This report was prepared by the Armour Research Foundation under USAF Contract No. AF 33(615)-7760, Project 7360, "The Chemistry and Physics of Materials." Task No. 736003, "Interaction of High Energy Neutrons with Materials." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, and the project engineers.

This report covers work conducted from January 1, 1962, to January 31, 1962.

Dr. H. C. Samuelsky directed the phase of the program involving low energy bombardment. Most of the experimental work on this phase was done by Mr. R. L. Kellner with assistance from Mr. H. G. Shaw and Mr. G. L. Johnson. Assists. R. Pohl and J. Brey contributed to the design and construction of equipment necessary for making electrical measurements on the germanium crystals.

Dr. F. L. Zemke directed the work on high energy bombardment with the assistance of several workers from the nuclear reactor facility of the Physics Division.

Data are recorded in AF Logbooks C 10521, C 10922, C 0261, C 1035, C 1117, and C 11706.
The effect of ion bombardment on carrier lifetime, photoconductivity, and surface structure of germanium (111) crystals was investigated after bombardment at voltages between 10 and 2000 V. It was found that the lifetime decreased significantly at bombarding voltages above 80 V and that the number of defects in the surface region increased simultaneously by several orders of magnitudes. These defects are most likely dislocations and vacancy clusters. Less stable defects were introduced at very low bombarding voltages but these too were found to affect the electrical properties of the bombarded surfaces appreciably.

Preliminary results of the effect of adsorbed gases on the properties of ion bombarded surfaces, and the effect of neutron bombardment on the catalytic exchange of hydrogen with deuterium on etched surfaces are included.

This Technical Documentary Report has been reviewed and is approved.

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RADIATION EFFECTS ON SEMICONDUCTOR CATALYSTS

I. INTRODUCTION

It has been recognized for some time that radiation-induced defects exert an important influence on the catalytic properties of solids. However, a complete understanding of the surface behavior of any solid involves a detailed study of the physical and the chemical properties of its surface. Furthermore, it is necessary to work with well-defined structures and clean surfaces. During this year's work the main emphasis was placed on investigation of the effect of low-energy ion bombardment on the electrical and structural properties of germanium(111) single crystal surfaces. Preliminary experiments dealing with adsorption of hydrogen on ion-bombarded surfaces and with hydrogen-deuterium exchange on neutron-bombarded specimens were also carried out.

A brief discussion is given below, first of catalytic properties of semiconductor surfaces and then of the effects of structural defects on catalytic and electrical properties of germanium.

A. Theory of Semiconductor Catalysis

In all chemical processes which are accelerated by catalysts the electronic interaction of the catalyst with the reacting molecules plays a decisive role. The electronic interaction may manifest itself exclusively in polarization or, frequently, in direct electron exchange. Experimental proof of electron exchange between a catalyst and reacting gases has been given by several workers.1,2

The electron theory of catalysis approaches the electronic mechanism of the phenomena through chemisorption which can be formally represented as chemisorption of the reactants, reaction in the adsorbed phase, and desorption of the products. In the stationary state the over-all reaction rate is determined by the rate of the slowest step. Whenever chemisorption on a semiconductor involves a charge transfer, the extent of adsorption is usually too small to be detected by standard adsorption techniques. Therefore, it has been investigated by electrical methods. Measurements of the electrical conductivity of oxides have shown that the conductivity is determined primarily by the boundary layer.3,4 These and other data have been treated in terms of the boundary layer theory.5

Catalytic reactions can be divided into two general classes, those in which electrons are transferred to the catalyst (donor reactions) and those in which electrons are transferred to the adsorbing species (acceptor reactions). In the first group are included hydrogenation and dehydrogenation reactions and in the second group acceptor reactions involving molecules with high electron affinity, such as oxygen. Therefore, donor reactions can be expected to be catalyzed by n-type semiconductors and acceptor reactions by p-type semiconductors.

Manuscript released by the author 31 January 1962 for publication as an ASU Technical Documentary Report.

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In the case of elemental semiconductors such as germanium, it may be possible to study the catalytic properties of both n- and p-type material. This has the obvious advantage that a reaction can be studied on a single chemical substrate while either electrons or holes are present in excess. Some work has been carried out on germanium of both types. It was found that the decomposition of formic acid proceeds on both conductivity types but that on freshly etched surfaces the activation energy of the reaction is less for the p-type than for the n-type material. Further results have been reported for the hydrogenation of ethylene. The reaction rate increased rapidly above 100°C on p-type germanium, but for either intrinsic or n-type material the reaction rate did not become appreciable below 300°C. The catalytic properties of germanium films have also been investigated. The hydrogen-deuterium exchange reaction has been studied at elevated temperature and the ortho-para hydrogen conversion at low temperatures.

All the results described above were obtained with polycrystalline germanium catalysts. In addition, the surfaces of these catalysts were contaminated in some of the experiments. Ideally, any study of surface properties should start with an atomically clean surface and a well-defined crystal structure. The bare surface itself contains surface energy states, since it represents a termination of the crystal lattice and in the presence of contaminants other surface states are possible at the solid-gas interface. There is no doubt that adsorption processes, which occur as a first step in heterogeneous catalysis, depend on the electrical properties of the surface and proceed in a different manner on bare surfaces than on oxidized or contaminated surfaces. In addition, the molecules involved in desorption are chemically different from those in adsorption, with the result that the chemical conversion step may make some demands on the type of semiconductor surface.

There is considerable specificity in catalysis and, depending on the rate-determining step involving charge transfer, there may be a steady-state decrease or increase of the charge defect concentration in a thin boundary layer of the catalyst. Under these conditions the surface charge formed by the charges of the chemisorbed atoms and molecules is compensated by equal and opposite charges in the boundary layer. If electron exchange between the catalyst and the reacting gases is accompanied by depletion zones and enrichment zones of conduction electrons, the process produces positive or negative space charges in these regions.

B. Structural Defects as Catalytic Centers and Recombination Centers

In theoretical studies of catalysis the surface of the catalyst is sometimes assumed to be homogeneous. However, it is well known that most catalytic reactions proceed only on a fraction of the exposed surface and that there are sites which are preferentially attacked by chemical reagents. In the absence of chemical impurities the most likely cause of a heterogeneous distribution of chemical forces at a solid surface is the presence of lattice imperfections, which are known to have unusual geometric and electronic properties.
The simplest imperfections are point defects, such as vacancies and interstitials. Solids also contain more complex defects such as screw and edge dislocations, which are more stable than point defects. Point defects and dislocations are usually introduced into the solid during solidification, but their number can vary, depending on the way in which the crystal is grown. Semiconductor crystals are commonly more perfect than metal crystals, especially those grown by special techniques by which the dislocation density can be reduced to a few hundred per square centimeter. In comparison, metal crystals contain a minimum of about $10^5$ dislocations per square centimeter.

In addition to grown-in point defects and dislocations, defects can be introduced by external means. For example, dislocations multiply rapidly as a crystal is plastically deformed. They can partly annihilate each other or can interact to form new dislocations. The over-all result is that the dislocation density rises as deformation proceeds. Imperfections can also be introduced into solids by irradiation. The interaction of energetic radiation and matter results in displacement of atoms from their equilibrium position, thus creating vacancy-interstitial pairs. Radiation effects have been found to cause deterioration comparable to that observed after cold work.

The pronounced effect of point defects and dislocations on the chemical and physical properties of solids is well recognized. Deformation studies concerned with germanium have shown that acceptor centers are introduced into germanium, resulting in a deformation-induced conversion of n-type germanium to p-type. The finding that these acceptor centers can be easily removed by annealing has led to the belief that they are point defects. Both low-energy and high-energy irradiation introduce point defects which may act as acceptors if they are vacancies and as donors if they are interstitials. In germanium a vacancy is surrounded by four unsatisfied electron orbitals, and although up to four electrons might be added to these orbitals, it has been suggested that their mutual electrostatic repulsion may be so great that only one or two electrons can be bound into these orbitals with energies lying in the energy gap. A vacancy would thus act as an acceptor. An interstitial atom which has four valence electrons not bound into orbitals might lose two of them and act as a double donor. Some evidence for this picture has been found in a study of germanium bombarded by fast neutrons.

Point defects acting as acceptor centers and donor centers in the surface region of the semiconductor could undoubtedly have a large influence on catalysis. However, at higher temperatures, at which the number of point defects is reduced to low numbers, dislocations are more likely to provide sites which can act as sources or sinks for electronic charges.

Radiation-induced catalytic activity has been observed in several solid-gas reactions. However, little work has been done correlating the changes in catalytic properties of the solid with the changes in the physical properties under comparable conditions. Such a correlation has been attempted in studies of the decomposition of formic acid on single crystals of silver bombarded with positive ions of various energies. It was shown that the catalytic activity of smooth single-crystal surfaces can be altered considerably. Since
the geometrical area of the crystals did not increase during bombardment, the increase of as much as $10^5$ in the preexponential factor was associated with an increase in active sites. The annealing experiments and electron diffraction experiments indicated that dislocation lines cutting the surface provided the sites for the reaction. An increase in the rate of hydrogenation of ethylene on platinum and nickel bombarded with argon ions had been reported previously. Examination of the surfaces by electron diffraction showed that defects of a complex nature were present after bombardment.

Most experimental work carried out on germanium irradiated with high-energy radiation has not been done under conditions which would result in a clean surface. However, electrical studies and adsorption studies have been made with germanium crystals cleaned by positive ion bombardment and freshly cleaved surfaces. The ion bombardment-annealing technique was developed to produce clean and defect-free surfaces, but the effect of bombardment alone on chemical and electrical properties has not been studied. So far there is little concrete evidence of the types and properties of defects introduced by ion bombardment into a semiconductor surface. However, there is no doubt that crystal orientation, number and type of defects present in the crystal prior to irradiation, size and type of the bombarding particle, and temperature of the crystal during and after irradiation may all contribute to the final structure of the surface. In addition, changes in the properties of the bulk may simultaneously occur as a result of the changes introduced into the surface.

The structural and associated electrical changes in the surfaces of germanium are expected to manifest themselves in different ways. From various experiments it is known that lattice defects can act as recombination centers for excess carriers. Thus recombination centers created by irradiation could act as donor or acceptor sites, depending on their electronic character, and thereby provide catalytic sites for a specific catalytic reaction. In order to investigate the catalytic properties of structural defects it is therefore necessary to consider the electrical properties of these recombination centers and their effect on the lifetime of charge carriers.

The lifetime of free carriers in the phenomenon of photoconductivity in semiconductors is a concept of basic importance. Excess carriers can be introduced into semiconductors by means of photoexcitation. These excess carriers consist of electron-hole pairs produced above those normally present at equilibrium. The excess carriers gradually recombine and the lattice is restored to its thermal equilibrium condition.

Two principal mechanisms are believed to control recombination processes. The first mechanism is direct recombination of electrons and holes accompanied by photo and phonon emission. The second mechanism requires the presence of localized energy states in the forbidden gap of the semiconductor. The presence of such states in a crystal increases the rate of recombination of electrons and holes. Impurities and lattice defects such as dislocations, vacancies, and interstitials are frequently known to introduce localized energy states, with the net effect of decreasing the lifetime of the excess carriers.
The theoretical picture of surface states has been used to describe many experimental results. It is generally believed that two kinds of states exist on the surface of germanium. The first type, fast states, are located at the interface of the semiconductor and the commonly present oxide layer. These states are believed to be responsible for surface recombination. It has been observed that the density of these states increases when the surface is mechanically damaged. The other group of states, slow states, exhibit much longer decay times than fast states. Their capture cross sections are also orders-of-magnitude lower than those of the fast states. These states are considered to be responsible for the variations in the work function with ambient but not for the observed recombination velocities.

The simple model of recombination via a center is a two-step process in which the electron capture by an empty center is followed by a hole capture at the same center, after which it is ready for further electron capture. The kinetics of this process has been discussed in the literature. The centers can be either chemical or physical in origin or both. An exact correlation of surface states with a definite type of imperfection has not as yet been achieved. Several authors believe that the simple model is basically correct but that actual recombination at surfaces is more complex and involves two or more levels.

Crystalline imperfections have been shown to introduce recombination centers into germanium crystals. Dislocations have been found to be regions of rapid recombination and it was found that the volume lifetime depends upon dislocation densities. In a different series of experiments it was shown that if $10^7$ dislocations per square centimeter are introduced in the course of plastically deforming germanium, the carrier lifetime is reduced below $10^{-6}$ sec. Recombination times have also been studied in plastically deformed $n$- and $p$-type germanium. It was shown that the cross section for electron capture in $p$-type germanium was $3.6 \times 10^{-15}$ cm$^2$, and in the absence of faster recombination paths the lifetime depended inversely on the dislocation density. Similar results were obtained in $n$-type material, but an analysis of the conditions is more complicated because space charge cylinders around dislocations are believed to act as acceptors and thereby create a region of negative space charge.

The theory of dislocation acceptors has been attributed to the "dangling bond" configurations along the extra plane of edge dislocations. The faulty coordination can be described as an unfilled orbital that can adsorb an additional electron. Dislocation acceptors could affect the mobility and the carrier lifetime in germanium surfaces. Electrons moving parallel to the space charge cylinders would probably not be much affected, but those moving normal to the cylinders would have to pass around and through them so that their mobility would be reduced. In addition, dislocation acceptor sites should act as recombination centers and therefore have a large effect on the lifetime of excess carriers.

When electron-hole pairs are generated in semiconductors so that nonequilibrium densities are present, they recombine until they approach the equilibrium distribution. The rates of recombination can usually be described
by an exponential decay law. When this is the case, the time constant of the minority carrier decay is called the lifetime. Short pulses of light are often used to introduce excess carriers, resulting in increase of the conductivity of the sample. Consideration of the surface region is important because the light has to enter the semiconductor at the surface. A clean surface is thought to contain fast surface energy states which have relaxation times of the order of 0.1 μsec and are presumably the ones that determine carrier generation and recombination at the surface. In the presence of oxygen an oxide layer is produced on the surface of materials such as germanium, and slow surface states may be introduced. Relaxation times from $10^{-3}$ sec to many hours have been associated with slow surface states, depending on the condition of the surface. It is believed that these long time constants arise because the states are in poor electrical contact with the semiconductor, being separated from it by the oxide film. Therefore, on a surface that is contaminated adsorption should be able to produce changes only in distribution of the slow states, since the fast states are not accessible to gases adsorbed at the oxide-gas interface.

There exists at a semiconductor surface a space-charge double layer which may originate from the presence of ions of one sign. The theory of the space-charge region indicates that the surface excess of charge carriers is due to the difference between the concentration found in the actual system and that found when the phases are homogeneous up to some arbitrarily chosen dividing surface. From these expressions one can calculate the net surface charge density and the excess conductivity due to mobile carriers near the surface. If carriers are constrained in the potential well due to a space charge, they frequently collide with the surface. Hence reduced mobility is expected. Experimental determination of the mobility of charge carriers in the surface region is quite difficult. At present there are insufficient data to decide either the direction or the magnitude of the charge transfer process.

As mentioned previously, the decay of photocconductivity can be used to measure the lifetime of minority carriers. Recombination of hole-electron pairs injected by light can occur via recombination centers or via traps. The process of trapping differs from recombination only in the relative values of the capture cross section. Trapping occurs when re-emission of the carriers from an energy level in the forbidden gap is more probable than the final step of recombination. Trapping effectively reduces the mobility of the carrier and gives an apparent long decay constant. This phenomenon is also associated with crystalline imperfections, both chemical and physical in origin. It has been established that hole traps are introduced into germanium crystals by electron bombardment and by copper atoms. From lifetime measurements it was calculated that for high-resistivity p-type material the cross section for electrons had a temperature dependence which would reduce the rate of electron capture to a negligible quantity at low temperatures. All the evidence indicates that imperfections can act as recombination centers at one temperature and as trapping centers at another temperature and that recombination centers become trapping centers at low temperatures.
II. EXPERIMENTAL

A. Specimen Preparation

Thin single crystals of germanium, $5 \times 1 \times 0.05$ cm, $2 \times 1 \times 0.05$ cm, and $2 \times 1 \times 0.1$ cm, were cut from larger crystals supplied by Sylvania Electric Products. Each specimen exposed the $(111)$ plane parallel to the surface. To remove the deformation introduced into the surface during cutting and to remove the thick oxide layer from the surface, the specimens were etched in a CP-4 solution, washed in distilled water, and dried in ethyl alcohol. The standard etchant used contained 25 cc nitric acid, 15 cc hydrofluoric acid, 15 cc glacial acetic acid, and 0.3 cc bromine. Occasionally it was necessary to increase the concentration of hydrofluoric acid in the solution in order to obtain a better surface finish.

After etching, the surfaces were investigated microscopically with a Bausch and Lomb Research Metallograph under oblique illumination at magnifications up to 1500. When sufficient care was taken during etching and the etchant was removed immediately after the process was completed, the surfaces had isolated conical etch-pits. The area in between the pits was very smooth and free of contaminants. It was found previously that dislocation lines cutting the $(111)$ surfaces of germanium are attacked preferentially, forming conical etch-pits identical to those found in this work. The number of dislocations, identified by counting etch-pits and by using various etchants, was approximately the same for different specimens, varying between $1 \times 10^3$ and $3 \times 10^3$ per square centimeter.

To obtain information about the changes occurring in the surfaces as a result of bombardment, each specimen surface was investigated microscopically not only after etching prior to bombardment but also immediately after bombardment. It was then reetched lightly in order to reveal the damage in the surface layer.

However, this method of revealing structural changes in the surface is applicable only when the damage to the surface is considerable and the depth of the damaged layer reaches far below the surface of the material. If the surface of the solid remains smooth during bombardment and the deformation introduced into the bulk of the specimen is confined to a few outer layers, a more sensitive method, such as electron diffraction, is necessary. Electron diffraction patterns taken by reflection are usually less sensitive to surface changes than those taken by electron transmission. Since the specimens used were too thick for such work, a method by which a specimen could be thinned down sufficiently to transmit electrons was adapted to germanium.

The electropolishing arrangement used to produce a thin region in a germanium crystal is shown in Fig. 1a and b. The electropolishing is performed on both sides of the specimen simultaneously by spraying the electrolyte onto it through platinum nozzles, which act as cathodes. The electrolyte is forced into the arms of the T-piece by applying slightly higher than atmospheric pressures of nitrogen on the top of the electrolyte. The specimen is covered on both sides with a quick-setting acrylic compound, except for two circular patches approximately $4 \text{ mm}$ in diameter directly opposite each other.
The platinum nozzles are fixed into the end of the arms of the polyethylene T-piece and are held pointing toward the exposed circular patches. By adjusting the flow of the electrolyte and the nozzle-to-specimen distance, the current density can be controlled until polishing is achieved.

A 10% sodium hydroxide solution was used in the trial experiments. The process of dissolusion was slow at current densities up to 100 ma/cm². In order to etch a specimen at a reasonable rate it was found advisable to increase the carrier density of the germanium electrode by illumination. A final experimental procedure was not developed, but sufficient experimental work was done to show that suitable germanium samples can be prepared by this method.

B. Ion Bombardment

Low-energy positive argon ions in the range between 5 and 2000 ev were produced in the discharge tube shown in Fig. 2a and b. The tube is made from pyrex and has two demountable joints. The cap at the end of the tube holds several tungsten leads, to which a tungsten filament, a cathode, and a cylindrical anode can be attached. The germanium specimen is attached either to one tungsten lead, as shown in Fig. 2a and 3a, or two leads are soldered to each end of the specimen as shown in Fig. 3b. A magnet is placed on the outside of the discharge tube parallel to the cylindrical anode. The discharge chamber is attached to a vacuum system consisting of two liquid air traps, a mercury diffusion pump, and a fore pump. The pressure in the vacuum system is measured with a Phillips ionization gauge capable of measuring pressures of better than 10⁻⁷ mm of mercury.

The d.c. power supply is shown diagrammatically in Fig. 4. The system consists of five power supplies, which are divided into two operationally independent units. The low-voltage unit covers the range from 1 to 100 v, and the high-voltage unit extends from 50 to 200 v. The high-voltage unit is divided internally into two separate supplies for reasonably efficient utilization of component ratings. The upper unit operates automatically above 400 v. Each unit can be extended upward by an additional factor of two if the power input is reduced. Thus a range between 1 and 4000 v can be covered.

The supplies include the necessary impedance employed with gas discharge devices. Since the required value of this impedance depends on the voltage and the current delivered, a sequence of resistors is provided by means of switches. The high-voltage unit has two selector switches which divide the voltage into four factor-of-four ranges. These switches vary the maximum emf and series resistance in such relation that the internal resistance can be maintained within a factor of two of the discharge integral resistance over the 100- to 2000-v range and over a power range from 0.15 to 10 w.

The ranges of the voltage and the current meters are changed by the same controls in such a way that readings are always in the upper half of the scale and overloads due to arc initiation or short circuits are limited to a factor of two greater than full scale.

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Figure 2b

ION BOMBARDMENT CHAMBER

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Figure 3

MOUNTING OF SPECIMENS
(a) For temperature measurements
(b) For electrical measurements
To obtain a self-sustained discharge over a wide range of applied voltages, a number of experiments were carried out to test the effects of gas pressure, magnetic field, and electron current on discharge conditions. By using different arrangements for the electrode arrangement shown in Fig. 2a, argon ions with energies from approximately 5 up to 2000 ev were produced.

The experimental procedure was as follows. A single crystal of germanium, previously chemically polished, was inserted in the ion bombarding chamber (cathode 1, Fig. 2a). The specimen surface was set perpendicular to the axis of the tube, and the system was evacuated to 10^-7 mm of mercury. After degassing the filament at high temperatures, a steady flow of argon was established through a pyrex leak valve and the discharge started. The argon gas used in the preliminary experiments was delivered from a cylinder and passed through liquid air traps. Since small oxygen impurities cannot be removed by this method, all later experiments were carried out with spectroscopically pure argon.

For bombarding voltages above 100 and up to 2000 v, cathode 1 (specimen) and cathode 2 were kept at the same potential (Fig. 5b). For all bombarding voltages below 100 v, a higher potential was applied between cathode 2 and the cylindrical anode than between the specimen and the anode (Fig. 5a). In all experiments the anode was kept at ground potential. To obtain a self-sustained discharge at low argon pressures electrons were emitted from a heated tungsten filament and made to move in helices under the action of a magnetic field which was provided by a magnet wound outside the glass envelope of the discharge tube. The magnetic field was made variable in order to obtain optimum discharge conditions for each set of current-voltage relation. Magnetic fields of up to 600 gauss were used. Under these conditions electrons ejected from the hot filament are accelerated in the cathode dark space and are forced to move in the magnetic field until they collide with argon atoms. As a result, a stable discharge at pressures as low as 10^-3 mm of mercury can be maintained and satisfactory ion currents can be collected by the specimen down to an applied voltage of 10 v. Since it is necessary to work at low argon pressures to avoid redeposition of the sputtered material, all experiments were made in an argon atmosphere of 10^-3 mm of mercury or less.

In a number of experiments the effect of the contact between the negative electrode and the specimen on discharge conditions was tested. It was found that the least satisfactory arrangement is a point contact, which results in a high contact resistance and a very uneven field distribution throughout the specimen. Significant improvement was achieved by providing an ohmic contact to one short edge of the specimen. However, the field throughout the specimen varied greatly. A specimen unto which a thin layer of polycrystalline germanium was deposited was bombarded successively with argon ions of 100 v. The deposited material was fully removed within 1 hr close to the side in contact with the sputtered tungsten lead, but some of the material at the other end was still present after 5 hr of sputtering. After applying a potential to both sides of the specimen, the remainder of the deposit was removed within a short period of sputtering.

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Figure 5
ELECTRODE ARRANGEMENT
In order to study the effects of ion-bombardment damage as a function of ion energies, it is necessary to establish whether other factors influence the formation of a disturbed surface during bombardment. It is likely that the defect pattern of a surface can vary appreciably with the current density of the bombarding ions and the time of bombardment. These factors determine the temperature of the specimen during irradiation and therefore influence the mechanism of the formation of structural defects.

In order to determine the temperature of the germanium crystal at different current densities, a platinum-rhodium thermocouple was inserted into the discharge tube (Fig. 3a) and the temperature was measured at the back of the germanium specimen. The equilibrium temperature of the specimen for a constant power input varied greatly according to the way in which the leads were attached. The temperature of a specimen hung from a tungsten lead did not exceed 60°C when the power input was kept at 0.02 w. Much higher temperatures were recorded for specimens which were in good ohmic contact with the leads. The equilibrium temperature exceeded 230°C even when the power input was reduced to less than 0.02 w. However, no accurate measurements were made at higher temperatures because the tin solder melted (m.p. 231°C). Attempts to use silver solder were unsuccessful. The differences in specimen geometry also made it difficult to extrapolate values obtained for one specimen to another. However, the temperatures of the specimens used in the final investigation never exceeded 220°C during ion bombardment.

C. Measurement of Carrier Lifetime

In order to investigate the role and the properties of surface defects introduced by bombardment as recombination centers, excess carriers were injected into the surface of germanium crystals by using either a Hanovia mercury-xenon arc lamp or a tungsten filament lamp. The decay in photoconductivity was measured as a function of various surface treatments.

The experimental system used is shown in Fig. 6a together with the ion bombarding apparatus. The system is shown schematically in Fig. 6b. The light was passed through a slit, chopped by a disc driven by a 14,500-rpm automobile-tire balancing motor, and focused by two quartz lenses. The change in sample conductivity was observed on an oscilloscope. The optical system was carefully adjusted with a photomultiplier to reduce the shape of the light pulse to a minimum. The slit was placed in a vertical position so that the light was focused only onto a narrow center part of the specimen. The slit width and the chopper speed were adjusted until the turn-off time was minimum. Under optimum conditions lifetimes of about 20 µsec were measured accurately.

Care was taken to focus the light beam always at the center part of the crystal and to mask the electrodes of the specimen. A high series resistance was placed into the power supply circuit to eliminate constant-current heating effects. The voltage applied to the crystal during carrier lifetime measurements was varied between 5 and 35 v. In this range the carrier lifetime was unaffected by the applied field. However, the photovoltage varied
Figure 6b

SCHEMATIC DIAGRAM OF PHOTOCONDUCTIVITY APPARATUS
linearly with the applied voltage. Care was also taken to ensure that the leads attached to the specimen were not rectifying. In a number of experiments the specimen was illuminated with a continuous light from another light source. No effect on carrier lifetime was found, indicating that trapping was absent.

D. Adsorption and Catalysis

To test which factors of surface preparation and environment can affect the catalytic properties of the semiconductor, a few adsorption and annealing experiments were made in the ion-bombardment chamber. Spectroscopically pure argon was supplied from the same source which was used in the ion-bombardment experiments. Pure hydrogen was obtained by passing cylinder hydrogen through a heated palladium tube. The same method can be used to obtain pure deuterium.

The effect of the adsorbed gas on carrier lifetime and photoconductivity was measured over a range of pressures and over a period of time. The effect of annealing by electron bombardment and the changes in surface properties in high and ultrahigh vacuum were also measured. However, in order to carry out catalytic experiments on the semiconductor surface it is necessary to transfer the catalyst into an ultrahigh vacuum system which does not contain metal parts. Furthermore, the specimen should be transferred under conditions which not only eliminate the possibility of contaminating the catalyst but also provide a means of effectively separating the bombardment chamber from the catalysis chamber.

A system for transfer of germanium specimens from the ion-bombardment chamber to the catalysis apparatus was designed and is shown in Fig. 7. It consists of a metal bellows, which holds the specimen, and a ground-glass joint just above the specimen. By contracting the bellows the specimen can be lowered into the catalytic chamber and the ground joint above the specimen is brought into contact with another ground joint sealed on top of the reaction chamber.

Depending on the surface finish of both joints, the leaks at the glass-to-glass interface can be minimized so that no additional provision for sealing off is necessary. Very small leaks may not interfere during catalytic experiments, because the ion-bombardment chamber can be evacuated to pressures below $10^{-8}$ mm of mercury and little or no back diffusion of the gases from the bombardment apparatus to the reaction chamber, which is at a much higher pressure, is likely to occur. However, if necessary, tests can be made to eliminate all leaks using indium solder or Viton O-rings at the outside end of the glass joint.

Preliminary experiments were performed to assess the effect of fast neutrons on the activity of germanium crystals used to catalyse hydrogen-deuterium exchange. Germanium (114) crystals enclosed in quartz were irradiated with neutrons in an atmosphere of mixed hydrogen and deuterium. The quartz used was the Suprasil variety obtained from the Amerasil Quartz Division of Engelhard Industries. This variety of quartz, fabricated from fused silica, is very low in sodium and does not darken under irradiation.
The single crystals used were intrinsic, with a measured resistivity of 23 ohm-cm. Their dimensions were 6 x 5 x 1 mm. Before being enclosed in the quartz tube, the crystals were etched in CP-4 and then washed with aqueous hydrofluoric acid, distilled water, and finally ethanol.

The quartz tubes were evacuated to a pressure of about \(10^{-6}\) mm of mercury and were filled to a pressure of 200 mm of mercury with a mixture of hydrogen and deuterium. The tubes were then sealed off. Four tubes were prepared. Tube 1 contained germanium but no gases. Tube 2 contained hydrogen and deuterium but no germanium. Tubes 3 and 4 contained both germanium and hydrogen-deuterium mixtures.

Tube 1 was prepared in order to test the handling procedures. It was important to ascertain whether there would be any residual radioactivity in the quartz or germanium after irradiation. The tube, cadmium wrapped, was given a total dosage of \(10^{13}\) nvt. It was found that the radioactivity was of such a low level that no safeguards in handling were needed. Tubes 2 and 3 were irradiated under similar conditions. Tube 4 was not irradiated but kept as a blank. The tubes were opened after 1 week and the contents analyzed by mass spectroscopy.
The experimental studies reported below were all made on (111) germanium surfaces. Three germanium crystals were used. They were all high purity, high resistivity, nearly intrinsic p-type specimens. The dislocation density of the crystals was determined by etch-pit counting and was found to be approximately $1 \times 10^5$ dislocations per square centimeter in each crystal.

In the first series of experiments crystal 1 (resistivity $31 \text{ cm} \cdot \text{cm}$) was bombarded with positive argon ions at voltages between 2000 and 15 $\text{v}$ and the carrier lifetime, $\tau$, and the photovoltage were measured as a function of bombarding energy. Initially, the carrier lifetime and the photoconductivity, $G$, of the sample of the etched specimen were measured in a vacuum of $10^{-7}$ mm of mercury, but all subsequent electrical measurements immediately after bombardment were made in a vacuum of $10^{-8}$ mm of mercury or better.

For the etched specimen $\tau$ was found to be 200 usec in vacuum and $G$ was approximately 2000 mv. After argon was admitted $\tau$ decreased from 200 to 170 usec, but $G$ increased slightly. Similar results were obtained with different samples. It seems that argon is adsorbed quite strongly on the oxidized germanium surfaces, since the original values of $\tau$ and $G$ could not be reproduced even after prolonged pumping.

In order to remove the oxide layer at the etched germanium surface, the surface was first bombarded at high voltages and then successively at lower voltages, at which the time of bombardment was increased. The increase in bombardment time is necessary because the initial surface damage formed at high voltages has to be removed before a surface representative of the damage caused by lower-energy ions can be investigated.

The carrier lifetime of the specimen bombarded at voltages between 2000 and 100 $\text{v}$ could not be determined accurately. In each case $\tau$ was less than 16 usec and $G$ decreased from approximately 2000 to 1 mv. After prolonged bombardment at successively lower voltages $\tau$ increased to 100 usec at 30 $\text{v}$ and $G$ increased to 100 mv. Further bombardment at 20 $\text{v}$ and then at 15 $\text{v}$ for 12 hr resulted in an additional increase in $\tau$, but $G$ decreased appreciably, to a value of about 7 mv.

These experimental results show three distinct types of behavior of the bombarded surface. At bombarding voltages above 100 $\text{v}$, at which an appreciable amount of material is being removed from the germanium sample, the marked decrease in $G$ is at least in part due to the removal of a chemical layer from the surface of germanium. This layer is most likely germanium oxide, formed during etching in the strong etching solution. The simultaneous large decrease in $\tau$ can be ascribed to an increase in the number of recombination centers, which are most likely structural defects introduced by the bombardment.
Due to stresses associated with thermal spikes it is possible to generate dislocation loops at voltages above 100 v. In addition, at these voltages and at much lower voltages it should be possible to produce dislocations in a crystal lattice if the bombarding ions can penetrate some distance below the surface. Under these conditions it is feasible that a large number of point defects generated below the surface may cause disturbances in the surface region due to a collapse of the lattice above the disturbed region. The depth of the damaged layer could be appreciable and will undoubtedly depend on various factors such as the arrangement of the atoms perpendicular to the incoming beam of the bombarding ions, the size of the bombarding particles, the ion energies, and also the defect structure of the bombarded solid. The depth of the damaged layer in germanium bombarded with argon ions in the region between 2000 and 100 v seemed to be quite high. It took many hours of bombardment at voltages below 100 v until a change in \( \tau \) could be found. Since material was being removed from the bombarded specimen, the increase in \( \tau \) with bombarding time and at lower bombarding voltages can be associated both with a decrease in the depth of the damaged surface layer and a decrease in the number of defects acting as recombination centers.

The increase in \( \tau \) of up to 100 \( \mu \)sec after bombardment at 30 v was followed by a simultaneous increase in \( \sigma \). However, when the bombarding voltage was decreased to 15 v, \( \sigma \) decreased continuously with bombarding time, reaching a value of about 7 mv after 12 hr of bombardment. A similar result was obtained with another germanium specimen bombarded first at 500 v and then at successively lower voltages. The initial \( \tau \) and \( \sigma \) of the etched sample were in this case much lower, and during bombardment at low voltages \( \tau \) increased only very slowly. However, \( \sigma \) decreased by a factor of 4 in the range between 50 and 30 v. It is not quite clear why an increase in \( \tau \) at low bombarding voltages should be followed by a decrease in \( \sigma \). One difficulty is that the conductivity is affected by any argon atoms remaining in the surface as well as by the bombardment damage itself.

In a second series of experiments crystal 1 was etched and then bombarded at low voltages only. The resistance of the sample, originally 1100 ohms, increased to 1500 after etching, and the thickness decreased from approximately 0.7 to 0.4 mm. Again \( \tau \) was found to be about 200 \( \mu \)sec, but \( \sigma \) was only 100 mv. Bombardment of the sample at 50 v for 1 hr resulted in a decrease in \( \tau \) to 20 \( \mu \)sec and a decrease in \( \sigma \) to 3 mv. Further bombardment at 30 v for 3 hr raised the value of \( \tau \) to 25 \( \mu \)sec and \( \sigma \) to 6 mv. An additional increase in \( \tau \) to 32 \( \mu \)sec was found after bombardment at 20 v, but \( \sigma \) remained constant.

The same specimen was etched for a third time. The resistance of the now very thin sample increased to 2800 ohms. \( \tau \) was again about 200 \( \mu \)sec, but \( \sigma \) had decreased to 500 mv. After bombardment at 100 v the sample was rebombarded for 4 hr at 46 v \( \tau \), which had initially decreased to less than 16 \( \mu \)sec, did not increase appreciably during this period. In order to obtain some information about the amount of damage still present at the specimen surface, the specimen was removed from the bombarding chamber and investigated microscopically. It was found that the center part of the bombarded surface was etched and that the number of large etch-pits, about 10\(^2\) per square centimeter before the specimen was subjected to bombardment for the first time, had increased by a factor of about 3 (see Fig. 8 and 9). The specimen
Figure 8
ETCHED GERMANIUM SURFACE BEFORE BOMBARDMENT

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Figure 9

GERMANIUM SURFACE AFTER ION BOMBARDMENT
was then slightly etched in a CP-4 solution. It can be seen (Fig. 10) that etching revealed a large number of flat-bottom etch-pits, which could be fully removed by further etching. The smooth pits may be associated with vacancy clusters and also with shallow dislocations.

The high recombination rates of the excess minority carriers found for this and other bombarded samples can be accounted for by the presence of these defects. In general, acceptor-type behavior is expected from either vacancies or dislocations, but coulombic repulsion causes low occupation of sites in line imperfections as compared with point imperfections.

Depending on the various factors governing the mechanism of defect production during ion bombardment, several types of defects can be introduced simultaneously. At high bombarding voltages dislocations and vacancy clusters are more likely to be introduced. At very low bombarding voltages in the region between 30 and 15 V, at which the actual ion energies are approximately 18 and 7 eV, respectively, atoms in the germanium lattice are most likely displaced into interstitial positions in the (-1, -1, -1) direction. However, even these low-energy ions could, if the depth of penetration is large enough, cause disturbances which may result in the formation of complex defects. A specimen surface bombarded with ions in this region was also etched, revealing a few etch-pits similar to those shown in Fig. 10; however, further work is necessary to establish if this result can be reproduced.

Some changes in the bulk density of dislocations were found at each time a surface was bombarded at voltages above 80 V. Successive etching resulted in the removal of the flat-bottom pits, but the large pits remained. The number of etch-pits per square centimeter, which was about 1 x 10^3 before bombardment, increased in the surface region after heavy bombardment by a factor of 10^3 or 10^4 and although most of the surface was again very smooth after a heavy etch, the number of dislocations had increased by a factor of 3.

In an attempt to obtain some information on the effect of adsorbed and absorbed gases on the germanium surface, experiments were performed using argon, hydrogen, and oxygen; and the changes in T and Φ were measured. A specimen surface bombarded at 10 V for 10 min and then successively at 20, 40, 100, and 500 V was heated by electron bombardment after each treatment. Even after bombardment at 10 V, T decreased appreciably. Since bombardment at this voltage is not likely to have removed the oxide layer from the germanium surface, the most likely cause of the decrease in T from 130 μsec to 28 μsec was argon embossed in the surface. Electron bombardment of the specimen after ion bombardment at 20 and 40 V showed a steady increase in both T and Φ (Fig. 11a and 11b) but electron bombardment of the specimen surface bombarded with 100- and 500-V ions resulted only in a slight increase in both parameters. The large effect of bombardment at the front of the specimen on the electrical properties of the unbombarded surface is shown in Fig. 11b.

A few experiments were made with hydrogen adsorbed on the bombarded surface. The hydrogen pressure was varied between 10^{-4} mm of mercury and 10^{-1} mm of mercury, and both T and Φ were measured over a period of time.
Figure 10
ETCHED GERMANIUM SURFACE AFTER ION BOMBARDMENT
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Figure 11
ELECTRON BOMBARDMENT ANNEALING
(a) Change in $\tau$ versus time of bombardment;
(b) Change in $\tau$ and $V$ at the front and back of the specimen.
Little or no change was found in $\tau$, but $\zeta$ increased by 3 mv at low pressures to 15 mv at higher pressures. After evacuating to 10$^{-8}$ mm of mercury the initial values obtained before adsorption were reproduced. In the presence of oxygen, however, $\tau$ and $\zeta$ increased irreversibly. Increases in $\tau$ up to 100 $\mu$sec were found, depending on the pressure and the time of exposure.

From the adsorption data it can be seen that adsorption of argon, hydrogen, and oxygen resulted in an increase in conductivity, but that the carrier lifetime is affected significantly only after oxygen adsorption. This could mean that the recombination centers introduced in the germanium surface were filled with electrons and electrons donated by the hydrogen were free to move in a space-charge region. The strong acceptor property of oxygen, on the other hand, may have caused a decrease in the number of the bound electrons at the recombination centers, so that their effectiveness for recombination was decreased and an increase in conductivity was therefore accompanied by a simultaneous increase in carrier lifetime.

Preliminary experiments were performed to assess the effects of fast neutrons on the activity of germanium used to catalyse hydrogen-deuterium exchange. The experiments performed thus far were designed to give gross effects. Germanium etched in a CP-4 solution was irradiated with fast neutrons in an atmosphere of mixed hydrogen and deuterium. The time of irradiation was 15 min, and the total dosage of neutrons about 10$^{13}$ nvt. It was found that the exchange reaction took place in the presence of germanium and that the amount of HD formed was about 3.5 times larger than the value obtained when hydrogen and deuterium were irradiated in the absence of germanium. Some hydrogen-deuterium exchange over etched germanium was also found in the absence of irradiation, but the amount of HD formed was found to be about 6 times less than with the irradiated sample.

In these experiments the germanium surface was undoubtedly oxidized. Therefore the data cannot be evaluated in terms of a clean surface. More work is necessary to determine whether the ion-bombarding technique can be used to remove the impurity layer after neutron irradiation without causing further damage to the surface and then to use these surfaces in catalytic studies. The main difficulty associated with the technique appears to be that argon atoms are embedded in the bombarded surface even at bombarding voltages as low as 16 v. To remove these atoms the specimen must be heated; however, by this process point defects are annealed out of the specimen. If dislocations are introduced by the irradiation, heat treatment at relatively low temperatures should not affect their number, and the catalytic properties of the irradiated sample could be studied as a function of dosage and energy of irradiation.

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The most important effect of the interaction of low-energy and high-energy particles with solids is the displacement of atoms from their equilibrium position. Imperfections such as point defects and dislocations, which are known to provide preferential sites for chemical attack, are introduced by this process. These defects, which also have unusual electronic properties, can act as recombination centers in semiconductors.

In this study germanium crystals with surfaces oriented parallel to (111) were bombarded with positive argon ions at voltages between 10 and 2000 V. The effect of bombardment on surface structure, carrier lifetime, and photoconductivity was investigated as a function of bombarding energy. It was found that the depth of the damaged surface layer was extensive after bombardment at voltages above 80 V. The defects introduced at higher bombarding voltages may be dislocations or vacancy clusters or both. Etching of the bombarded surfaces revealed that the number of defects in the surface region had increased by a factor of about 10^3. The decrease in carrier lifetime from 200μsec to less than 16 μsec was associated with these defects.

Electron bombardment annealing of a germanium specimen bombarded at voltages between 10 and 40 volts indicated that imperfections responsible for the decrease in carrier lifetime were less stable than those introduced at higher bombarding voltages. The most likely point defects introduced at low bombarding voltages are interstitial germanium atoms and argon embedded in the surface of the germanium crystal.

A few adsorption experiments carried out with argon on etched surfaces and hydrogen and oxygen on bombarded surfaces showed that the carrier lifetime of germanium was only appreciably affected in the presence of oxygen.

In order to study the effect of defects introduced by neutron bombardment on the catalytic properties of germanium a few samples containing a mixture of hydrogen and deuterium were irradiated both in the presence and the absence of etched germanium crystals. It was found that the rate of exchange was higher in the presence of germanium. However, the surfaces of the etched germanium crystals are undoubtedly oxidized, and further work will be necessary to develop a method which will ensure cleanliness of the germanium surfaces during catalysis.
REFERENCES

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