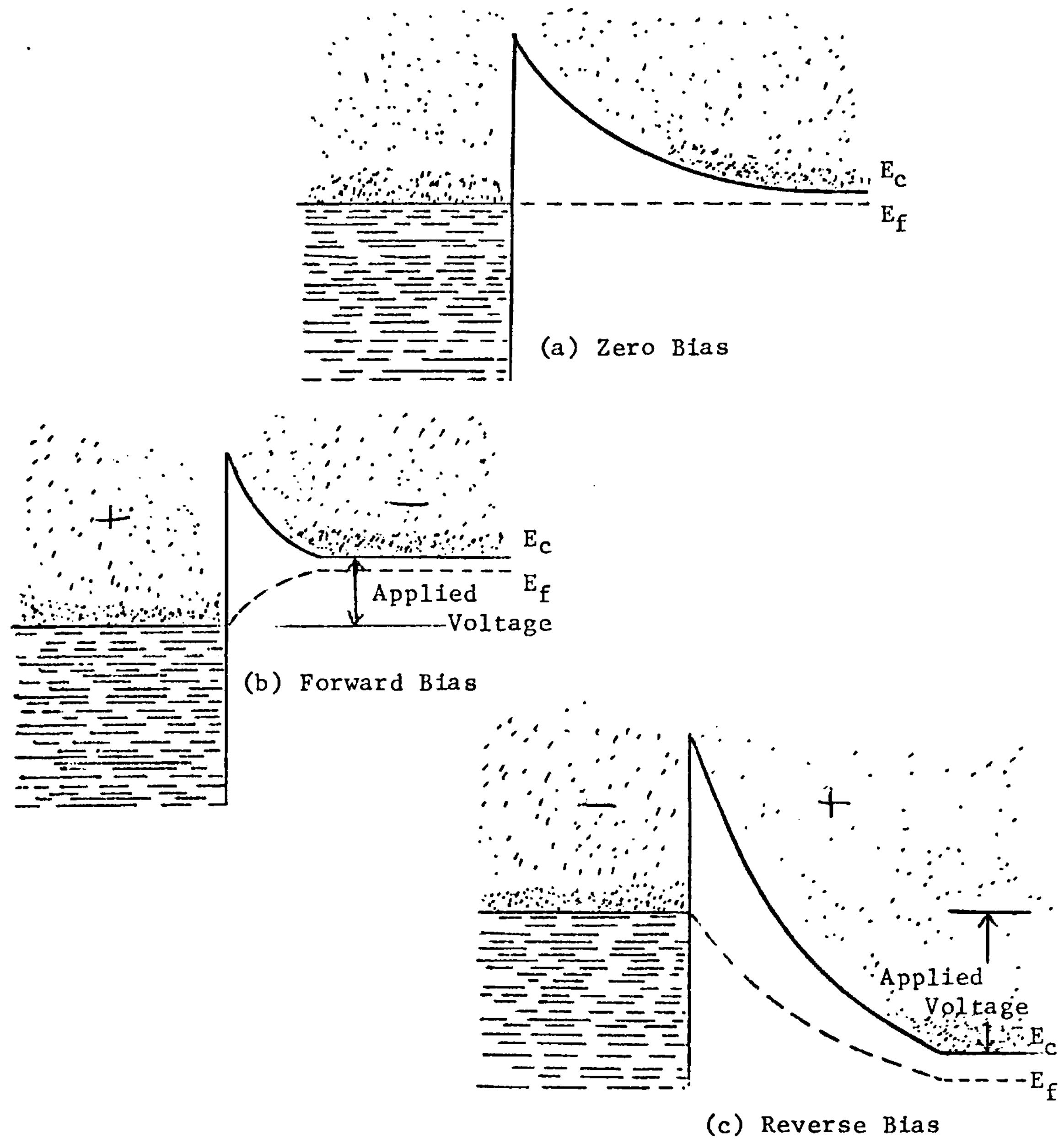

Fig. 2.7 Energy Diagrams Showing Schematically the Thermal Electron Energy Distribution with Applied Bias

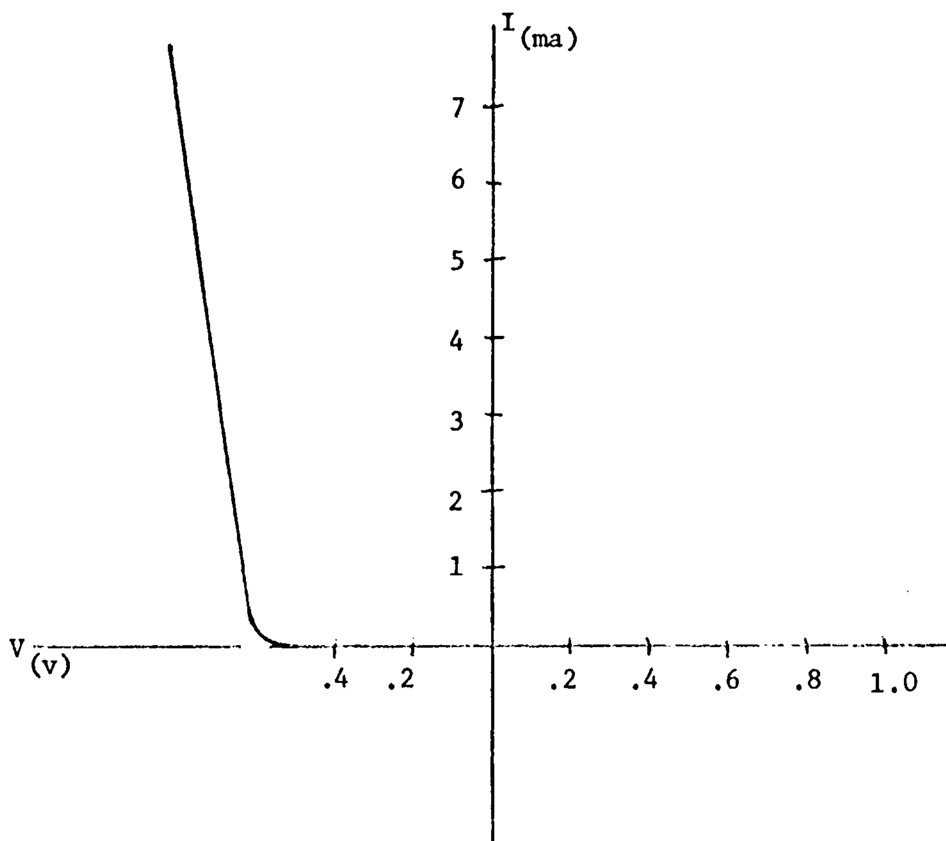

Fig. 2.8 Current Voltage Characteristic of Typical Metal Semiconductor Contact; This Sample Is Gold on Gallium Arsenide $\phi \approx 0.9$ eV

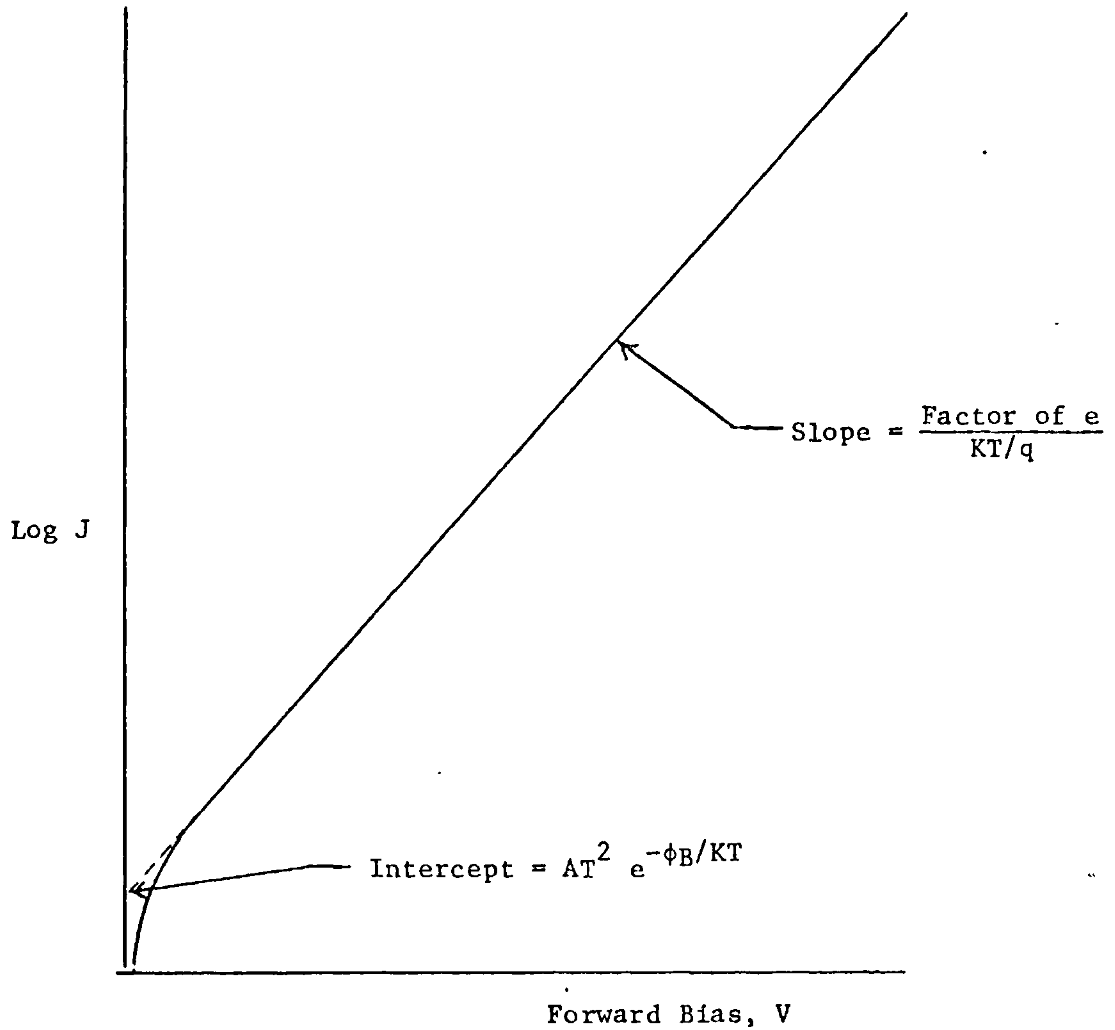

Fig. 2.9 Schematic of Fig. 2.5; I Versus V Plot for Metal Semiconductor Contact

shown in Fig. 2.10. From either of these two plots the metal semiconductor barrier energy can be deduced and the thermal nature of the current established.

If this were the entire story, the only possible way of making an ohmic contact to a semiconductor with a metal would be to decrease the barrier energy so that the thermally excited electron current, or thermal current, which flowed in the reverse direction is large enough for the particular device application. Referring again to Fig. 2.9, it can be seen that, for currents less than, or of the order of the intercept current, the characteristic is ohmic up to voltages of 1 or 2KT. By making the barrier sufficiently small, this current can be made quite large, i.e., a barrier of 0.25 eV can support currents in either direction of up to 10^4 amps/cm^2 and still remain ohmic.

However, as we have seen with many of the covalent materials, the barrier energy on n-type material, for example, is approximately two-thirds of the energy gap of the semiconductor and does not change appreciably with the metal used. Hence, the approach of making the barrier energy arbitrarily small cannot be used for ohmic contacts to these materials. With some highly ionic materials, such as zinc sulfide, another difficulty is often encountered which is shown in Fig. 2.5. That is, metals do not exist with electronegativity sufficiently small to make the resulting barrier energies low enough to form ohmic contacts for device purposes. Thus, if one considers only the thermally excited electron currents which can flow in the

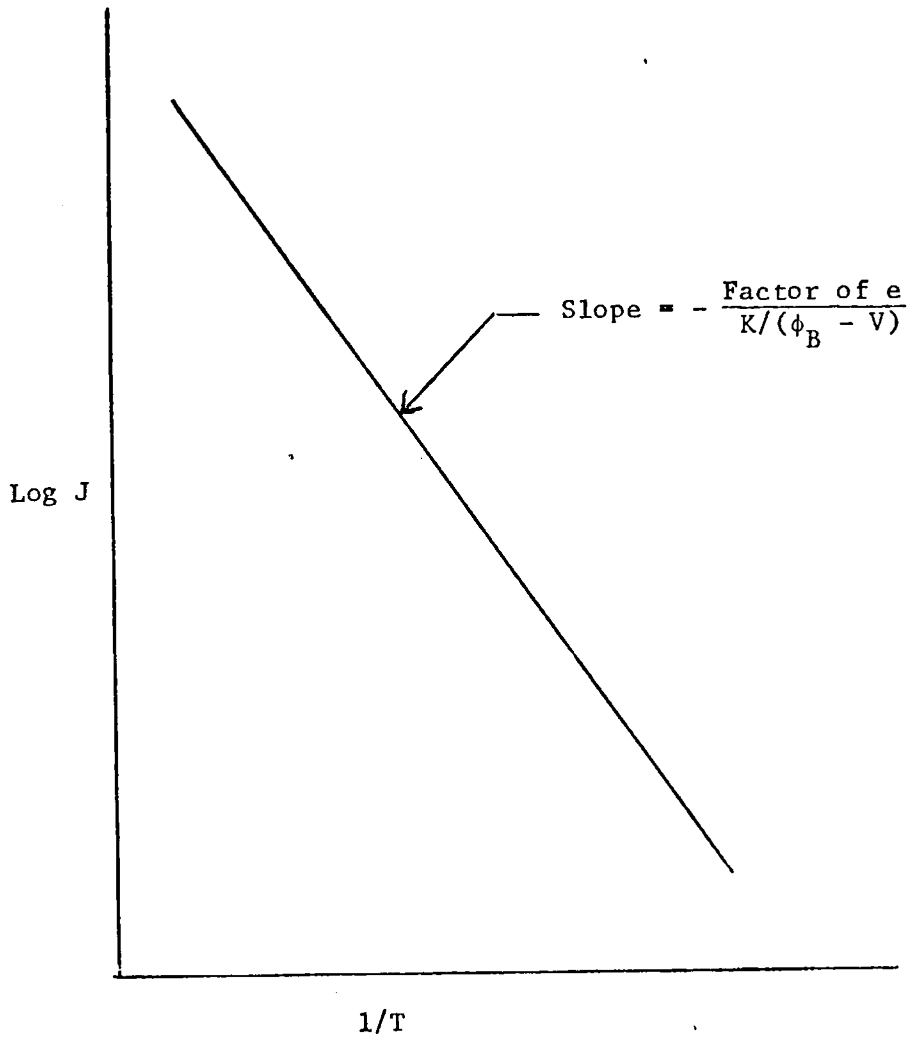

Fig. 2.10 Schematic Arrhenius Plot for Forward Biased Metal Semiconductor Contact

metal-semiconductor system, the number of semiconductors to which ohmic contact can be made becomes very small.

Thermal current, however, is not the only current which can flow in a metal semiconductor system. As the carrier concentration in the semiconductor is increased, the width of the depletion layer is decreased. At very high carrier concentrations, the depletion layer becomes sufficiently small that quantum mechanical tunneling can take place. This tunneling results from the fact that the electron probability distribution in the forbidden region is damped exponentially with distance, and hence can penetrate a barrier if it is sufficiently thin. Referring again to Fig. 2.7(b) and 2.7(c), it can be seen that in both the forward and reverse directions, the distance through which the electrons must tunnel decreases as the applied bias is increased. If the depletion layer is sufficiently thin, current in either direction increases markedly with voltage. The type of current-voltage characteristic resulting from tunneling of this sort is shown in Fig. 2.11. The solid line, curve A, is a typical curve for a device with low carrier concentration. In the forward direction the thermal current increases exponentially with voltage, as we have seen earlier. In the reverse direction only a very small saturation current flows until sufficient electric field is developed for avalanche breakdown to take place. However, if the carrier concentration in the semiconductor is increased, tunneling currents begin to flow in both the forward and reverse directions. In the forward direction tunneling current increases exponentially and is often difficult to distinguish from

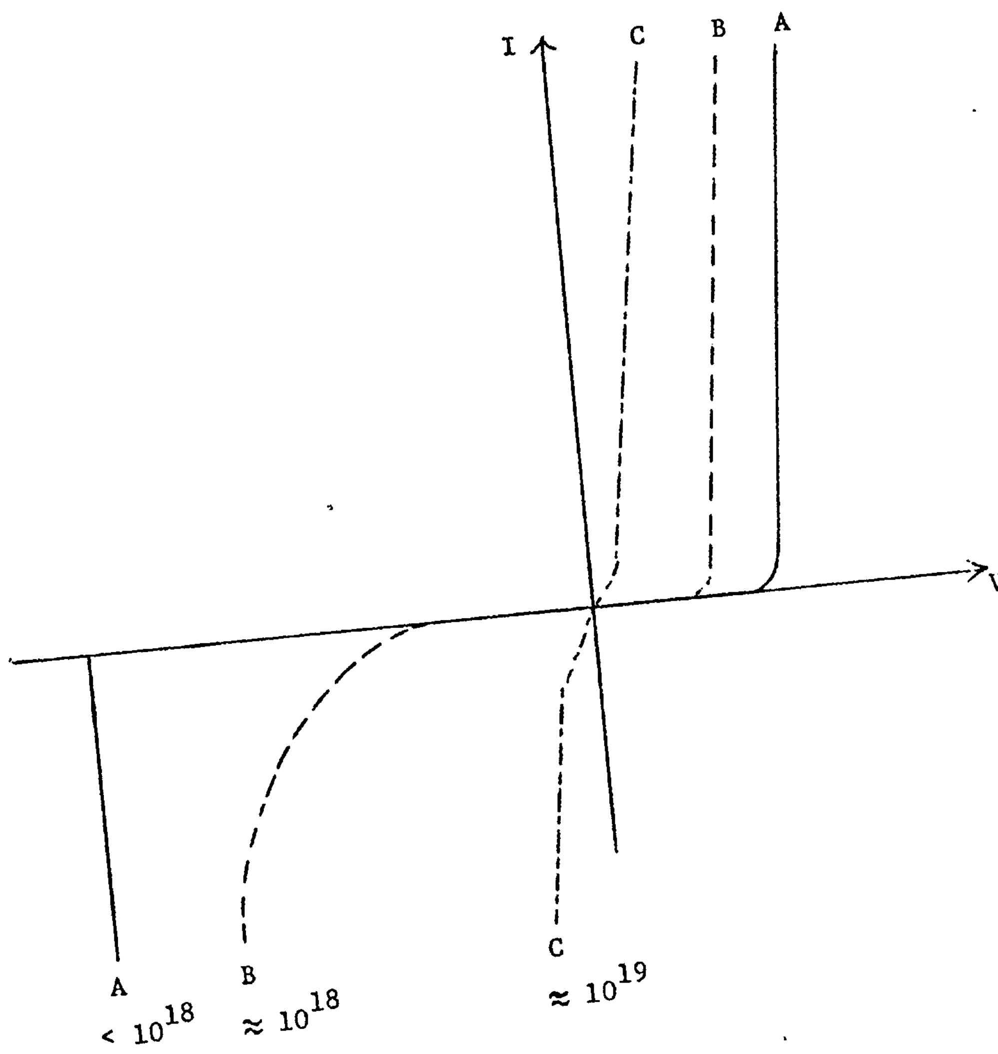

Fig. 2.11 Current Voltage Curves for a Metal Contact on Semiconductor Samples of Progressively Higher Carrier Density

thermal current. In the reverse direction tunneling current increases exponentially but less steeply than in the forward direction. For carrier concentrations in the intermediate range, of the order of $10^{18}cm^{-3}$ for typical semiconductors such as gallium arsenide, the situation is illustrated by the dashed lines, curve B in Fig. 2.11. As the carrier concentration is increased still further to $10^{19}cm^{-3}$, the currents conducted in both the forward and reverse directions again increase exponentially but at very much lower voltages and there is a broad crossover range where the current is essentially ohmic. This is shown by the dot-dash line, curve C, in Fig. 2.11. This then is the general approach used in making ohmic contacts to the traditional semiconductors: place a metal contact on a region of very high carrier concentration and allow tunneling to take place through the barrier.

For the above reason it is important to understand in detail the nature of the tunneling process and how it is characterized in a given semiconductor. The exponential damping of the electron probability distribution in the semiconductor forbidden gap, to which we referred earlier, is quantitatively characterized by an exponential damping constant, q, which is shown in Fig. 2.12 as a function of electron energy. Near the conduction and valence band edges, q is small and the electron penetrates deeply into the semiconductor. However, near the center of the forbidden gap, q is relatively large and the electron distribution damps very quickly. Although the actual characteristic, q, versus energy curves has been measured for only a small number of semiconductors,

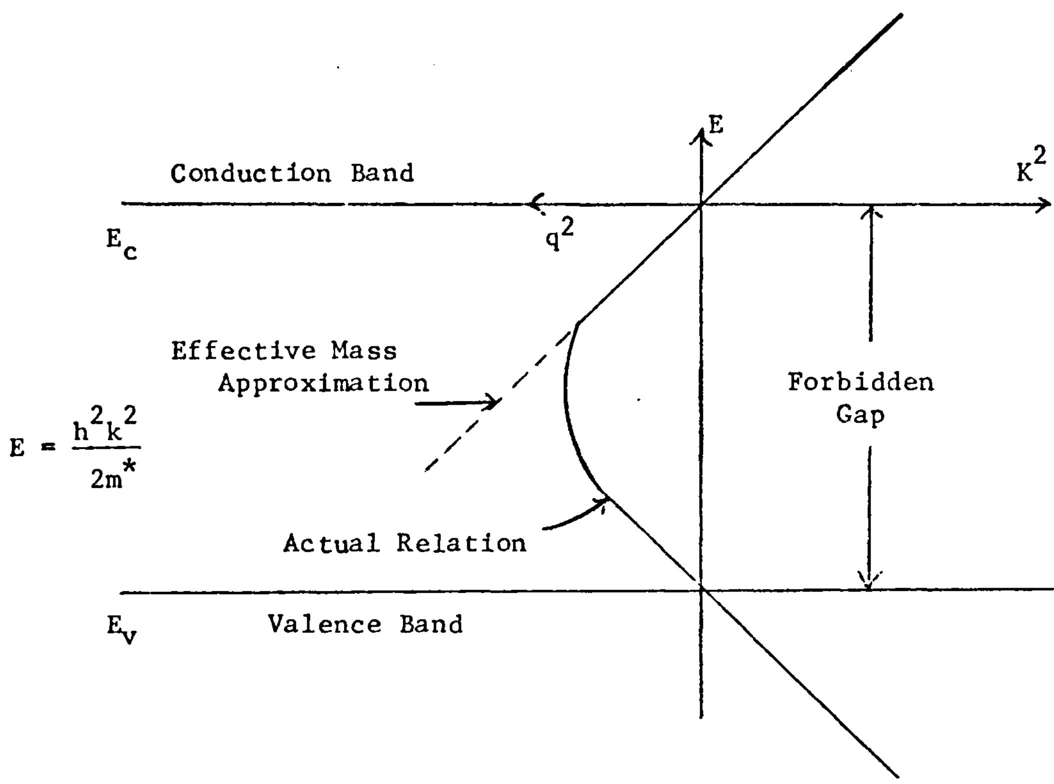

Fig. 2.12 Propagation Constant of Electrons in a Semiconductor Showing the Attenuation Constant q in the Forbidden Gap as a Function of Electron Energy

the relationship to be used in any given semiconductor can often be estimated from the equation:

$$E^2 = \left(\frac{Eg}{2}\right)^2 + \frac{\hbar^2 q^2 Eg}{2m^*} \tag{2.2}$$

where E is the electron energy measured from the center of the forbidden gap, Eg is the gap energy, and m^* is the effective mass of the majority carrier in the semiconductor.

In Fig. 2.11 current-voltage characteristics of a typical metal semiconductor contact were plotted for various semiconductor carrier concentrations. If we plot the logarithm of current versus the applied voltage for the forward direction instead, curves such as those shown in Fig. 2.13 are obtained. For low carrier concentrations the current increases by a factor of e for every KT of applied voltage. As the carrier concentration is increased, current due to tunneling becomes important and a nearly exponential characteristic results with smaller slope and larger intercept on the current axis. At still higher carrier concentrations, appreciable currents flow in the neighborhood of zero bias. These currents are of interest when the contact is used as an ohmic contact. However, a great deal of information can be obtained about the density of electrons just under the contact by studying the forward characteristics. To a first approximation the current is given by the expression

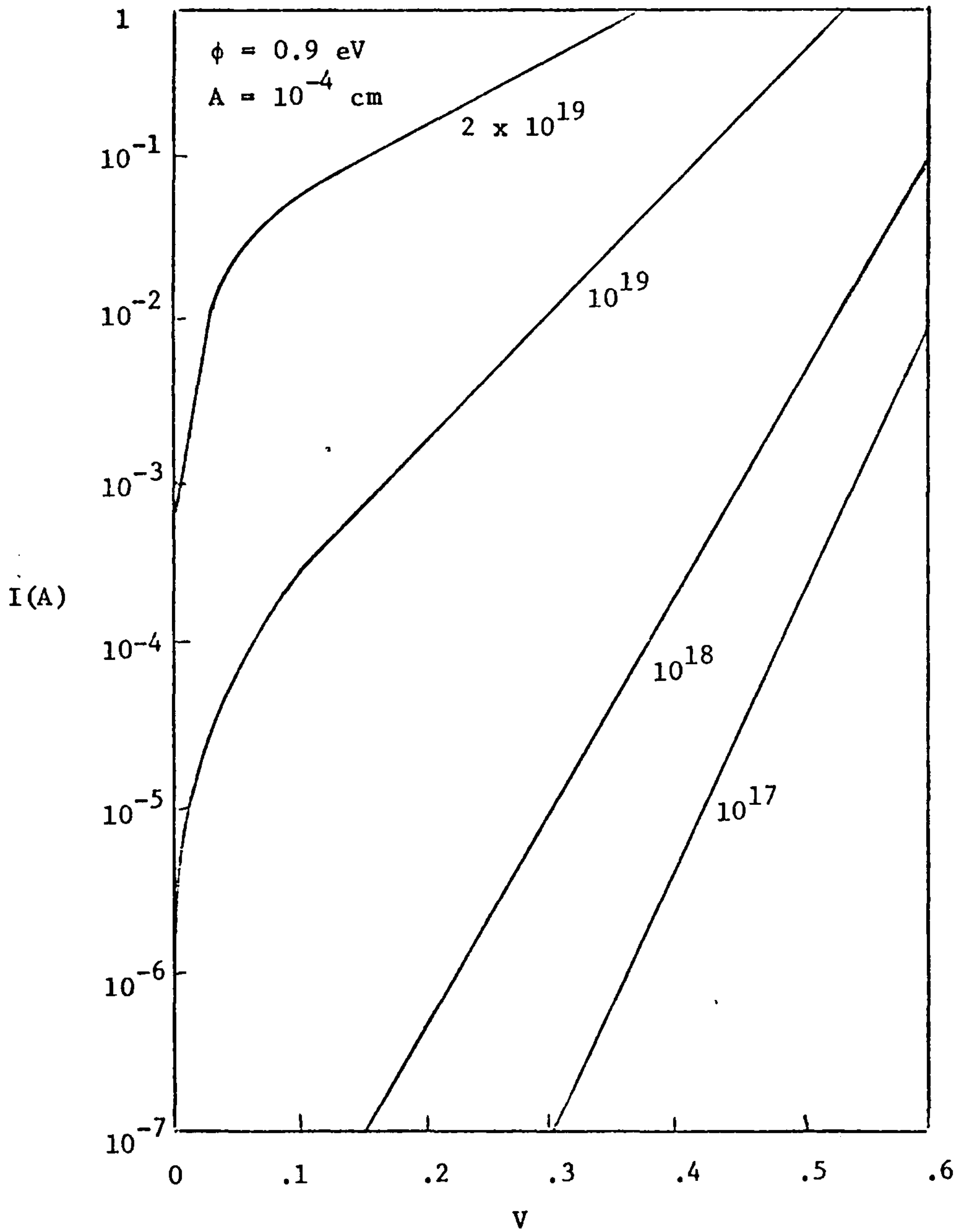

Fig. 2.13 Schematic Log Current Versus Voltage Plot for Similar Progression of Samples as Shown in Fig. 2.11

$$I \propto \exp \left[\frac{2\varepsilon_s V}{qN} \right]^{-1/2} \tag{2.3}$$

where N is the net donor, or acceptor, concentration and V is the applied voltage. Thus, the forward characteristics in the tunneling range are very sensitive to the carrier concentration; if the effective mass of the carrier involved is known, the actual carrier concentration can be estimated from the slope and from the intercept the general magnitude of current which can be carried by the contact as an ohmic contact without unreasonable voltage drop.

It should be emphasized again that the origin of these current-voltage characteristics is the exponential attenuation of the electron probability distribution in the forbidden gap of the semiconductor. In other words, the current which flows decreases in a generally exponential way with the width of the depletion layer through which the electron must tunnel, in accordance with the attenuation constant given in Fig. 2.12. For this reason, one would expect the ohmic contact resistance to depend exponentially upon the depletion layer width at zero bias and, hence, upon the square root of the carrier density in the semiconductor. Figure 2.14 illustrates some measurements [Mead, 1966] of ohmic contact resistance as a function of (carrier density)$^{-1/2}$, it can be seen that contact resistance varies exponentially with this quantity over a wide range, as is expected from this mechanism.

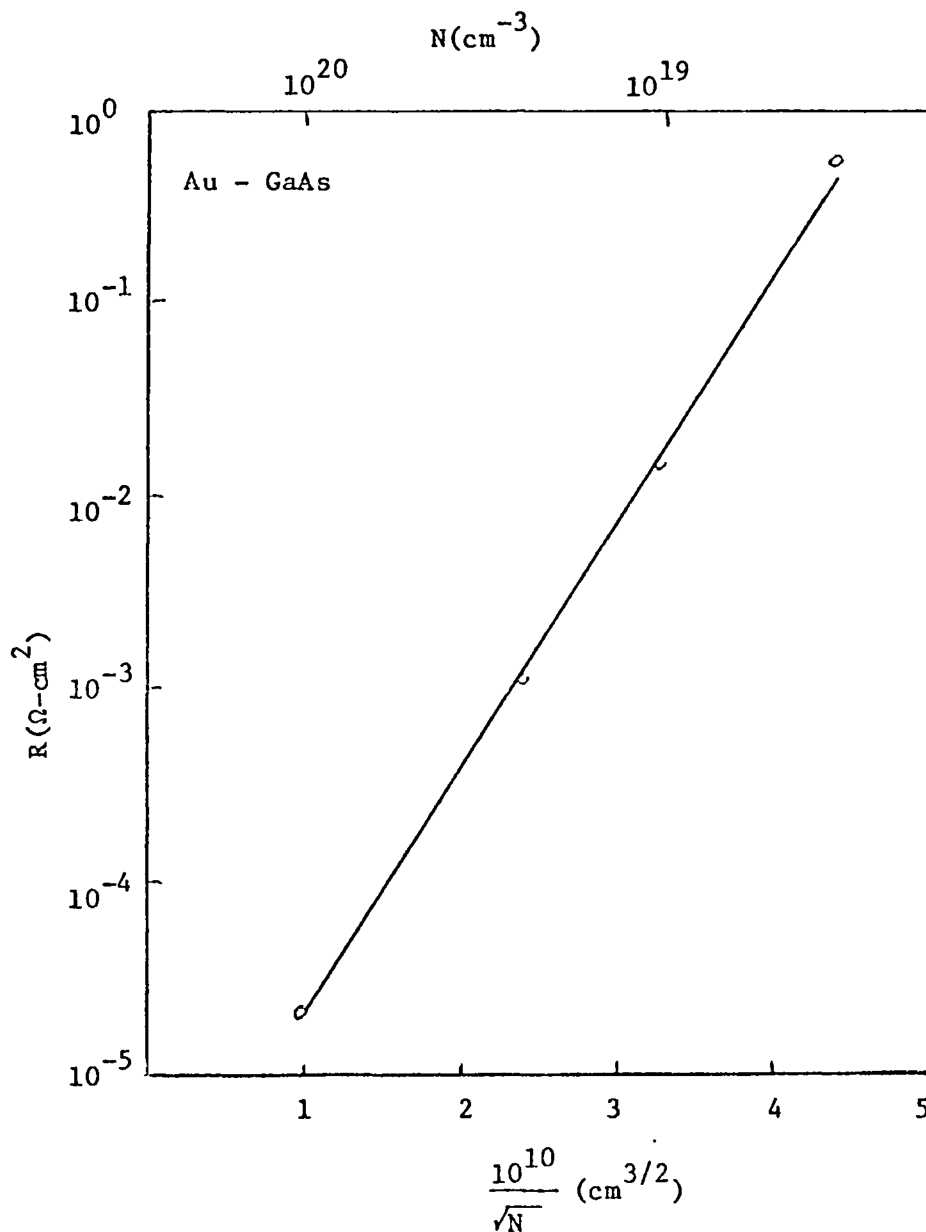

Fig. 2.14 Contact Resistance of Gold on Gallium Arsenide Contacts as a Function of Gallium Arsenide Carrier Concentration

In summary, it can be said that there are two general classes of semiconductors with respect to their contact behavior. First are those to which ohmic contact can be made when the barrier energy is sufficiently small that the thermal currents which flow are sufficiently large for the device application involved. This is the case, for example, in the cadmium sulfide photocell. The second class is materials where this cannot be done; in general, ohmic contacts can be made by making the carrier density in the materials sufficiently large that quantum mechanical tunneling can take place. Quantitative studies of the characteristics of a particular contact can be very helpful in establishing the carrier density of the materials just under the contact and in characterizing over what range of current the contact is useful.

CHAPTER 3

DEVELOPMENT OF PROCEDURES AND MATERIALS

Investigation of ohmic contacts on silicon carbide commenced with a search for the proper procedure to utilize in achieving an ohmic contact. The scarcity of silicon carbide made it advantageous to seek this proper procedure with a semiconductor material other than silicon carbide, thus precluding any damage to, or destruction of, the available silicon carbide crystals in early experimental efforts.

The availability of silicon wafers made this semiconductor material a logical choice to be used in the efforts to determine a feasible approach to putting ohmic contacts on a semiconductor material. Silicon wafers with a resistivity of .01 - .1 ohm-centimeters were selected since there was a plentiful supply of this type and this resistivity for n-type silicon was amenable to a wide variety of contacting materials that could be investigated.

A silicon wafer was thoroughly cleaned with trichloroethylene (TCE) and isopropyl alcohol before being placed in a prebake oven at 160°C for twenty minutes. This prebake was performed to dehydrate the wafer prior to beginning the photoresist process and thereby insure a good adhesion of the resist.

Centrifuged, 5:1 KMER was then spun on the wafer, after which the wafer was placed in a post bake oven at 95°C for ten minutes to

drive off any solvent remaining in the photoresist film. This drive off assured that the photoresist coating could be developed without lifting or developing pin holes.

The mask selected was a pattern consisting of a square pattern made up of 30 mm x 30 mm, center to center, squares imprinted on a 2 in. x 2 in. glass slide. The square window area pattern was selected because visual inspection of the pattern uniformity was more easily accomplished than with other available geometric designs.

Using a clean mask, the photoresist coated wafer was then exposed to ultraviolet light for fifteen seconds after which it was developed for ten seconds. The wafer was then observed under the microscope to ascertain that a uniform, sharp pattern had indeed been printed into the photoresist and the resist had been developed. This visual check confirmed that the pattern was as desired.

The patterned wafer was then placed in a curing oven at 160°C for twenty-five minutes. This curing step is mandatory since the resist must be completely polymerized as resist adhesion depends on polymerization. If the resist is not completely polymerized, the etching solution can lift the resist from the silicon wafer.

After this curing step, the silicon wafer was placed in a 10:1 hydrofluoric acid (HF) etch for five minutes. Upon removal from the etch microscopic examination revealed that window areas in the pattern had been opened through the coating oxide to the silicon itself. This examination also confirmed that the pattern had not been disrupted by the etch and apparently did provide the desired window isolation.

The photoresist process was performed on a number of silicon wafers to place the pattern on them. Each time it was accomplished, one or more of the parameters given above were changed, i.e., straight KMER, reduced/increased post bake, prebake times, etc., to determine if the pattern installation process affected the contacting procedures in any way. This parameter varying simply confirmed the findings of R. C. A. Harris that the stated parameters are the optimal to be used in the photoresist process [Harris, 1968]. This investigation was undertaken to assure that the pattern would withstand the further testing accomplished of the contacting procedures and would not, of itself, be a cause of any negative or undesirable results that may arise. The patterned silicon wafer was to be the test vehicle for the further experimentation on contacts and its repeatability and stability were essential. Splitting the prepared wafer into two pieces for results comparison and to conserve wafers, the first contacting material to be investigated was now prepared for application onto the pattern.

The material to be tested as a contact material was an unfluxed platinum paste commercially available from Engelhard Industries, Incorporated. After a thorough stirring, which insured uniformity of the solution, the paste was brushed onto the patterned wafer with a q-tip. One piece of the wafer was covered with an excess quantity of the paste, while the second piece had a light and uniform layer of the platinum paste brushed onto it. Both coated pieces were allowed to dry for a period of three hours, at which time the piece with the excess quantity of paste was again brushed with a clean dry q-tip to remove the applied

excess. Two additional hours of drying followed this second brushing to assure that the contacting material on both pieces was uniformly dry on the patterned surface. All drying was done at room temperature. After the five hours of drying, each piece was visually inspected under the microscope to determine the uniformity and relative thickness of the coating on each piece. The application of an excess quantity of coating material did appear to afford a denser concentration of the paste in the windows of the pattern.

One of the half wafers prepared above was placed in J-100, heated to 100°C for three minutes, removed, cleaned with acetone and blown dry. The J-100 removed the remaining photoresist and the platinum paste covering it. The window areas retained a uniform deposit of platinum. The second half wafer was sintered in a furnace at 550 ± 5°C for two minutes, then stripped in the J-100. This stripping removed all remaining photoresist and all of the platinum paste. With the melting point of platinum at 1770°C, this sintering carried out was completely ineffective in assisting any bonding of the platinum but did affect the adhesion of the platinum paste enough to permit its removal by the J-100.

Another prepared wafer was utilized to determine if the remaining photoresist with its adhering platinum paste could be removed by heat. This would again leave the platinum in the isolated window areas of the square pattern, as desired. A temperature of 1015 ± 5°C was selected for this step to insure the complete removal of the resist. Upon placing the wafer into the tube of the horizontal furnace, there

was an immediate and violent flare-up. The flames died out immediately and the wafer was left in the furnace for two minutes in a second attempt to sinter the silicon and platinum. Examination under a microscope showed that all the resist had been removed; however, the adhering platinum paste had not been removed in a uniform pattern. Deposits of platinum did remain in the window areas, but was also deposited irregularly on the oxide, precluding any hope for the desired window isolation. This process was attempted several times with various temperatures and heating times; however, it was not possible to achieve any window isolation. The resist strip J-100 step remained the best method for achieving the desired isolation and was the method utilized for the remainder of the experimental work.

All of the foregoing work was duplicated several times using the platinum paste as the contact material; however, the paste was diluted with toluene in varying quantities each time to give a less viscous solution. This was accomplished to determine if the density, thickness, and uniformity of the platinum solution would have any effect on the contacting procedures. Through this process it was determined that a less viscous platinum solution, capable of being spun onto the wafer, gave a contacting material coverage that was consistently more uniform in density, thickness, and distribution.

This completed the work to determine a reliable procedure to place the contacting material onto the semiconducting material. It was now possible, with the above method, to place the contacting material onto the silicon carbide with assurance that window isolation could be

maintained and that reliable testing could be accomplished on any contacts achieved.

Four 6H silicon carbide α-crystals were now cleaned with TCE and isopropyl alcohol, prebaked at 160°C for twenty minutes and then put through the complete photoresist process, as previously outlined for silicon, to install the square pattern on each of them. After etching the oxide off of the window areas, three crystals were given two spin-on coatings of the less viscous plantinum solution.

For comparison purposes, one crystal was not platinum coated and one platinum coated crystal was placed in the furnace at 1015 ± 5°C to burn off the photoresist with its adhering platinum coating. This resist burn-off step again proved unsatisfactory, as it had with silicon, since it continued to fail to provide the desired window isolation. The remaining three crystals, after an adequate drying period of several hours, were stripped in heated J-100 to again isolate the platinum coated window areas.

All four of the crystals were then placed into the evaporation system and given an aluminum coating, thus assuring good probe contacting when testing the contacts themselves. After evaporating on the aluminum, another photoresist processing was accomplished utilizing a negative square pattern mask. Upon completion of this negative mask installation, each crystal was placed in a heated aluminum etch to restore the desired window isolation and then placed in heated J-100 for ten minutes to strip off all remaining resist. After cleaning with acetone, isopropyl alcohol, and blowing each crystal dry, the crystal

that had been placed in the furnace to remove the resist was placed on the probe station for a preliminary test that was to be indicative of what to expect on the remaining two platinum coated crystals. The probe station trace of this crystal appeared to be back-to-back diodes, as shown in Fig. 3.1.

The remaining three crystals, two platinum coated under the aluminum and one with just aluminum, were then sintered for three minutes at 510°C to insure good bonding of the aluminum. These crystals were then placed, individually, on the probe station to determine if contacts had been formed and, if formed, to inspect their characteristics as indicated by the oscilloscope trace. The first sample inspected was the crystal having only the aluminum and, as seen in Fig. 3.2, the trace indicates that a very poor diode had been formed. The trace displays some characteristics of both rectifying and ohmic contacts. With the work function of aluminum at 4.25 eV and the work function of the α-silicon carbide being 4.6 eV, the dual characteristics of the trace are understood. These work functions are close to being a match and the electronegativity of the aluminum approaches that required for ohmic contact, yet it remains too high and, therefore, results in a rectifying contact. When combined, these two tendencies result in the diode-like trace seen in Fig. 3.2.

The two crystals with the platinum coating were then placed on the probe station and the observed traces were nearly identical. Both crystals displayed characteristics of rectifying contacts, as seen in Fig. 3.3. The work function of the platinum, as determined by the

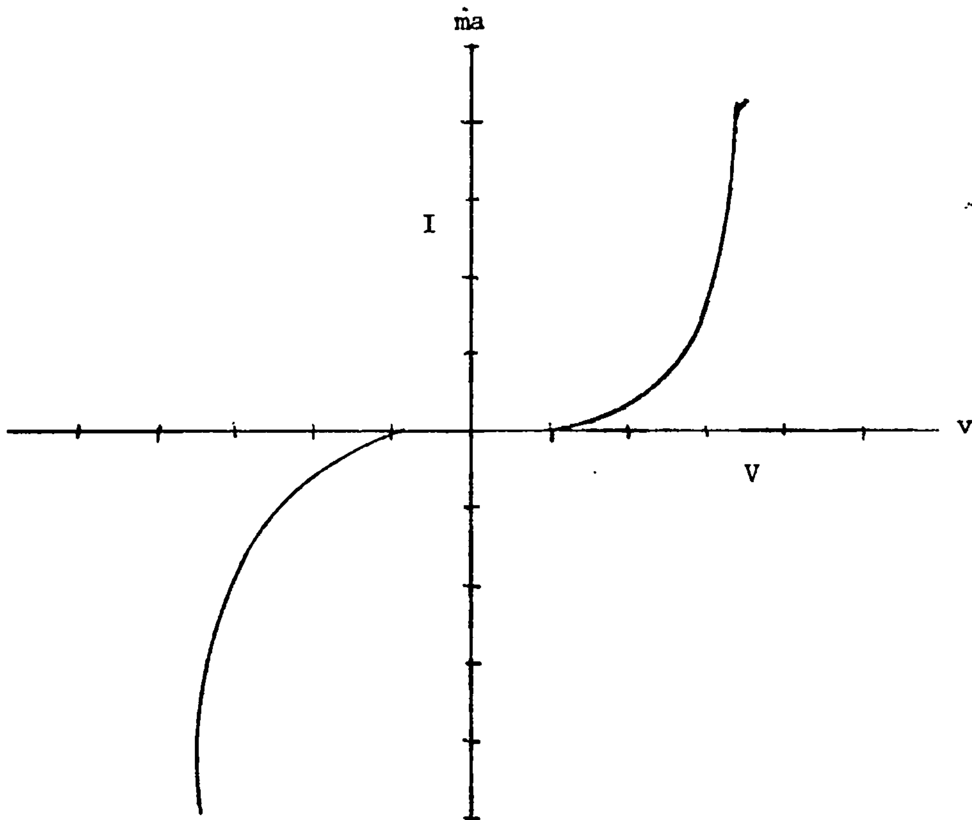

Fig. 3.1 Probe Station Trace of Platinum Coated, Aluminum Evaporation, 6H α-Silicon Carbide Crystal Showing the Back to Back Diode Characteristic

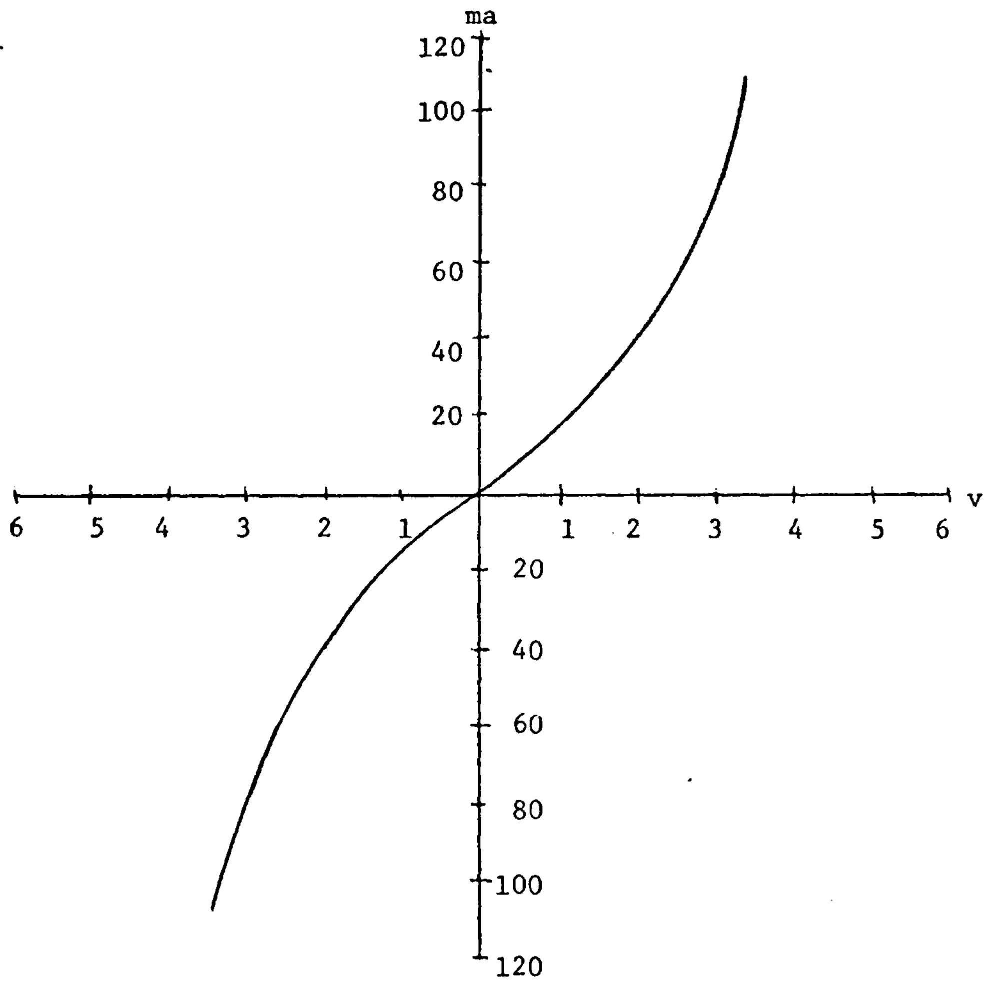

Fig. 3.2 Green 6H α-Silicon Carbide with Aluminum Coating Only. Probes Set on Two Adjacent Window Areas

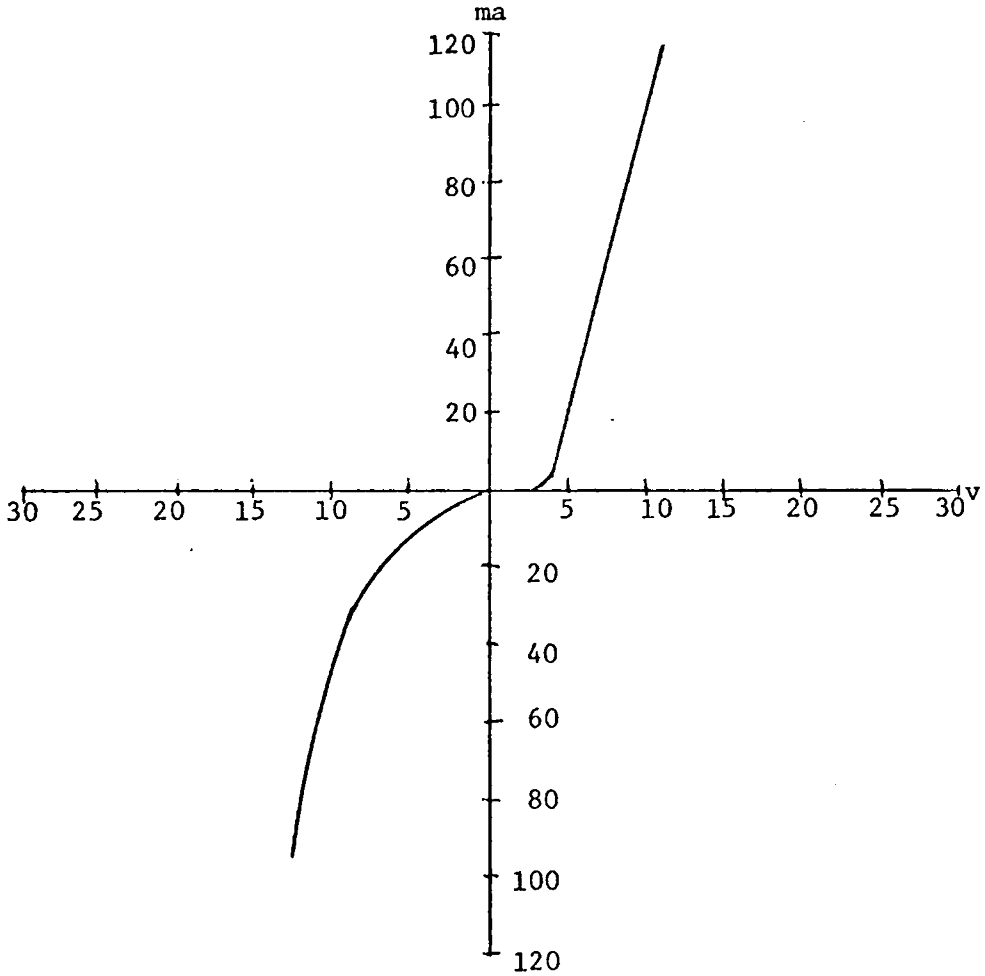

Fig. 3.3 Green 6H α-Silicon Carbide with Aluminum Coating Over Platinum. Probes Set on Two Adjacent Window Areas

contact potential method, was 5.36 eV and this work function value resulted in the observed rectifying contacts.

The observed results with the platinum paste were due to an insufficient bonding of the platinum to the silicon carbide. The melting point of platinum, as previously stated, was too high for the equipment available to achieve, hence, the insufficient bonding with the resulting failure to lower the barrier energy of the platinum into the range where ohmic ontacts could be expected. The contacting process was repeated utilizing an antimony solution and then an arsenic solution as the contacting material. Each time the results were similar to platinum in that only rectifying contacts could be achieved. An evaluation of all contacts formed thus far, that is by spin-on of solution, appear to be consistent in resulting in rectifying contacts.

CHAPTER 4

FUSION TO SILICON CARBIDE

Since the application of contacting materials in solution form resulted in only rectifying contacts, a different method of application had to be attempted. Looking again for an inexpensive and plentiful contacting material, silicon once more appeared to be an ideal choice, only this time to be utilized as the contacting material rather than the semiconducting material. The melting point of silicon, 1410°C, could be achieved on available equipment and this temperature was well below the melting point of silicon carbide, 2700°C. The melting of silicon on silicon carbide should result in the fusion of the two materials with a concurrent lowering of the barrier energy between them. With the work function of silicon at 4.2 eV, and that of silicon carbide at 4.6 eV, the fusion process should result in the formation of ohmic contacts.

Ohmic contacts had been made by Hall [1958] and Violin and Kholuyanov [1964] on silicon carbide by fusing appropriately doped silicon. This process appeared an ideal solution to the formation of ohmic contacts since all required materials and processes were available. The above cited processes for fusion of silicon to silicon carbide all required temperatures in excess of 1600°C to insure proper alloying of the contacting to the semiconductor material. It appeared that the

high temperature requirement resulted from the dopant utilized in the silicon and could be circumvented through the use of phosphorus as the silicon dopant.

Selecting a phosphorus doped silicon wafer with resistivity of .01 to .1 ohm-centimeters as the contacting material, the wafer was scribed. The wafer was selected with the stated resistivity because this resistivity most closely matched the resistivity of the silicon carbide, which was .03 to .3 ohm-centimeters. After scribing the wafer, it was broken into numerous pieces of about one square millimeter in size and, with two silicon carbide crystals, all were thoroughly cleaned in TCE and isopropyl alcohol. Upon completion of the cleaning, the silicon carbide crystals and about twelve pieces of the silicon were placed in a 10:1 hydrofluoric acid etch for ten minutes to remove any oxides that may have accumulated on them.

Concurrent with the above cleaning process, a horizontal tube furnace was raised to 1432°C. The temperature was measured with the use of a Pt-Pt 13% Rh thermocouple inserted into the furnace tube. With an argon atmosphere flowing in the tube, the silicon-silicon carbide samples were prepared.

Removing the silicon carbide and the silicon preforms from the HF etch, each was thoroughly rinsed in distilled water and blown dry. The silicon carbide crystals were placed on a quartz boat and four pieces of silicon were placed in a straight line on each crystal, insuring that each piece of silicon was isolated from other neighboring pieces. The quartz boat was then placed at the end of the furnace tube

for a ten minute preheating to preclude introducing a room temperature boat suddenly into the 1400°C range. It was then placed into the aforementioned heating zone for a period of ten minutes, after which it was removed from the furnace. Visual inspection indicated that the silicon had melted and the surface tension of the molten silicon had caused the formation of circular peaks of silicon for each piece of silicon placed on the silicon carbide. This surface tension caused a contraction of the silicon as it melted and peaked, thereby further insuring the isolation of each piece of silicon on the silicon carbide.

After cooling, the samples were checked mechanically for fusion of the contact material and semiconductor material. Several efforts to physically dislodge the silicon from the silicon carbide with tweezers and by dropping the samples through a distance of four feet onto a hard surface proved unsuccessful. Following this physical check, the samples were placed on the probe station for an electrical check. Curve traces of the I-V characteristics were observed between each of the contacts and in various combinations between the contacts. Each time the curves were nearly identical and are shown in Figures 4.1 and 4.2.

The nonlinearity shown in Fig. 4.1 was a result of poor contact between the silicon and the probe itself. Figure 4.2 is a plot of the I-V characteristic for the contacts when the probe did make good contact to the silicon. The nonlinearity was greatly reduced on the traces of all contacts after each sample was lapped to put a flat surface for probe contact on the silicon contacts. The nonlinearity caused by the probe was completely eliminated by the use of pressure probes to

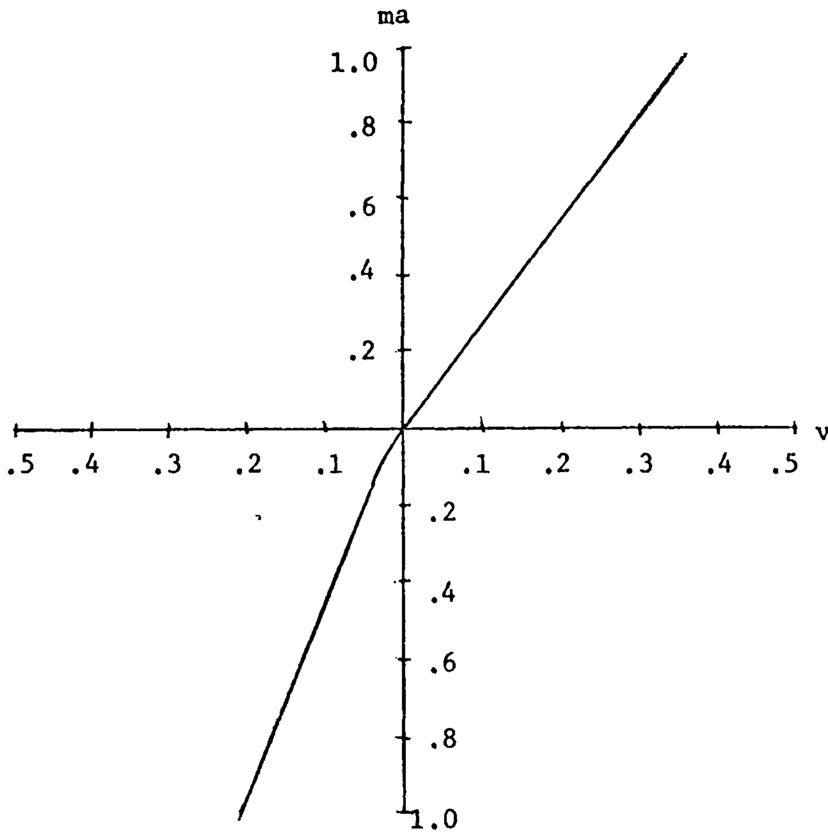

Fig. 4.1 Probe Station Trace of Silicon Fused to Green Silicon Carbide Showing Probe Caused Nonlinearity

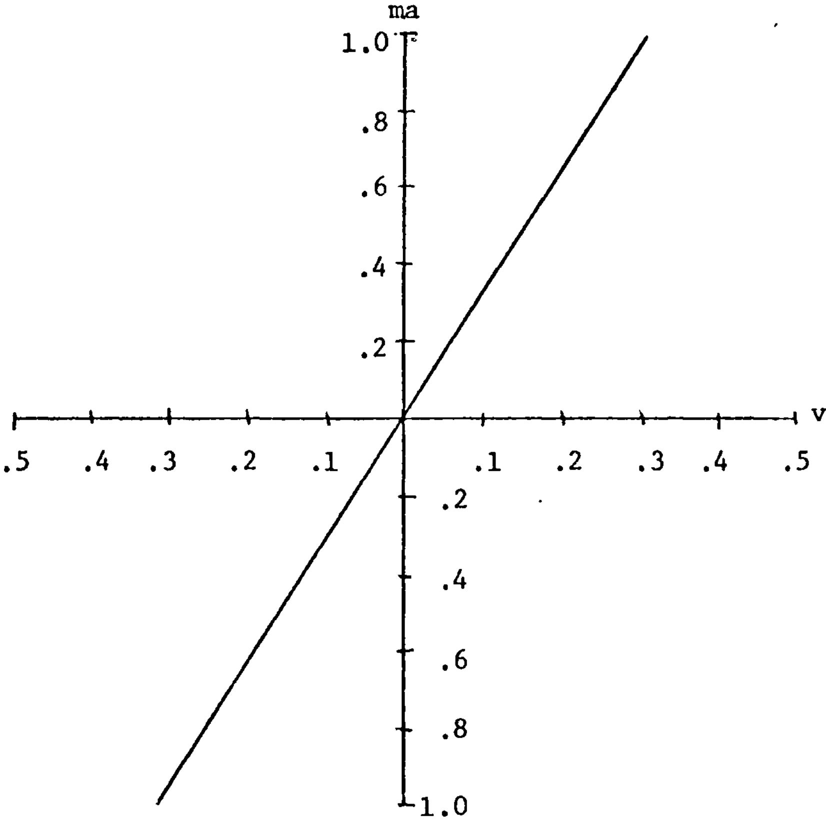

Fig. 4.2 Probe Station Trace of I-V Characteristics of Silicon Fused to Green Silicon Carbide

insure intimate contact between the probe and the silicon contacting material.

This fusion of silicon to the silicon carbide process was repeated several times and each time, the end result was good ohmic contacts. The silicon carbide in each of these experiments was green silicon carbide with a doping level of $9 \times 10^{18} cm^{-3}$. This heavy doping meant there was a very thin space-charge layer width and one through which carriers could easily tunnel. This tunneling current was in addition to any thermally generated electron current over the barrier and is commonly called thermionic field emission [Padovani and Stratton, 1966]. Any increase in the doping level would have led to an even thinner depletion width which would permit carriers at the Fermi level to tunnel through the barrier. This additive component of tunneling current flow made the current-voltage characteristics, as observed at the probe station, linear over a large current range and resulted in the ohmic behavior seen in Fig. 4.2.

The typical current-voltage characteristic between adjacent contacts on the green silicon carbide was used to determine the total resistance between contacts. This total resistance consisted of the two contact resistances plus the distributed resistance of the silicon carbide crystal between the two contacts. The total resistance taken from Fig. 4.2 is approximately 300 ohms and is linear.

No attempt was made to determine the actual contact resistance since it was impossible to ascertain accurately the area of the contact. The fusion of the silicon to the silicon carbide was irregular and

resulted in areas of actual fusion that were invariably smaller than the measured contact areas. At best, only the order of magnitude of the contact resistance could be determined and no further work was done in this area since total resistance was satisfactory for the purposes of this experiment. A more detailed explanation of contact resistance determination is presented by Harris [in preparation].

Fusion of silicon to lightly doped, transparent, silicon carbide did not result in ohmic contacts, but rather blocking contacts. The doping level of the transparent silicon carbide was $3 \times 10^{16} cm^{-3}$. This relatively low doping level resulted in a space charge layer width that was too wide for any tunneling to take place. Furthermore, the work function of this transparent silicon carbide was 4.8 eV which presented a higher barrier than that of the green silicon carbide. This higher barrier prevented any thermionic emission over the barrier until approximately forty volts had been applied, at which point there was a soft turnover in the current-voltage characteristic.

Since ohmic contact to lightly doped silicon carbide was highly desirable for use in MOS devices, an investigation of platinum as a contacting material was undertaken. However, as previously stated, there was no furnace equipment available capable of producing the 1770°C required to melt platinum. It was, therefore, decided to fuse platinum to the lightly doped silicon carbide in an evaporation system where in the vacuum, fusion temperatures could be reached. The platinum source to be used as the contacting material was 99% pure platinum thermocouple wire which was flattened and cut into small preforms. After etching the

silicon carbide crystal in an hydrofluoric acid solution to remove any oxide, the crystal was placed on the tungsten strip of the evaporation system. Three platinum preforms were then placed in a straight line configuration across the crystal. The system was evacuated to a pressure of 1×10^{-5} mm of mercury at which time the filament temperature was raised. The platinum melted when the tungsten strip temperature was 1340 ± 10°C, and the crystal surface was at 1100 ± 10°C. All temperature measurements in the evaporation system were performed with a micro-optical pyrometer. The above cited temperatures were maintained for five minutes in a vacuum pressure of 5×10^{-5} mm of mercury after which the filament temperature was slowly lowered. There was a good possibility that the silicon carbide and the tungsten filament would fuse together since these two materials will alloy at approximately 1900°C at normal pressure [Hall, 1958]. There was no fusion of the tungsten and the transparent silicon carbide; however, there was some fusion of the green silicon carbide and the tungsten on subsequent attempts at platinum fusion.

Upon removing the crystal from the evaporation system, a physical check was performed on the contacts to attempt to remove them from the crystal. Mechanically trying to pick the contacts off with tweezers and, again, dropping the crystal in an attempt to dislodge the contacts proved unsuccessful. The platinum apparently had fused with the transparent silicon carbide. Placing the sample on the probe station for an electrical check confirmed that fusion between the two materials had occurred and that the contact thus formed, was an ohmic contact.

The I-V characteristic for this contact is seen in Fig. 4.3 and the total resistance between the contacts, as previously defined, taken from Fig. 4.3 is approximately 400 ohms and is linear.

The fusion of platinum to lightly doped silicon carbide invariably resulted in ohmic behavior. The linear I-V characteristic of this contact is not analogous to the results found by Yu [1970] when placing platinum on n-type silicon in that rectifying contacts are not formed. The platinum and silicon carbide did not form an abrupt junction, but rather an alloy of the two materials. This alloying caused disruptions in the crystalline structure and led to dislocations, vacancies, recombination centers, and other surface effects which are only now being studied with reference to silicon carbide. The energy barrier between these two materials still existed; however, the height and form of this barrier through the alloyed region is a subject of much conjecture and investigation and is beyond the scope of this experiment.

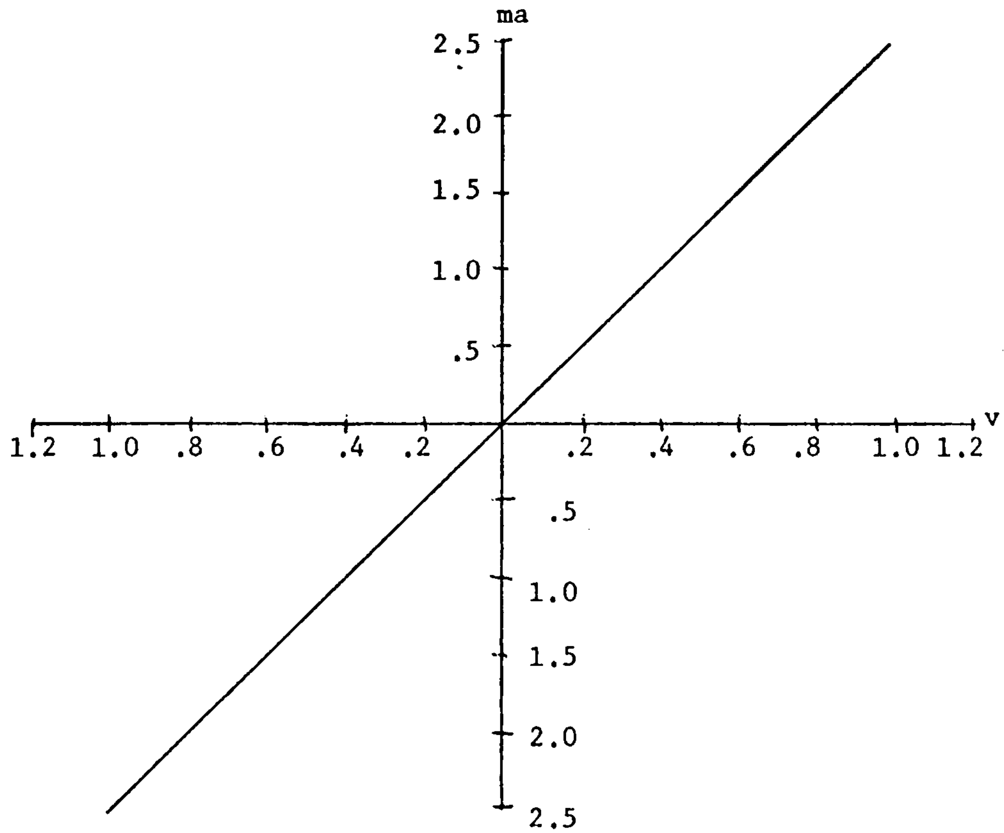

Fig. 4.3 Probe Station Trace of I-V Characteristics of Platinum Contacts Fused to Lightly Doped Silicon Carbide

CHAPTER 5

CONCLUSIONS

The primary goal stated in Chapter 1 for this thesis and its associated experimental work was to form ohmic contacts on silicon carbide utilizing inexpensive, plentiful contacting materials and relatively low temperatures. A secondary goal was to determine a process for making the above contacts that was simple to perform and utilized no highly sophisticated equipment that was not readily available in most solid state engineering laboratories.

With the fusion of silicon on heavily doped silicon carbide and the resulting ohmic contacts, as discussed in Chapter 4, both of the above goals were realized. The thermally generated electron current over the energy barrier between the two materials plus the tunneling current through the thin space charge layer assured ohmic behavior. The resultant linear I-V characteristics are also shown in Chapter 4.

The fusion of silicon to lightly doped silicon carbide resulted in blocking contacts rather than the desired ohmic contacts. Fusing platinum on lightly doped silicon carbide in a vacuum pressure of 5×10^{-5} mm of mercury, where the fusion temperature could be achieved, accomplished the primary goal of making ohmic contacts; however, it is only a partial realization of the secondary goal in that the process is not as simple as the fusion of silicon at normal pressure and does require the use of relatively sophisticated equipment.

The fusion of platinum resulted in an alloying of the two materials rather than the formation of an abrupt junction. The alloying further led to many possible surface effects phenomena which, at this time, are not well understood and continue to be investigated. The barrier energy between the platinum and silicon carbide still exists after fusion; however, its position and form through the alloyed region is another unknown presently being investigated in various research efforts.

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