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EFFECTS OF ADSORBED MOLECULES AND GAMMA RADIATION ON THE SURFACE PROPERTIES OF GERMANIUM DIODES

THESIS

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Preface

This investigation resulted from an interest in the unusual electrical properties of germanium diodes in gamma radiation. Previous studies of these unusual effects included a complex, time-consuming procedure for surface treatment. I hope that the simple experimental technique and the agreement of the results, reported in this paper, will increase the flexibility for future investigations.

I am indebted to the personnel of the Electronic Technology Laboratory and Materials Laboratory of the Wright Air Development Division for making available the necessary facilities and equipment. A special acknowledgement is given to Dr. W. L. Lehmann for his guidance and assistance in the interpretation of the data. Finally, I wish to acknowledge the assistance and encouragement given so generously by my wife.

David M. Verrelli

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Abstract

The reverse current-voltage characteristics of a germanium grown junction are measured both before and during Cobalt-60 gamma irradiation of 5.65×10^7 ergs/gm C-hour. The ambients are dry oxygen, ozone, and water vapor. For a dry oxygen ambient in radiation, the current rises with increase in voltage until, at a critical value of the voltage, the current drops sharply. No such drop is observed in ozone or water vapor. A theoretical interpretation whereby oxygen molecules are desorbed from the surface is offered to account for the sharp drop. The magnitude of the current below the critical voltage is attributed to an excess surface charge resulting from the transfer of electrons across the oxide barrier.

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EFFECTS OF ADSORBED MOLECULES AND GAMMA RADIATION ON THE SURFACE PROPERTIES OF GERMANIUM DIODES

I. Introduction

The purpose of this investigation is to observe the reverse current-voltage characteristics of a germanium p-n diode in various ambients, before and during gamma irradiation. The ambients are ozone (26°C), wet oxygen (26°C), and dry oxygen (-72°C to 65°C). The intensity of the radiation field is 5.65×10^7 ergs/gm C-hour.

The surface condition and ambient influence the reverse characteristics of a germanium diode. Currents in excess of the saturation current of the bulk are induced by the adsorption of gas molecules onto the surface, resulting in surface conduction. There are four possible mechanisms for this surface conduction:

1. Adsorbed molecules produce a net surface charge which induces an inversion layer across the junction region. The inversion layer is a thin layer of material just below the surface that has different charge carriers than the bulk material beneath. This mechanism is of primary importance and has been substantiated by theory and experiment (Ref 5).

2. Current multiplication in an inversion layer can take place at applied potentials lower than the avalanche breakdown voltage of the bulk junction. This mechanism is required to explain some of the abnormally high reverse currents obtained (Ref 16).

3. A thick layer of adsorbed molecules gives shunting conductance across the surface. This type of conduction is similar to that in molten

semiconductors. For the case treated here, the mobility of the charge carriers in this layer is of the order of 10^{-3} cm^2/volt-sec and is of minor importance (Ref 16:169).

4. Ionic conduction may take place on adsorbed liquid films. This mechanism of conduction has not been observed and is assumed of minor importance (Ref 9:165).

In radiation, germanium diodes exhibit unusual electrical properties. Specifically, a peak occurs in the reverse current-voltage characteristics of diodes in a dry oxygen ambient (Ref 11). Further, the presence of water vapor in the ambient alters the critical voltage at which the peak occurs. As the humidity is increased, the prominence of the peak diminishes until at 100% humidity, the peak disappears (Ref 6).

Presently, the occurrence of the peak is attributed to the effect of gamma ray ionization on the surface properties of the diode. However, the mechanisms of interaction are not substantiated.

This paper reviews briefly the types of surface states, methods of surface conduction, and mechanisms of interaction between ambients and the surface of a semiconductor. The effects of adsorbed molecules on the surface properties are discussed and correlated with experimental data. A theoretical interpretation is offered for the observed characteristics in gamma radiation. This interpretation is also tested against published data.

II. Surface Phenomena of Semiconductors

Surface States

In addition to the energy states located within the bulk material of a semiconductor, a high density of states exists at the surface. These states result from the termination of the crystal lattice, formation of an oxide layer, and adsorption of impurity atoms.

Tamm States. Within the bulk material the systematic arrangement of atoms produces a periodicity of the potential field in which an electron moves. The sharp end of this periodicity at the surface introduces new energy levels in which electrons can exist. There energy states, first discovered by Tamm, exist at well defined energy levels. Handler suggests that his data indicates the occurrence of Tamm states; however, others question his interpretation because of the rigorous proof required for establishing the presence of a clean semiconductor surface (Ref 9:23).

Fast States. An oxide layer, described later in this chapter, is invariably present at the surface of an etched semiconductor. At the interface of the bulk material and the oxide layer, mechanical faults, vacancies, and adsorbed impurities introduce surface states intimately in contact with the bulk. These states have lifetimes in the order of a few microseconds. The density of these "fast" states depends critically on the preparative history of the sample. These states are of prime importance in the recombination process (Ref 2:578).

Slow States. On the surface of the oxide layer, adsorbed impurities and atoms of the surrounding ambient give rise to additional surface states. These outer states, removed from the bulk material by the oxide layer, have reaction times with charge carriers of the bulk in the order of 0.1 second to minutes. From field effect and inversion layer experiments, the density of "slow" states is estimated in the order of 10^{13} per cm^2 (Ref 2:569).

The density and population of slow states is not only a function of the number of adsorbed molecules but also a function of the type. Table I lists various materials which are known to give different surface charges. This surface charge results from the trapping of either holes or electrons in the slow states. Therefore, the population of the slow states determines the conductivity of the surface.

Table I

Some Materials Which Give Surface Charges Upon Adsorption

Positive Charges	Negative Charges
Ammonia	Boron Trifluoride
Acetone Vapor	Ozone
Water Vapor	Oxygen
Dioxane Vapor	Chlorine
Pyridine Vapor	
Methyl Alcohol Vapor	

Ref 9:143

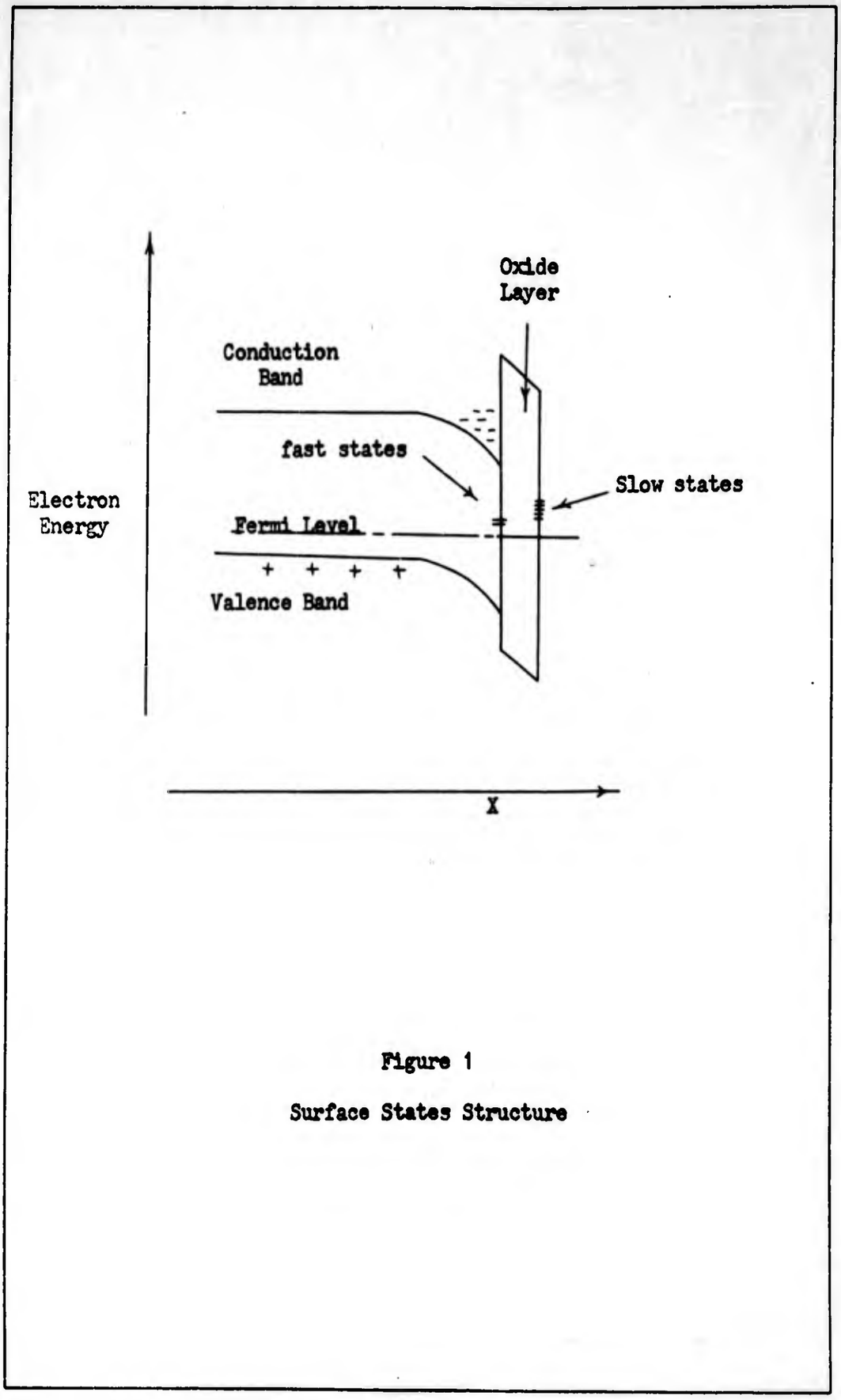


Figure 1

Surface States Structure

In summary, the termination of the crystal lattice, mechanical faults, and adsorbed impurities introduce a complex, high density of energy states at the surface of a semiconductor. Figure 1 illustrates the location of both "fast" and "slow" surface states. The high density of these recombination centers, localized at the surface, considerably effects the electrical characteristics of a semiconductor in various ambients.

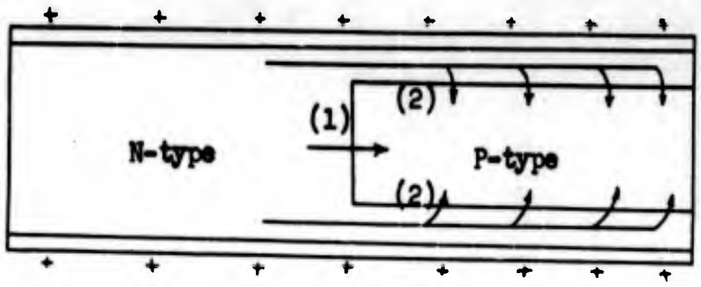
Methods of Surface Conduction

The theoretical relationship for the reverse current across the bulk junction of an ideal semiconductor diode is

$$I = I_o \left[\exp (qv/kT) - 1 \right] \qquad (1)$$

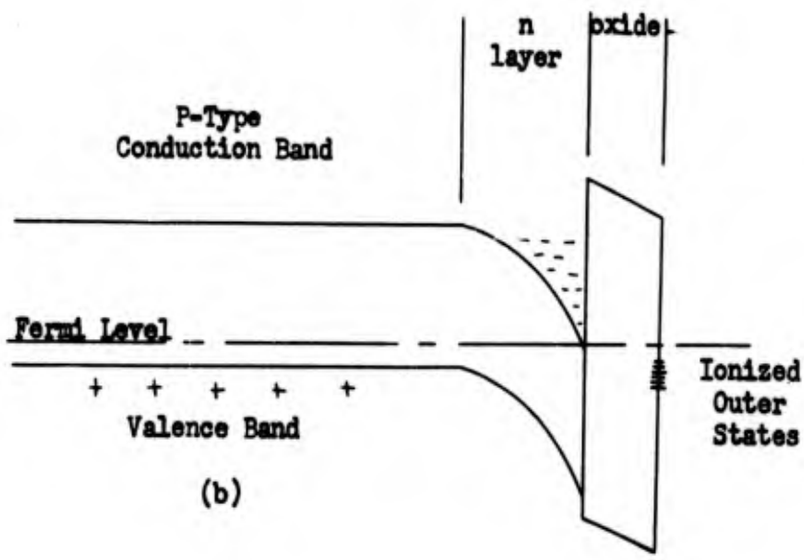
where I_o is the generation current, q is the electronic charge, v is the applied potential, k is the Boltzmann constant, and T is the absolute temperature. Sometimes, excess currents are obtained from a diode and can not be explained by the properties of the bulk material. These variations occur when molecules are adsorbed onto the surface. Inversion layer conduction across the junction region and current multiplication at the inversion layer-bulk interface are primarily responsible for these excess currents. Ionic conduction on the surface and outer states conduction may also contribute to the excess current, but their influence is negligible.

Inversion Layer Conductance. Because of the high density of recombination centers, it is possible for trapped holes or electrons to produce a net charge on the surface of a diode. This surface charge attracts



(a)

(1) bulk junction
(2) inversion layer-bulk interface



(b)

Figure 2

N-Type Inversion Layer
(a) Schematic (b) Energy Level Diagram

oppositely charged carriers (repels like charge carriers) in the region adjacent to the surface. Thus a depletion layer, formed by the influence of the surface charge, extends into the crystal for a distance of 10^{-6} to 10^{-4}cm. If this charged layer is opposite to the majority carrier concentration of the bulk material beneath, the active area of the original junction is increased. In order to induce an inversion layer, the surface charge must exceed a minimum amount (Ref 9:140). The schematic model and electron energy diagram for an n-type inversion layer, such as would be created by a water ambient, are illustrated in Figure 2.

The theory of Eriksen, Statz, and de Mars gives for inversion layer conduction

$$I = C(2j_o)^{\frac{1}{2}} \left(\int g(v')dv' \right)^{\frac{1}{2}} \qquad (2)$$

where I is the current that flows for an applied voltage V, C is the circumference of the diode, $g(v)$ is the conductance of a square of inversion layer at bias V, and j_o is the saturation current per cm^2 across the surface junction. Graphical integration of Equation (2) gives the inversion layer current as an approximate logarthmic function of voltage (Ref 5:134). Thus an inversion layer should result in a linear plot of log V vs I.

Surface Current Multiplication. It has been shown that reverse biased junctions breakdown as a result of minority carrier multiplication analogous to multiplication breakdown in a gas. The minority carriers diffuse to the high field region of the junction, where they are accelerated, and produce hole-electron pairs by collisions with the atoms of the crystal lattice. The created holes and electrons themselves are capable of being

accelerated and of producing additional carriers. Thus the net current across the junction is multiplied by a factor dependent upon the magnitude of the electric field. As the applied voltage is increased the current multiplication factor increases until at a particular value of the reverse voltage, called the breakdown voltage, the multiplication of the minority carriers is essentially infinite. This process is termed avalanche breakdown of the bulk junction.

It has been shown by many experimenters that high intensity fields exist in the localized region where the inversion layer meets the bulk p-n junction. The magnitude of these fields depends upon the distribution of the surface charge as well as the applied potential across the bulk junction. Since these fields can be greater than those across the bulk junction, avalanche breakdown in this localized, critical region can occur at applied potentials less than the breakdown voltage of the bulk junction.

Since the magnitude of the electric field at the inversion layer-bulk interface is critically dependent upon the surface charge, the applied bias at which current multiplication sets in is a function of the ambient. This phenomenon was first reported by Bernstein and Kingston for p-n-p bars in a nitrogen ambient containing water vapor (Ref 1:1566). Statz and de Mars also report surface current multiplication (Ref 16:180).

Ionic Conduction. When the amount of condensable vapor on the surface of a semiconductor reaches the multilayer region, the outer, adsorbed molecules become quite mobile. An electrolytic film on the outer adsorbed molecules is thus free to transport charge under the influence of an

electric field. Although ionic conduction is possible under the above circumstances, it has not been substantiated by experimental data.

Slow Surface States Conduction. Statz and de Mars have shown that surface charge, trapped in the outer states, is free to move under the influence of an electric field. The mobility of these charges has been estimated to be less than 10^{-3} cm^2/volt-sec. Therefore, this type of conduction is negligible when compared with inversion layer conduction (Ref 16:169). However, it is noted that the movement of charge in the surface states may cause a change in the inversion layer beneath the oxide layer and thus indirectly produce a substantial effect.

Interaction of Ambient with Surface of Semiconductor

As indicated above, the surface states markedly effect the electrical properties of a semiconductor. A thorough understanding of the interaction between ambient atoms and the surface of the semiconductor requires a detailed and well defined model of the semiconductor surface. No one, to date, has formulated such a model. Therefore, the following paragraphs, designed to give a general but brief mechanism of interaction, represent thinking in the field of semiconductor surface physics.

Oxide Layer Formation. An etched germanium surface is invariably covered with an oxide layer whose structure and composition are not well known. The thickness of the oxide layer depends critically on the surface preparation technique. Electrolytic etching produces thin oxide layers ($\sim$ 10Å) whereas chemical etching produces thicker layers (> 30Å).

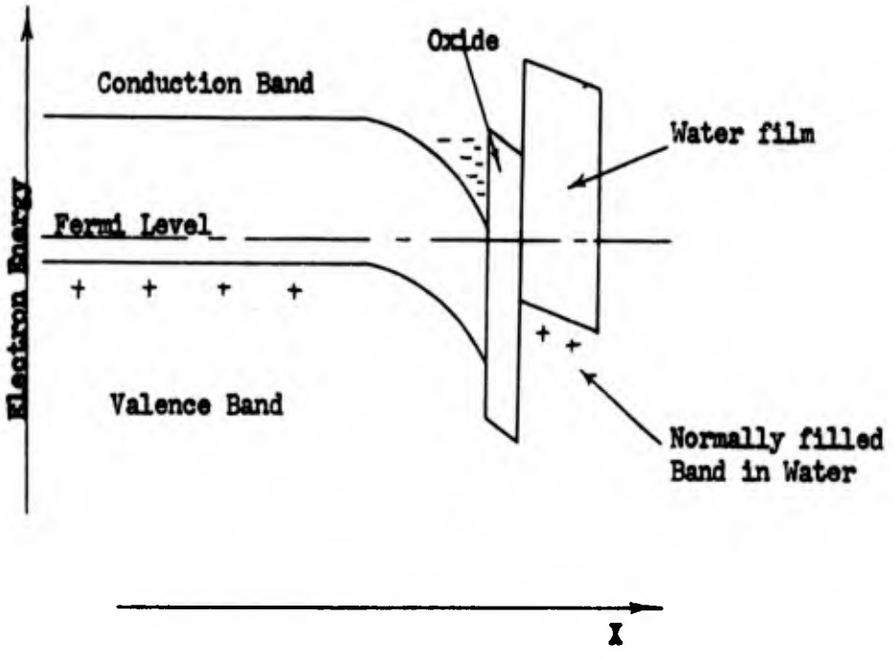


Figure 3

Slow States Conduction
in Water Film

The effect of a thick oxide is to reduce ambient changes on the underlying semiconductor space-charge region. Very thick oxide layers can be grown by prolonged heating in oxygen at elevated temperatures (Ref 9:198).

Oxygen Up-Take. When oxygen comes into contact with a freshly etched oxide surface, a monolayer of oxygen atoms rapidly covers the surface. Continued exposure to an oxygen ambient does not increase the adsorption above 1-2 monolayers.

Adsorption measurements in an oxygen ambient indicate a slight, negatively-charged surface. However, this charge is not sufficient to induce a p-type-inversion layer across the n-region of a diode. Thus, an oxygen ambient does not produce excess reverse currents (Ref 9:329).

Water Vapor Adsorption. Adsorbed water molecules produce a positively charged surface. Thus an n-layer is induced over the p-region of a diode. The initial layer of water molecules is tightly bound to the oxide. This layer does not contribute to excess currents. Its only effect is to decrease the surface recombination velocity (Ref 2:596). As additional layers are adsorbed, the water molecules become quite mobile, and are capable of transporting charge. The multilayers of molecules induce the n-layer over the junction region. This could be explained if the normally filled valence band of the water film lies close to the Fermi level of the underlying bulk material. Thus some electrons would be excited out of the valence band leaving a positive surface charge in the water film. Hole conduction within the water film could result. Figure 3 illustrates a possible energy level diagram for formation of an inversion layer and slow states conduction in the water film.

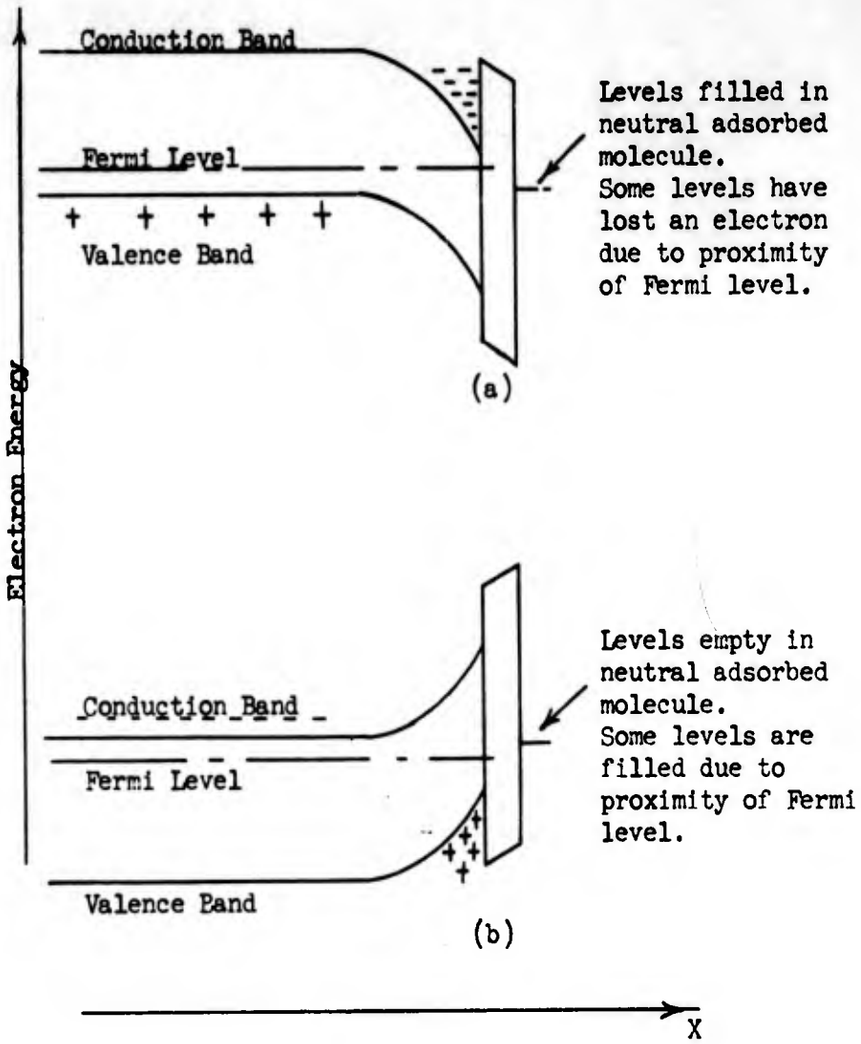


Figure 4

Energy Bands at Surface With Adsorbed Molecules

(a) Water Vapor (b) Ozone

Ref 9:144

The multilayers of adsorbed water molecules can be removed by cycling of the ambient from wet to dry oxygen. However the initial layer of adsorbed molecules can only be removed by a high vacuum (Ref 2:584). When the surface of the diode is freshly etched, cycling of wet and dry oxygen must be performed six or seven times before reproducible data can be obtained (Ref 13:2082). Thus the complex structure of a semiconductor surface is again demonstrated.

Ozone Interaction. Ozone is known to interact with the surface of a semiconductor diode and produce an excess negative charge. A p-type inversion layer is also induced (Ref 9:143). This could be explained if the ozone were to introduce energy levels slightly above the normal position of the Fermi level. These normally-empty states could serve as electron traps and a negative surface charge could result. Figure 4 compares the energy level diagrams for adsorbed ozone and water vapor molecules.

The excess surface charge of a diode in an ozone ambient can not be reduced significantly by cycling to a dry oxygen ambient. However, if the surface is exposed to a wet ambient and then cycled to a dry ambient only a slight negative charge results (Ref 14:2277). Thus the effect of ozone on the surface properties is readily counteracted by water molecules but not by dry oxygen molecules.

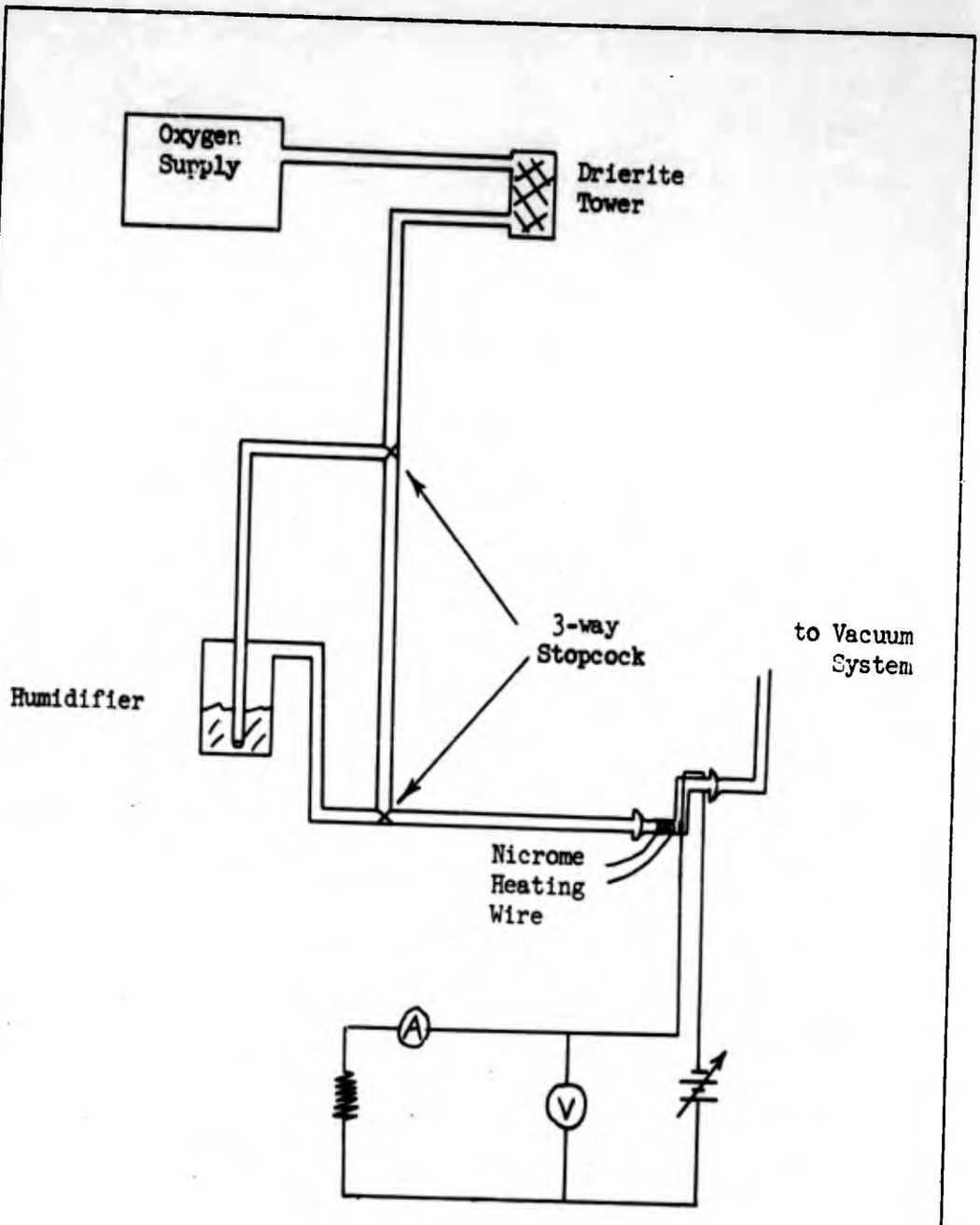


Figure 5

Ambient-Variation and Electrical Circuit

III. Experimental Procedure

The following paragraphs contain a general discussion of the experimental procedure. Detailed explanations of techniques are included as Appendices to this paper.

Commercially available, grown junction, germanium diodes (Western Electric #1876) were used in all experiments of this investigation. The surface of the decapsulated diode was chemically etched, washed, and vacuum dried. Reverse current-voltage characteristics of the diode were then obtained in dry oxygen, wet oxygen, and ozone without gamma radiation. Figure 5 is a schematic representation of the experiment.

Ambient Variation

Oxygen was dried in a calcium sulfate drying tower and was permitted to flow continuously across the surface of the diode. A wet ambient was obtained by bubbling the dry oxygen through distilled water. Ozone was generated by a discharge from a Tesla coil.

Measuring Equipment and Procedure

All electrical measurements were obtained with a Hewlett Packard, Model 410B, vacuum tube voltmeter and a Signal Corps, I-176 ammeter. These equipment were utilized because of the finite time required to obtain steady state conditions. This time lag is attributed to the finite time required for the surface states to come into equilibrium with the bulk. The current in the circuit was permitted to flow continuously.

Gamma Facility

Irradiation of the specimens was performed in the 19,000 curie

cobalt-60 source of the Materials Laboratory, Wright Air Development Division. The intensity of the radiation field was 5.65×10^7 ergs/gm C-hour.

This facility contains a hollow, cylindrical, test cell in which the specimens were placed. Electrical and gas leads were fed through a spiral lead plug from the test cell to the control panel. This enabled cycling of ambient and variation of the bias during irradiation.

The cobalt-60 source is stored in a swimming pool unit directly beneath the test cell. A hydraulic lift raises the source into position for irradiation. The experimental technique for recording the reverse characteristics during irradiation were identical with those performed prior to irradiation.

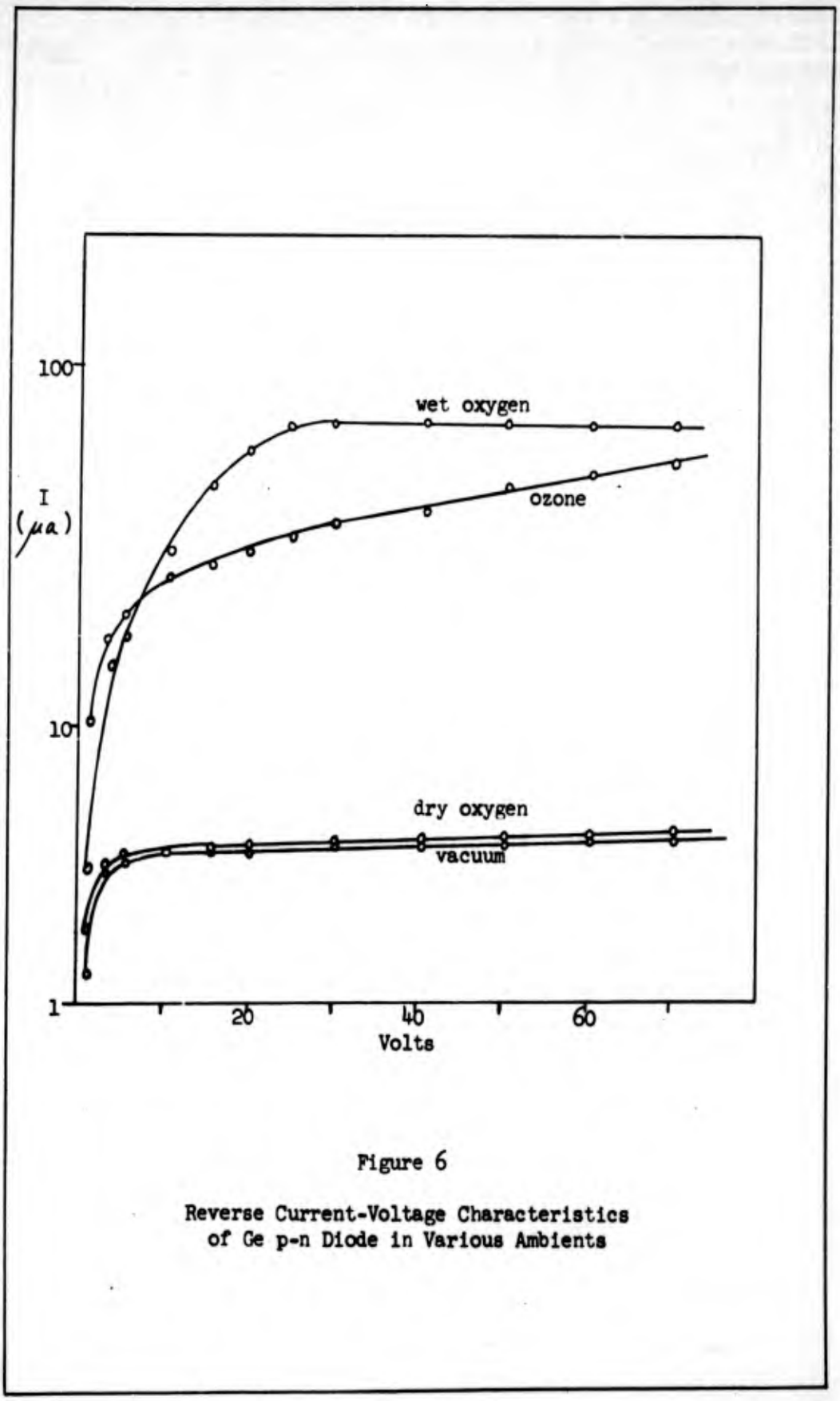


Figure 6

Reverse Current-Voltage Characteristics
of Ge p-n Diode in Various Ambients

IV. Effects of Adsorbed Molecules on the Surface Properties of Germanium Diodes

The results of the initial experiments of this investigation are in qualitative agreement with those reported in the literature. Eleven diodes were exposed to various ambient conditions. The effects of adsorbed molecules are discussed in terms of present theories of surface conduction.

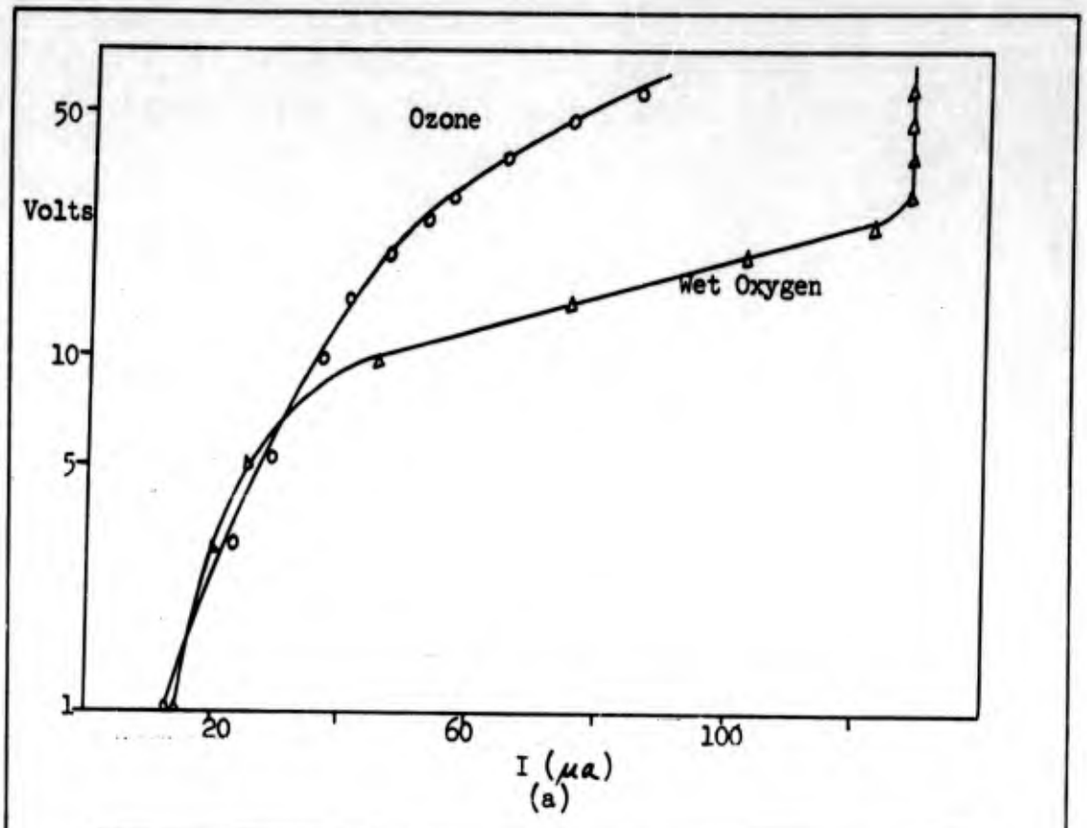
Figure 6 illustrates the reverse characteristics of a representative diode in vacuum, dry oxygen, ozone, and wet oxygen. These characteristics clearly demonstrate that adsorbed ozone and water molecules cause surface conduction across the junction of a germanium diode. The bulk characteristics must lie at or below the vacuum case.

Effect of Dry Oxygen

The characteristic of a diode in a dry ambient was not considered acceptable unless the reverse current was less than 5 μa over the range of 0-70 volts bias. In Figure 6, the characteristics of the diode in both vacuum and dry oxygen are approximately the same. At 70 volts bias the reverse current is 4.4 μa for the vacuum case and 4.8 μa for the dry oxygen case. Although the surface is not neutral in the dry ambient, the slight negative surface charge is less than the minimum amount required to produce an inversion layer (Ref 9:140). Excess currents are not obtained from the adsorption of oxygen molecules.

Effect of Ozone

In the ozone case, the diode produces reverse currents that are



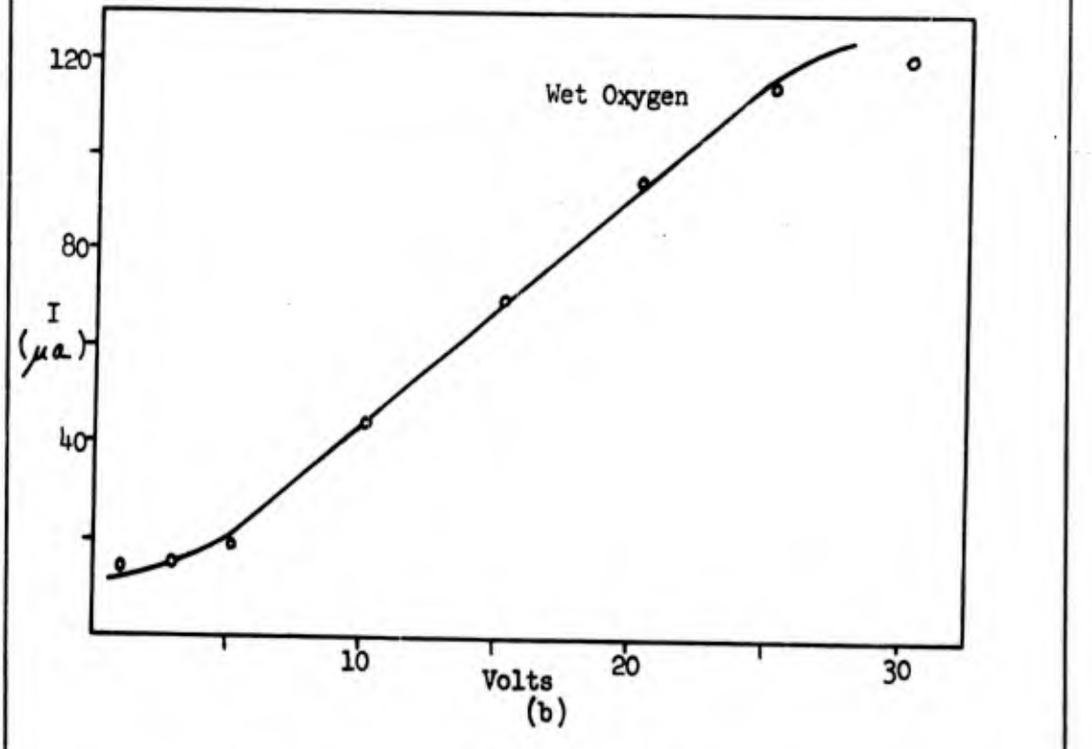


Figure 7
Reverse Characteristics of Ge Diode
in Ozone and Wet Oxygen
(a) Inversion Layer Response (b) Ohmic Response

higher, by an order of magnitude, than those in either a vacuum or a dry oxygen ambient. The current increases steadily over the range of 0-70 volts bias.

The work of Brattain and Bardeen indicates an excess surface charge when a germanium sample is exposed to an ozone ambient (Ref 3). The excess surface charge induces a p-type inversion layer. From the theory of Statz and de Mars the reverse current for inversion layer conduction is an approximate logarithmic function of the applied voltage (Ref 5:134). A plot of log V vs I is included as Figure 7a. These data indicate that inversion layer conduction can satisfactorily explain the excess current below 15 volts. At high voltages the response of the diode begins to vary from the linear relationship of log V vs I. Current multiplication at the inversion layer-bulk interface apparently sets in at the higher applied voltages.

Effect of Water Vapor

The excess currents resulting from a wet oxygen ambient can not be explained simply in terms of inversion layer conduction. Below 5 volts bias, the current response is approximately logarithmic and is attributed to channel conduction. (It is noted that the initial slopes of the two curves in Figure 7a are similar.) As the applied voltage is increased, the response of the diode appears ohmic until the reverse current saturates at 121 μa for an applied potential of 32 volts. Figure 7b illustrates this ohmic response.

The efforts of Eriksen, Statz, and de Mars have shown conclusively that ionic conduction on the water film and hole conduction within the

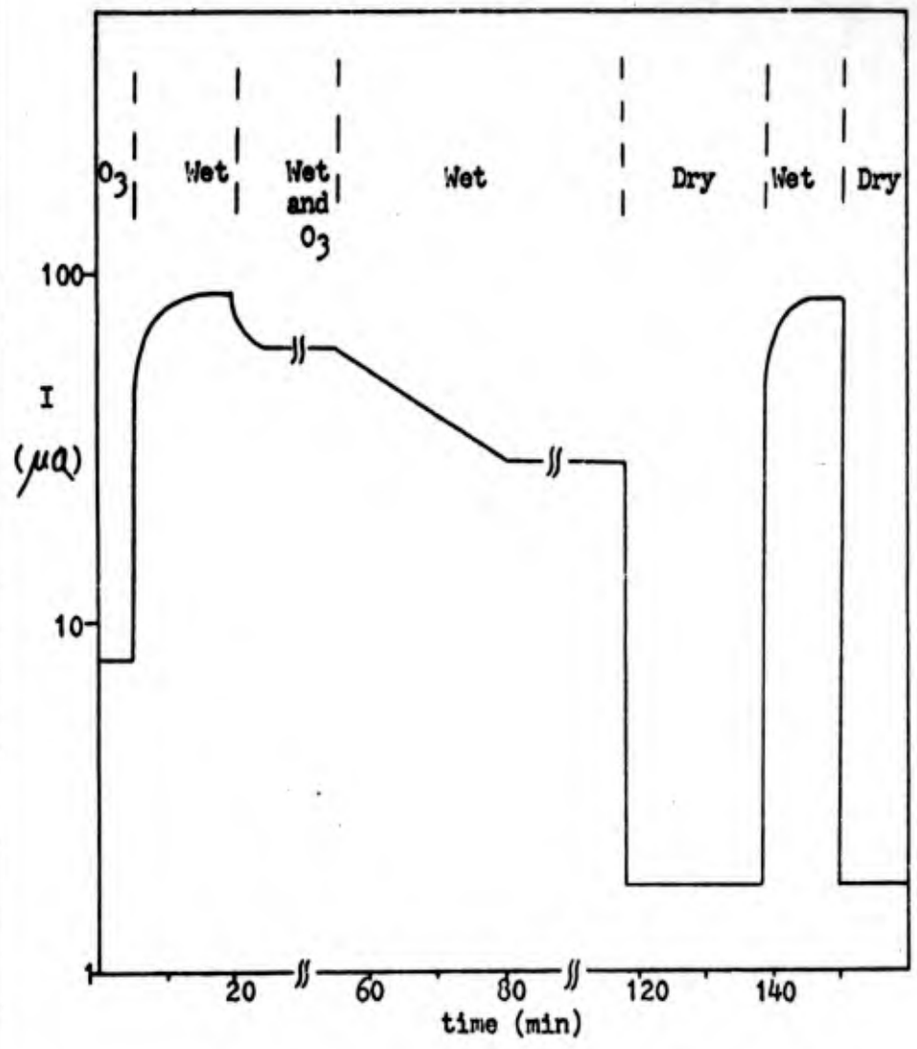


Figure 8

Cycling of Ambients at
30 Volts Reverse Bias

film can not account for the excess current (Ref 16:169). They propose an anomalous current multiplication discussed earlier in this paper.

Cycling of Ozone, Wet and Dry Oxygen

The effect of ambient cycling between ozone and dry oxygen is irreversible. The saturation current of a diode in the dry ambient can be increased by repeated exposures of the surface to an ozone ambient. This result is similar to the observations of Kikuchi (Ref 8). However, if the surface is exposed to a wet ambient and then cycled to a dry ambient, the initial saturation current can be regained (Ref 14:2277). An experiment was performed to observe the effects of a mixed ambient of wet oxygen and ozone. Only a small amount of ozone was generated. The results are illustrated in Figure 8.

The wet ambient produces a saturation current of 86 μa . As ozone is introduced, the saturation current decreases to 66 μa . The effect of ozone in this cycle is to reduce the total surface charge on the diode.

When the ozone is removed from the ambient, the current decreases to a saturation value of 30 μa . This phenomenon can not be interpreted from present theory. A simple attachment or oxidation process does not explain the results. The data suggest a complex structure of the mixed ambients at the surface.

When the ambient is cycled from wet to dry oxygen, the initial characteristics of the diode are regained. Thus the effect of ozone has been removed by the influence of the water molecules.

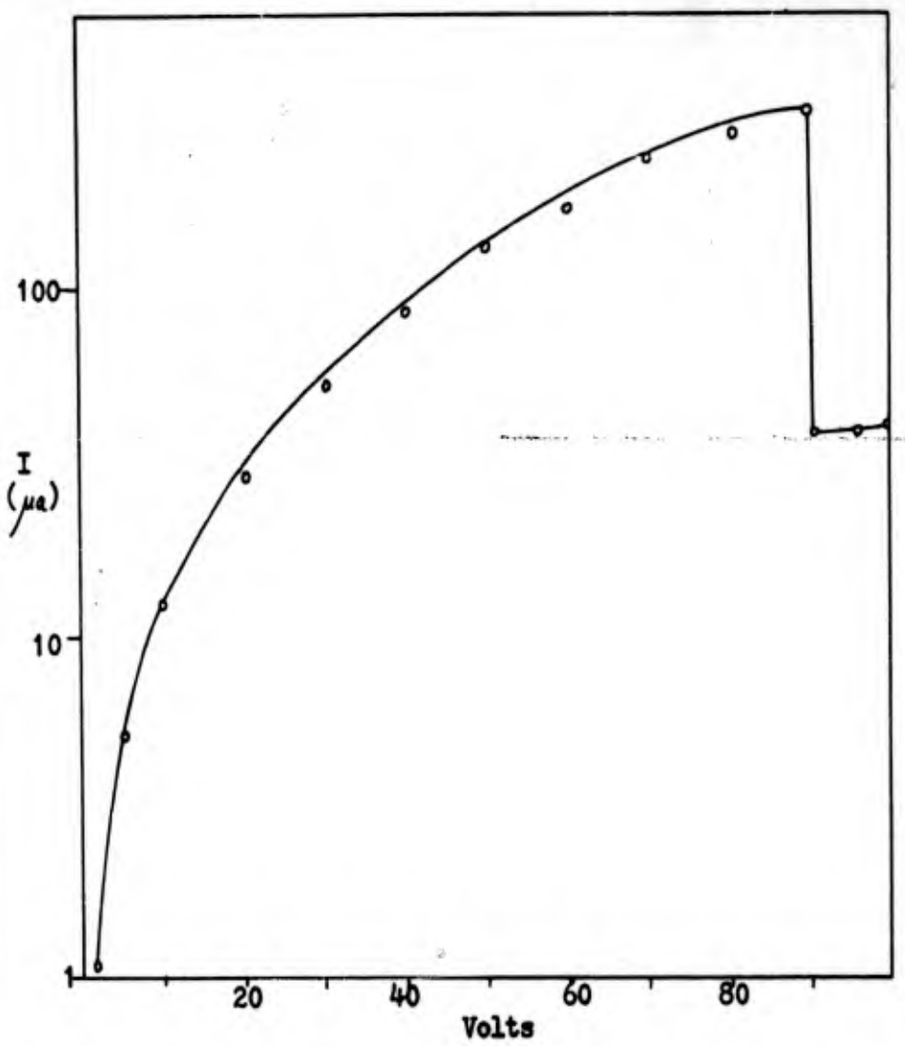


Figure 9

Reverse Characteristics of Ge Diode
in Dry Ambient with Gamma Radiation

V. Effects of Gamma Radiation on the Surface Properties of Germanium Diodes

Unusual effects are observed when a germanium diode is exposed to gamma radiation. The mechanism of interaction between the radiation and the surface properties of the diode is not clearly understood. These unusual effects will be discussed in terms of outer states disturbance, surface current multiplication, and molecular desorption.

Effects of Gamma Radiation on Adsorbed Oxygen Molecules

Results. Three diodes were chemically etched, cycled between dry and wet oxygen, and then irradiated in the gamma facility. The ambient during the irradiation portion of the experiment was dry oxygen. Figure 9 is typical of the response of these diodes. As the reverse bias on the diode is increased, the current increases rapidly until a critical voltage is reached. At this critical voltage the magnitude of the current decreases significantly and saturates for further increase in potential. For these three diodes, the magnitude of the current just below the critical voltage varied from 180 to 320 μa and the saturation current above the critical voltage ranged from 9 to 40 μa . The critical voltage varied from 70 to 88 volts.

A fourth diode was heated in an oxygen ambient at 100°C for 48 hours to obtain a thicker oxide layer. The response of this diode was similar to that described above, however the magnitude of the current just below the critical voltage of 72 volts was only 25 μa . The saturation current was 9 μa .

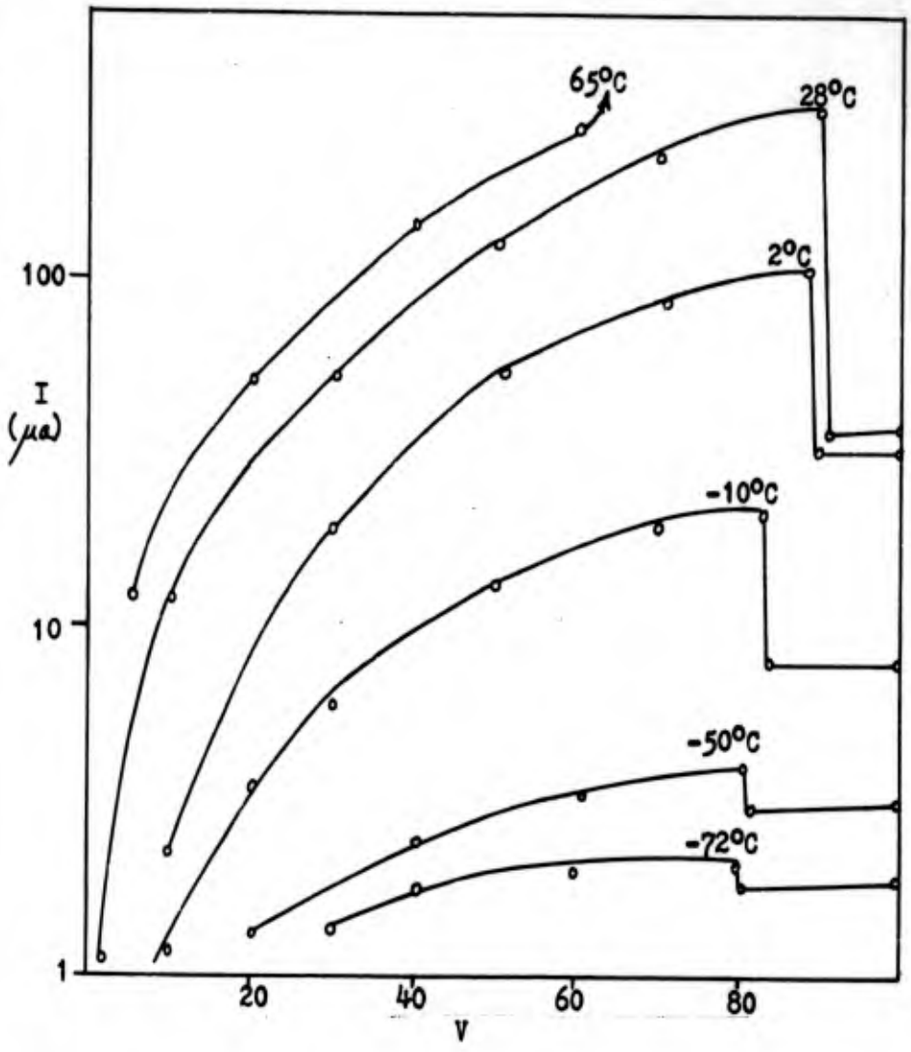


Figure 10

Variation with Temperature of the Reverse Characteristics of Ge Diodes in Radiation Environment

Oscillations of the reverse currents as a function of time were observed at the critical voltage of all four diodes. The period for oscillation varied from 30 seconds to one minute. A hysteresis effect was also observed on each diode; the critical voltage was 20 to 25 volts lower for decreasing voltage than for increasing voltage.

The critical voltage of one of the above diodes was altered by changing the temperature of the ambient. As the temperature was increased in arbitrary increments from -72°C to 65°C the critical voltage increased accordingly from 82 to 90 volts (See Figure 10).

Two diodes did not contain the peak in the reverse characteristics. The first of these diodes was exposed to an ozone ambient immediately before irradiation in a dry ambient. A methanol wash was not included in the surface treatment of the second diode. However, after irradiation in a dry ambient, this second diode was rewashed (including methanol) and re-irradiated. The peak appeared at an applied potential of 73 volts.

The occurrence of the peak in the reverse characteristics is similar to that reported by Metscher in 1957 (Ref 12) and by Freyer in 1960 (Ref 6) Both of these experimenters used electrolytic etching for surface treatment. Metscher obtained thick oxide layers by prolonged exposure to oxygen. The critical voltages at which his peak occurred varied from 15 to 20 volts and the magnitudes of the currents just below the critical voltages varied from 100 to 320 μa. Saturation currents ranged from 3 to 5 μa; the bulk photo current is assumed to be limited to these saturation values. Electrolytic etches result in thin germanium oxide layers. Therefore, it is assumed that Freyer's diodes were coated by thin oxide

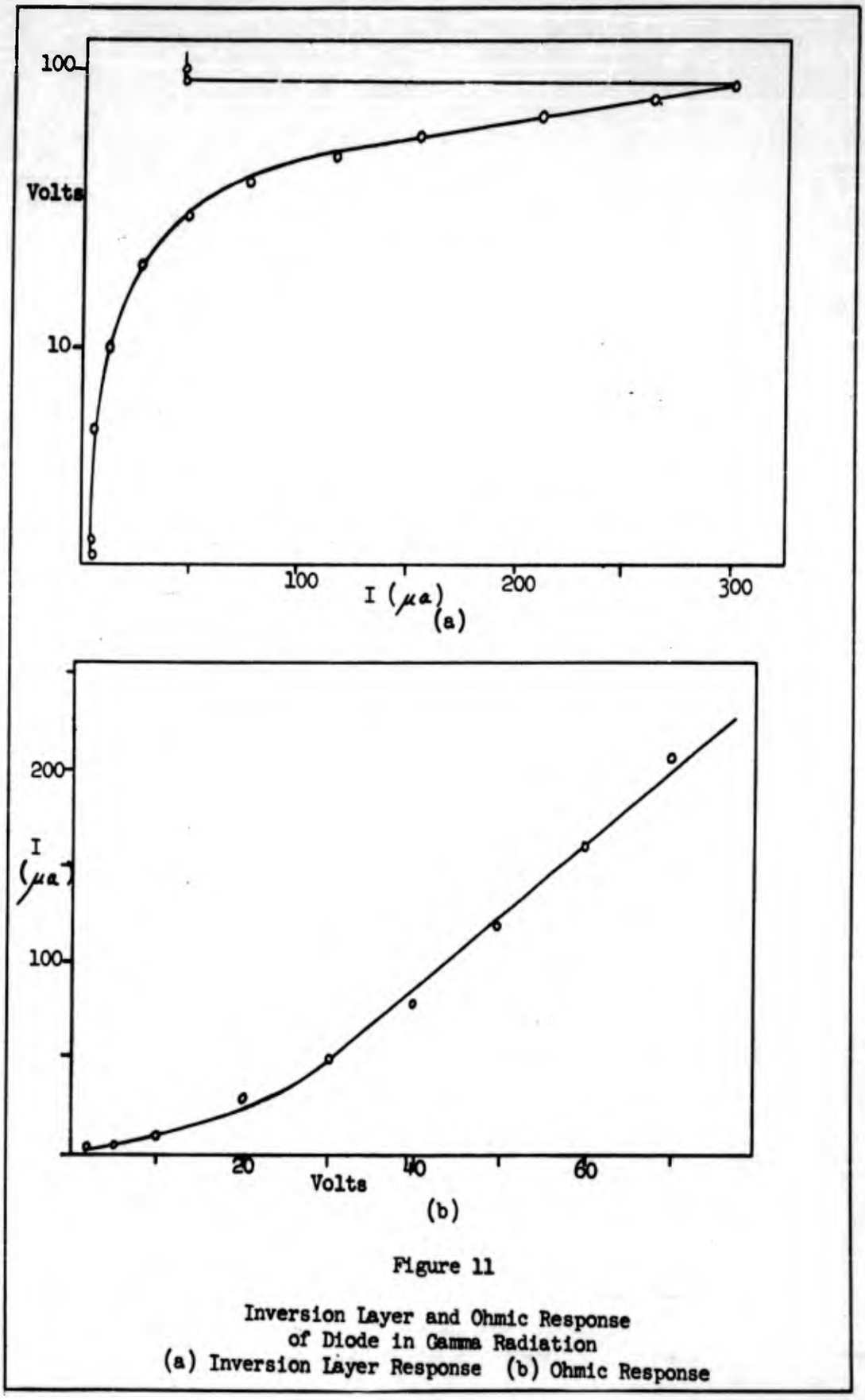


Figure 11

Inversion Layer and Ohmic Response
of Diode in Gamma Radiation
(a) Inversion Layer Response (b) Ohmic Response

layers. He obtained currents of approximately 350 μa at critical voltages from 25 to 55 volts. Freyer also observed oscillations of the current at the critical voltage as well as the hysteresis effect. Thus the phenomenon of the peak during irradiation was present over a wide range of oxide layers and independent to some extent of the details of surface treatment.

The excess currents obtained in a dry oxygen ambient can be decreased by evacuating the diode holder to 5×10^{-5} mm Hg (Ref 11). Thus, the assumption that the electrical properties of a germanium diode in gamma radiation are governed primarily by the surface condition is substantiated.

Discussion of Results. It was shown in Chapter IV that an inversion layer is not present on the surface of a diode in a dry oxygen ambient, without gamma radiation (Ref page 13). However, the adsorbed oxygen atoms introduce energy states at the surface (electron traps) that are capable of becoming occupied. Several investigators have disturbed the surface equilibrium by illumination and heating (Ref 9:174). It is interpreted that this disturbance of the slow states is affected by transfer of charge carriers across the oxide barier (Ref 9:182). Thus, the effect of gamma radiation could be to increase the net surface charge on the diode. By populating the electron traps (placing a negative charge on the outer surface of the oxide), a p-type inversion layer could be induced across the bulk junction. Figure 11a, a plot of log V vs I, demonstrates that inversion layer conduction can not fully explain the results since the response is far from logarithmic. Moreover, Figure 11b, a linear plot of I vs V, suggests a current multiplication phenomenon similar to that observed in a wet ambient without gamma radiation (Ref Figure 7b, facing page 14).

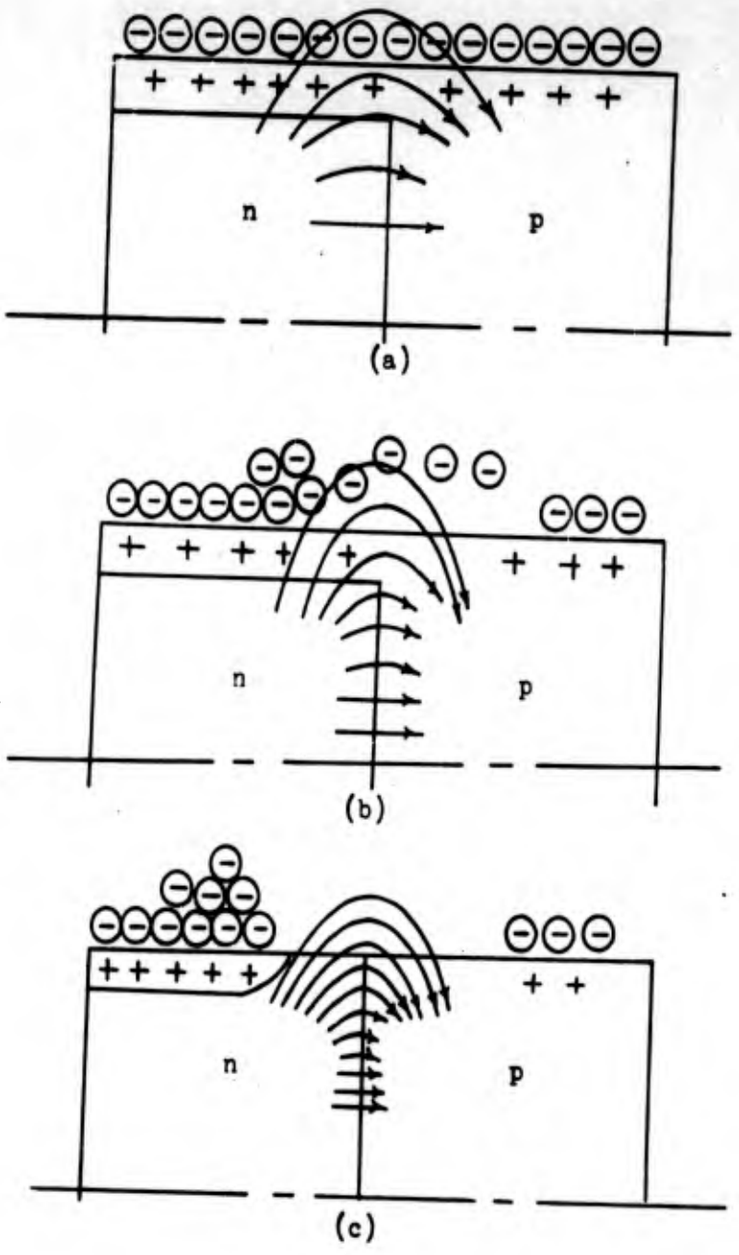


Figure 12

Proposed Model for Desorption
(a) Inversion Layer Induced by Adsorbed Oxygen Molecules
(b) Oxygen Molecules Desorbed by Electric Field
(c) Inversion Layer Pinched at Bulk Junction

Because of the high intensity of the radiation field (5.65×10^7 ergs/gm C-hour), the excess, negative, surface charge could result in higher intensity electric fields in the critical region where the inversion layer meets the bulk junction than in the bulk junction itself. Thus current multiplication could take place in this localized region. In addition, avalanche breakdown within a portion of the oxide layer is also possible.

The above can satisfactorily explain the magnitude of the excess currents obtained from diodes in a gamma field, but it does not account for the sharp decrease in the current at the critical voltage. Another process must account for this phenomenon.

Figure 12 depicts a proposed model for the reduced current above the critical voltage. In Figure 12a, the excess surface charge has induced a p-type inversion layer over the n-type material. The voltage drop across the bulk junction is represented by electric field lines which, near the surface, exert forces on the adsorbed, negatively-charged oxygen atoms. As the applied voltage is increased, the influence of the field at the surface increases and the charge in the outer surface states is capable of redistributing itself along the lines of force. At the critical voltage, the normal component of the field is of sufficient magnitude to eject the adsorbed atoms from their lattice sites, as illustrated in Figure 12b. Another alternative is that the parallel component of the field redistributes the surface charge such that a depleated-charge region is formed on the surface. The desorbed molecules or the altered surface charge distribution would effect the material beneath the oxide layer by pinching

the inversion layer where the inversion layer-bulk interface meets the bulk junction. If the inversion layer is pinched, as illustrated in Figure 12c, the only current that could contribute to the characteristics would be that across the bulk junction. The desorption mechanism is deemed more plausible than the charge redistribution because of the sharp decrease in current at the critical voltage.

The above postulate can be used to possibly explain some of the unusual effects observed, namely the hysteresis effect and the temperature shift of the critical voltage. Once the oxygen molecules are desorbed, the influence of the normal component of the field is greater than that before adsorption because of the reduced surface charge in the charge-depleted region. Thus, a lower critical voltage must be applied before re-adsorption can occur. The effect of increased temperature on the surface properties is similar to that of radiation in that the total surface charge is increased. The increased surface charge could shield the valence electrons of the oxygen molecules from the influence of the normal component of the electric field. Higher applied voltages would then be required for desorption. This is offered as a possible explanation for the shift in critical voltage as a function of temperature (Figure 10, facing page 17).

Effect of Gamma Radiation on Adsorbed Water Molecules

The response of a diode in a wet ambient with gamma radiation is similar to that without radiation. The saturation current is slightly less than that obtained without radiation. This result is similar to that obtained by Freyer. In contrast with the dry oxygen case, the

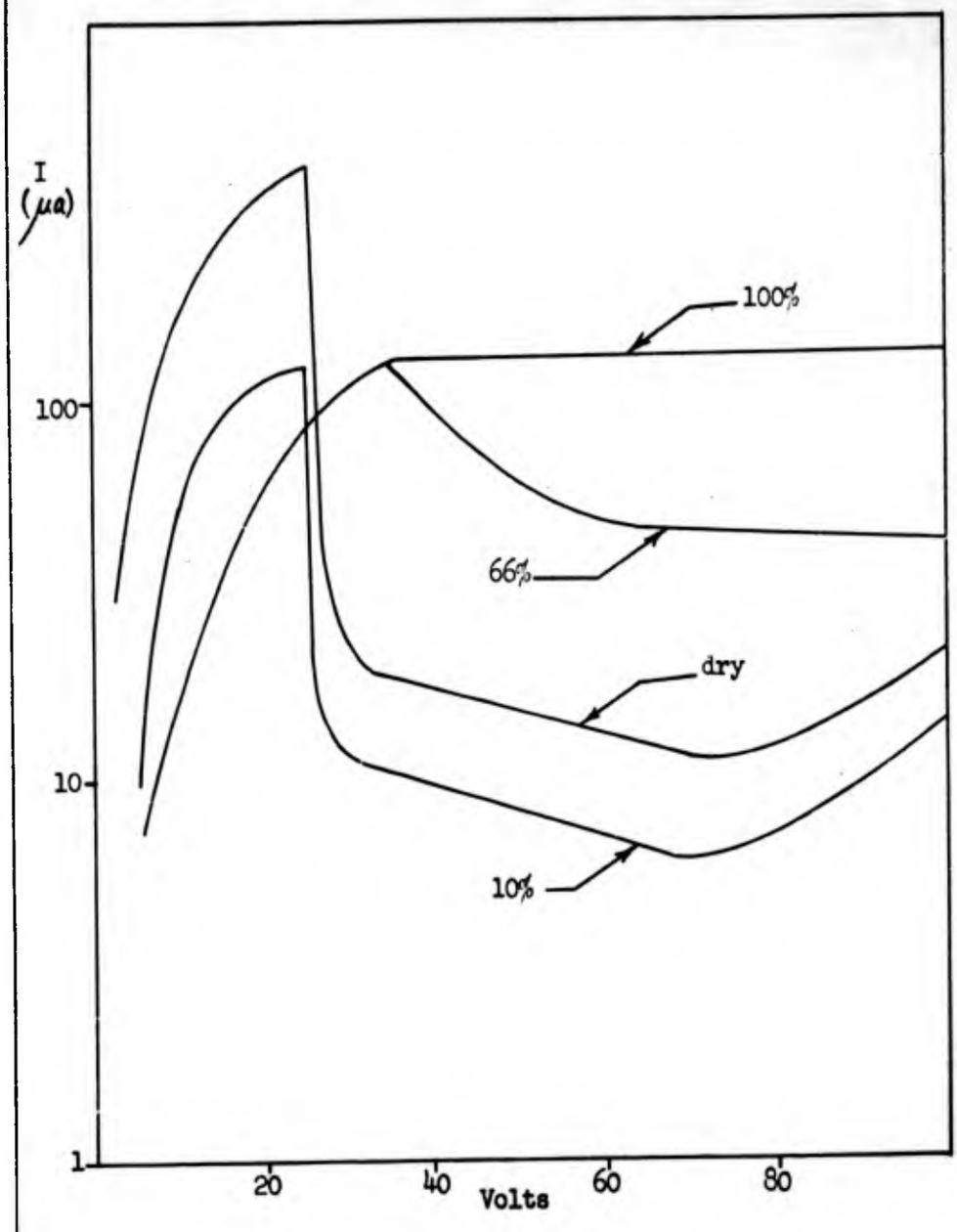


Figure 13

Reverse Current-Voltage Characteristics
in Dry Ambient and 10%, 66%, 100%
Relative Humidity During Irradiation

Ref 6:23

characteristics in a wet ambient do not contain the peak. This can possibly be explained by a stronger chemical combination between the water molecules and the surface. In addition, since water is adsorbed in multilayers onto the surface, the multilayers could distort the electric field vector such that desorption could not occur in the voltage ranges used in this investigation (0-100 volts).

Additional results published by Freyer, illustrated in Figure 13, indicate that the critical voltage for desorption shifts with the humidity of the ambient until at 100% humidity, the peak disappears. As water molecules are adsorbed, the initial effect is to reduce the surface charge. Therefore, a lower bias would be required for desorption. This could possibly explain the shift for the 10% humidity case. As the multilayers of water are adsorbed, the net surface charge should change from negative to positive with the minimum current being obtained when the surface is neutral. In Figure 14, facing page 22, the effect of cycling between wet and dry oxygen is illustrated. The minimum reverse current obtained is attributed to the neutral charge of the surface as the initial layer of water molecules is adsorbed.

Unexplained Effects of Gamma Radiation on Surface Properties

During the course of this investigation some unexplained results were obtained. The characteristics of two diodes in a dry ambient did not contain the peak. Intentional deviations from the prescribed experimental procedure had been performed on each of these diodes.

The first of these diodes was exposed to an ozone ambient immediately before irradiation. It was shown in Chapter IV that dry oxygen does not

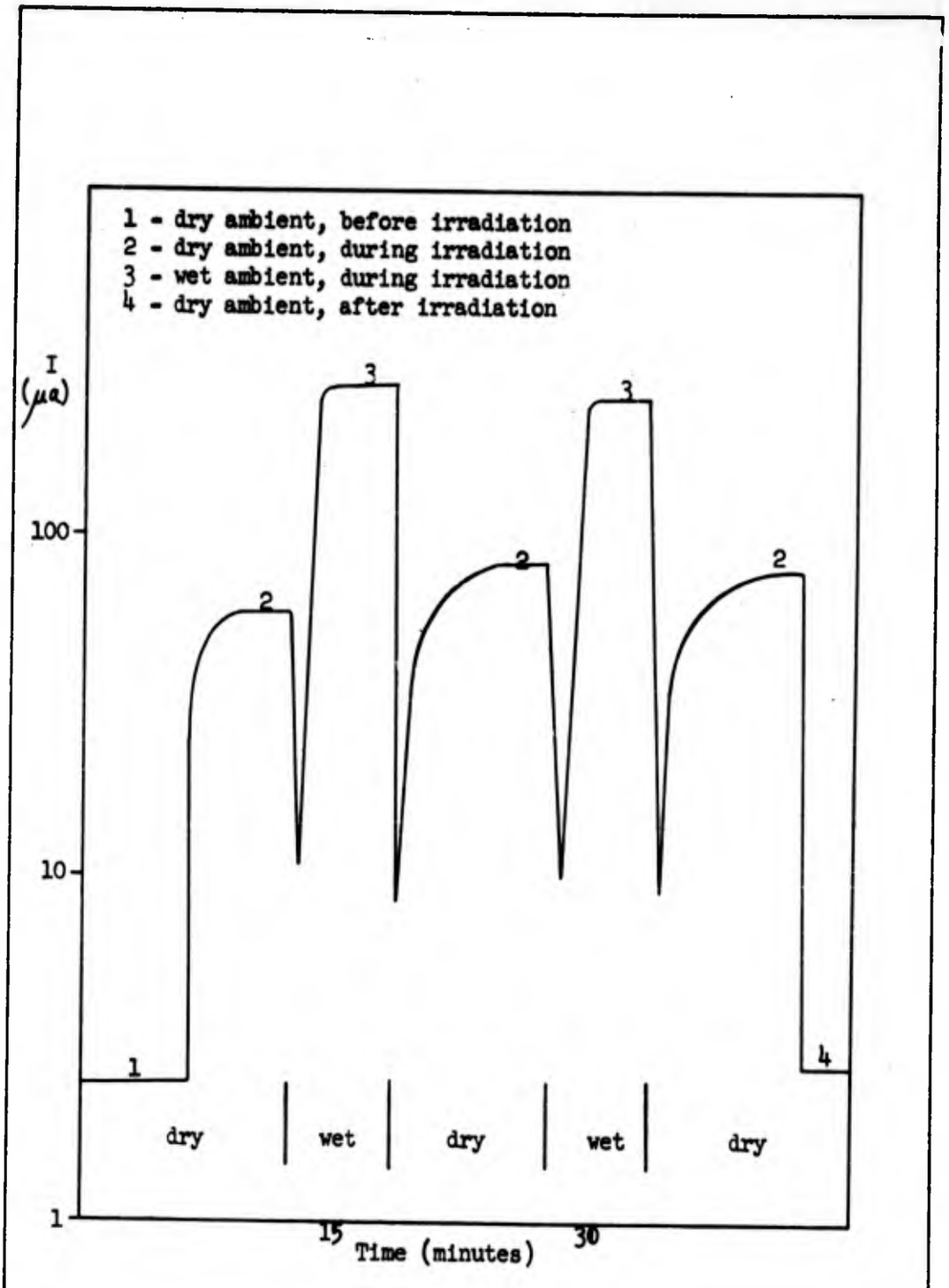


Figure 14

Reverse Current vs Time During Ambient Cycling at 20 Volts Reverse Bias

Ref 6:24

counteract the effect of ozone on the surface (Ref page 15). Therefore, a possible explanation of the result is that the chemical bonding of the ozone with the surface is greater than that of oxygen. Therefore desorption could not take place in the range of voltages used in this investigation.

A methanol wash was not included in the surface treatment of the second diode. This result can not be interpreted from either theory or the proposed model of desorption.

VI. Summary

A thorough understanding of the surface behavior of semiconductor materials requires the correlation of experimental data with theory. This investigation provides data on the reverse characteristics of a germanium p-n diode in ozone, dry oxygen and wet oxygen, before and during gamma irradiation. The following paragraphs summarize the interpretation of the data.

The adsorption of ozone and water molecules onto the surface of a diode disturbs the density and population of the outer states. Excess charge, trapped in the outer states, induces an inversion layer across the junction of the diode. Localized, high-intensity fields produce current multiplication in the critical region where the inversion layer meets the bulk junction.

The effect of gamma radiation on the surface properties of a diode in a dry ambient is to disturb the surface equilibrium by exciting charge carriers across the oxide layer. The resulting surface charge induces an inversion layer and leads to current multiplication. At a critical applied bias, the normal component of the electric field vector ejects the adsorbed oxygen molecules from the surface. This disturbance of the surface charge pinches the inversion layer at the bulk junction and only the generation current across the bulk junction contributes to the characteristics.

Increased temperatures supplement the effect of radiation. At elevated temperatures, a slight shift in the critical voltage occurs because of a shielding of the valence electrons. Desorption does not occur in a wet ambient because of the strong bonding between the water molecules and the surface.

VII. Recommendations

The interpretation of the data reported in this paper depends critically on two basic postulates. The first attributes the increased surface charge to a transfer of electrons across the oxide layer; the second explains the sudden decrease in conductivity by a desorption mechanism. Since the application of a bias on a junction will shift the quasi Fermi level at the surface, the disturbance of the surface equilibrium by gamma radiation compounds a complex study. Additional data is required to thoroughly test the above postulates.

A parametric analysis of changes in contact potential of semiconductor materials as functions of ambient and radiation would be invaluable in testing the proposed model. This analysis could be supplemented by field effect experiments to prevent desorption.

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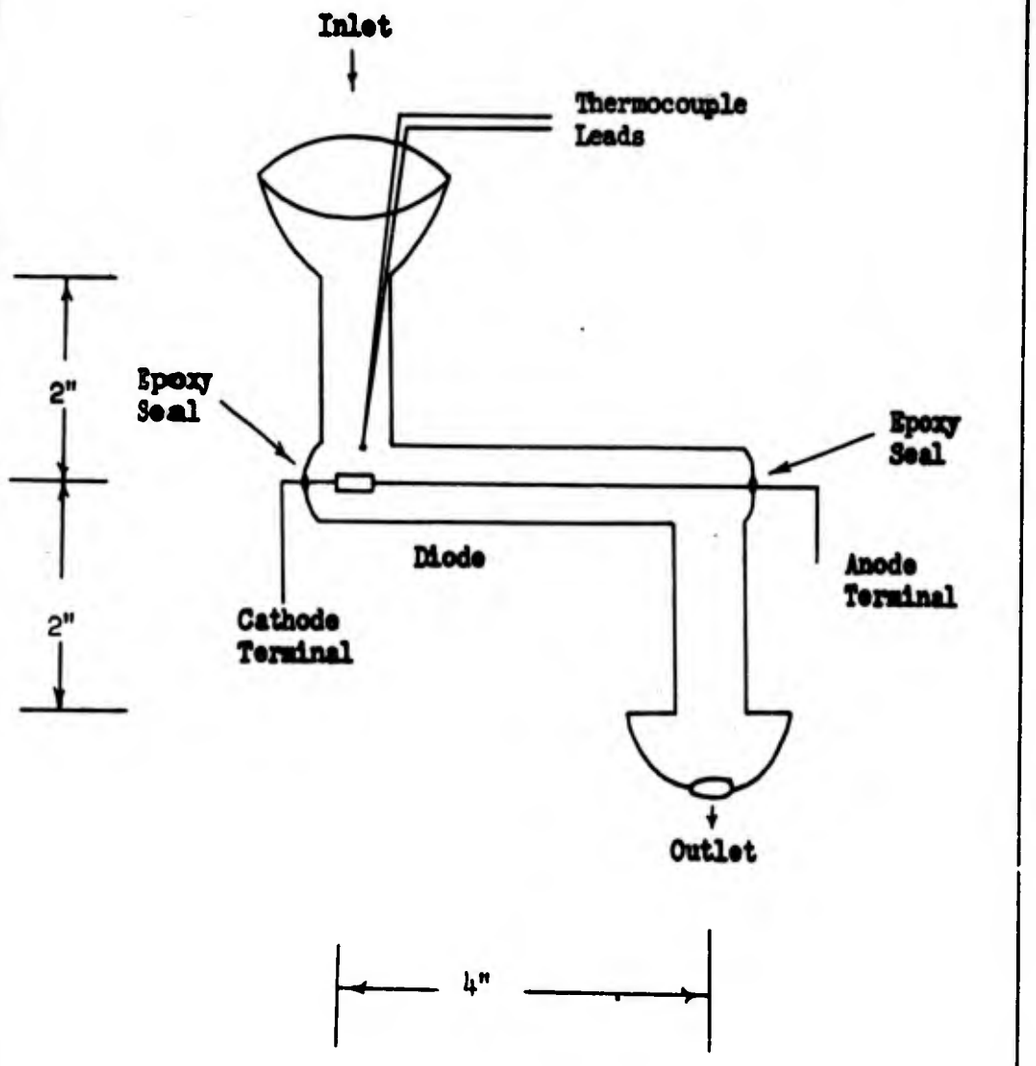

Figure 15

Diode Holder

Appendix A

Diode Preparation

The purpose of surface treatment is to remove the superficial layer of disturbed material resulting from the mechanical preparation of each diode. Unless removed, this disordered layer would provide harboring sites for adsorbed moisture and foreign atoms.

An acid etch, such as the modified CP-4 etch used here, provides a bright, smooth, and glossy surface. Such a surface is superior to those produced by other types of chemical etches. The composition of the modified CP-4 solution is concentrated nitric, 43% hydrofluoric, and reagent grade acetic acid in a volume ratio of 5:3:3. The nitric acid and hydrofluoric acid serve as oxidant and oxide solvent respectively, while the acetic acid moderates the reaction of the etch with germanium (Ref 5:323). Because of the hazards involved in handling hydrofluoric acid, the preparation of the etching solution is performed under a hood. The etching solution is contained in polyethylene beakers. The acid solution will attack the copper leads of the diode unless special precautions are taken. An epoxy resin is used to coat the leads. This resin eliminates the variability of acid-etched diodes due to the presence of copper ions on the surface. After treating the leads, the diode is swabbed with carbon tetrachloride and sealed in the diode holder illustrated in Figure 15. Epoxy resin also serves as a sealing agent.

The diode holder, constructed of pyrex glass ware, contains vacuum ball joints for easy attachment to a vacuum system. A nicrome wire, wound around the holder, serves as an ambient heater.

Etching of the diode surface is performed by continuously pouring the acid solution over the diode for three minutes. During this operation, the diode holder is inclined at about 30° so that the diode surface is always beneath the level of the liquid. The pouring rate must be sufficient to prevent bubbles from adhering to the surface. The adherence of bubbles will result in a non-uniform etch rate across the surface. The diode is then washed thoroughly with water, methanol, and again with water. Care is taken to assure continued submergence of the diode beneath the liquid. The residue wash solution is then poured from the holder. A copper-constantan thermocouple is placed in close proximity with the surface and the holder is attached to the vacuum system. During this process (about 15 seconds), the surface of the diode is exposed to air. The final step in surface preparation is to vacuum dry the surface until the reverse current-voltage characteristics of the diode are acceptable. A maximum current of 5 μa at 70 volts bias constitute an acceptable characteristic.

Appendix B

Ambient Variation

The reverse characteristics of the treated diode are obtained in various ambients. Figure 5, facing page 11, depicts the schematic for the ambient-variation technique.

After the diode is vacuum dried, dry oxygen is permitted to flow continuously over the diode surface. The oxygen is dried through a calcium sulfate gas drying unit. The flow rate of the dry ambient is of no significance in this experiment. Three-way stopcocks permit by-passing of the dry oxygen to a humidifier. (An alternative method not used here is to vary the humidity of the ambient by utilizing various salt solutions.) However, the flow rate of the oxygen through the humidifier determines the ultimate humidity of the ambient. In this experiment the flow rate is adjusted such that the reverse current is a maximum at an arbitrary applied bias.

An ozone ambient is provided by a discharge from a Tesla coil in the gas line about 18 inches upstream from the diode holder. Temperature variations are performed in a dry oxygen ambient. The lowest temperature is obtained by encasing the diode holder in dry ice. Higher temperatures are provided by the nicrome wire heater.

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