High-Vacuum Studies of Surface Recombination Velocity for Germanium*†

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(Received March 3, 1958)

The surface recombination velocity, s, of minority carriers for (100) faces of germanium crystals has been studied under various vacuum conditions. Values of mean lifetime were obtained by the decay-of-photoconductivity method and the corresponding values of surface recombination velocity were determined from geometrical considerations. Increases in s were observed due to initial evacuation of the experimental tube. Following outgassing of the samples in vacuum at temperatures above 500°C and for a time in excess of 30 hours, s was found to be insensitive to exposure to oxygen at pressures as high as 10^{-4} mm Hg. As a result of cleaning the surfaces of samples by the ion-bombardment technique, s increased to a value of (5 to 7)$\times 10^3$ cm/sec. Heating the ion-bombarded crystals in vacuum at temperatures above 500°C for prolonged periods of time, followed by slow cooling, resulted in a decrease in s to a value below 500 cm/sec but greater than the value obtained following a CP-4 etch and the value obtained after pumping. The recombination velocity of clean and annealed (100) germanium surfaces was found to be insensitive to room-temperature adsorption of oxygen at pressures as high as 5×10^{-5} mm Hg. Exposure of these clean surfaces to oxygen at temperatures of about 100°C resulted in small decreases in mean lifetime, corresponding to a possible increase in s, assuming that this was entirely a surface phenomenon. The clean-surface value of s could be restored by heating at 500°C in vacuum for short periods of time. The characteristics of a well-outgassed oxide-covered surface and a clean surface are found to be similar. The observed similarities are discussed and the conclusion drawn that the oxide layer, of itself, has little or no effect on the surface recombination process.

I. INTRODUCTION

RECENT attempts to study the recombination process at the surfaces of clean germanium single crystals have incorporated a procedure of simultaneously performing two or more experiments on the same surface.[1] This procedure has been used to provide enough parameters so that the separate experimental results could be compared using the statistical theory of semiconductor surfaces developed by Brattain and Bardeen[2] and by Stevenson and Keyes.[3] These experiments, however, have been unsuccessful in unambiguously determining the physical constants associated with the recombination process at clean germanium surfaces. The reason for this failure appears to be due to the experimental difficulties involved when combining the requirements of two or more experiments with those necessary for obtaining clean surfaces. It has been shown that the electrical and physical properties of clean germanium surfaces are reproducible,[4,5] when proper precautions are taken. Hence, it follows that the results of separate experiments on surface con-ductance, surface recombination velocity, field effect, and work function, for similar crystal faces of germanium, may be used in a comparison of experiment with theory. In the present work, a part of which has been discussed earlier,[6] we have limited the objective to a study of surface recombination velocity.

II. EXPERIMENTAL

1. Method

The investigations included methods of using both thick and thin crystals. These two methods are fundamentally different only in the manners of supporting, heating, and ion bombardment of the crystals. In both cases the mean lifetime was determined by the decay of photoconductivity and the values of surface recombination velocity were obtained from geometrical considerations, having previously determined the bulk lifetime and diffusion constant. In the thin-crystal method the geometry of the sample was such that volume effects were reduced relative to those of the surface. Since the method of determining mean lifetime has been described by Stevenson and Keyes,[7] only brief consideration of this part of the experiment will be given.

The method of decay in photoconductivity utilizes a short pulse of light to create extra hole-electron pairs in the sample. By adjustment of the intensity of this light pulse, the excess conductance of the sample is made directly proportional to the density of excess current carriers. The mean lifetime is obtained from a determination of the time dependence of the excess

[1] G. Wallis and S. Wang, Bull. Am. Phys. Soc. Ser. II, 1, 52 (1956); Autler, McWhorter, and Gebbie, Bull. Am. Phys. Soc. Ser. II, 1, 145 (1956); J. T. Law and C. G. B. Garrett, J. Appl. Phys. 27, 656 (1956).
[2] W. H. Brattain and J. Bardeen, Bell System Tech. J. 32, 1 (1953).
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[4] R. E. Schlier and H. E. Farnsworth, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1956), p. 3.
[5] J. A. Dillon, Jr., and H. E. Farnsworth, J. Appl. Phys. 28, 174 (1957).
[6] H. H. Madden and H. E. Farnsworth, Bull. Am. Phys. Soc. Ser. II, 1, 53 (1956).
[7] D. T. Stevenson and R. J. Keyes, J. Appl. Phys. 26, 190 (1955).
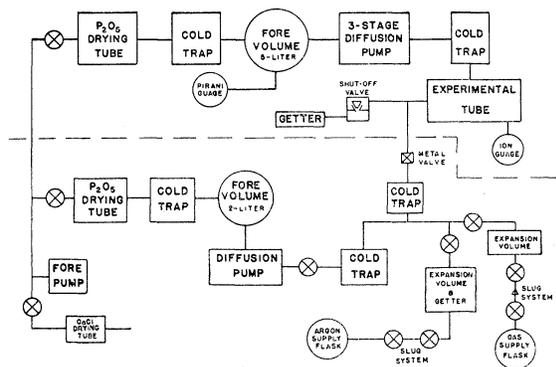
FIG. 1. Block diagram of vacuum and gas-handling systems.

conductance. This determination of small changes in conductance was made by sending a constant current through the sample and observing the resulting proportional voltage changes by means of an oscilloscope.

For the final experiments the light pulse was produced by a rotating mirror placed several meters from the crystal and passed through a converging lens. A battery-operated light source eliminated ac ripple which was a cause of distortion in the observed waveform of decay in photoconductivity in the case of two crystals. A battery in series with an external, noninductive, wire-wound resistance and the crystal furnished the constant current. The value of the resistance was chosen to keep the electric field in the sample from changing the observed lifetime and to produce a sufficient voltage change across the sample to be measured. A Tektronix type 121 wide-band preamplifier and a 511AD oscilloscope were used as measuring instruments.

2. Vacuum System

A diagram of the vacuum system is shown in Fig. 1. The main tube was pumped by a three stage diffusion pump using Octoil-S. A side tube, with molybdenum filaments which were flashed to produce a gettering film, was connected to the experimental tube by a magnetically controlled ball-and-socket ground Pyrex valve. This valve remained open when argon was admitted to the main system for ion bombardment and was shut when oxygen or other gases were admitted. The experimental tube and getter were separated from the diffusion pump by a trap cooled by a dry ice-acetone mixture during the out-gassing and later by liquid nitrogen. A dry ice-acetone cooled trap was also used between the diffusion pump and the fore pump. A gas-handling system, pumped by a single stage oil diffusion pump, incorporated two separate gas supply lines. A molybdenum getter was built into the expansion volume of the supply line used for argon. The other gas supply line was used for oxygen. A metal vacuum valve, which was outgassed in an oven, separated the gas-handling system from the main tube.

Pressure was measured in the high-vacuum side of

the main system by means of a Westinghouse WL 5966 ionization gauge. A thermistor was used for measurement of pressures above 10^{-4} mm Hg. Both the high-vacuum side of the main system and the metal valve were initially heated by ovens at about 350°C for several hours. During this heating the molybdenum getter envelope and all tubulation not enclosed in the ovens were heated with an air-gas flame. After the system had cooled to room temperature, the filaments and getters were outgassed, and the cold traps were allowed to warm to room temperature for a few minutes to remove condensible vapors. After replacing the dry ice-acetone mixture on the cold traps, the baking process was repeated. The dry-ice mixture was later replaced by liquid nitrogen. The residual pressure in the experimental tube was of the order of 2×10^{-9} mm Hg although the presence of the getter insured that the residual pressure of active gases was much less than this.

3. Crystal Mounts

The following conditions were realized in constructing the mounts. (1) The contacts at the ends of the crystal were ohmic and used no metal which might diffuse into the sample when heated. These conditions were realized by using pressure contacts between electrodes of pile graphite and ground surfaces at the ends of the crystals. (2) All leads connected to the crystals were shielded with quartz or glass tubing to prevent sputtering of metal onto the crystal during argon-ion bombardment. (3) Plastic deformation of the crystal was avoided during heating in vacuum.[8] This was
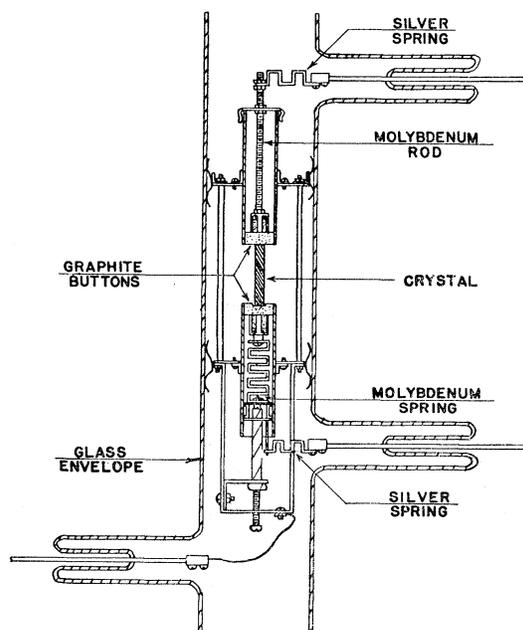
FIG. 2. Schematic diagram of thick-crystal mount.

[8] R. A. Logan and M. Schwartz, Phys. Rev. 96, 46 (1954).

accomplished in different manners for the thick and thin crystals as described below.

A schematic diagram of the thick crystal mount is shown in Fig. 2. The smallest dimension of the crystals used with this mount was 2.5 mm. The crystal was supported between two disks which were made from pile graphite. These disks were cleaned and outgassed in vacuum for over five hours at temperatures above 1000°C prior to assembly of the crystal mount. The lower graphite disk was supported from below by a molybdenum spring. This spring was designed to support the crystal in a vertical position and to avoid plastic deformation during the heating of the germanium crystal in vacuum. The compression of this spring was adjusted so that it was only slightly greater than that required to produce reliable electrical contacts between the graphite disks and the ground-surface ends of the germanium. The crystal was heated by conduction with an alternating current. This heating current was carried to the upper graphite disk by a threaded molybdenum rod, and to the lower disk by the molybdenum spring. Because of the large currents needed for heating the crystal, flexible silver-strip leads were used to connect the molybdenum spring and rod to the glass-to-metal seals of the tube envelope. These leads were annealed in vacuum prior to assembly of the experimental tube in order to minimize strain on the crystal mount introduced when making the connections to the glass-to-metal seals. The first experimental tube contained one crystal mount. The second tube contained two similar crystal mounts so that observations on two crystals could be made under the same conditions. In order to check the design of the thick-crystal mount for its effectiveness in supporting the crystals during heat treatment in vacuum without changing their bulk properties, the bulk lifetime and resistivity of one of the crystals was measured following the experiment. These bulk parameters were found to be substantially unchanged.
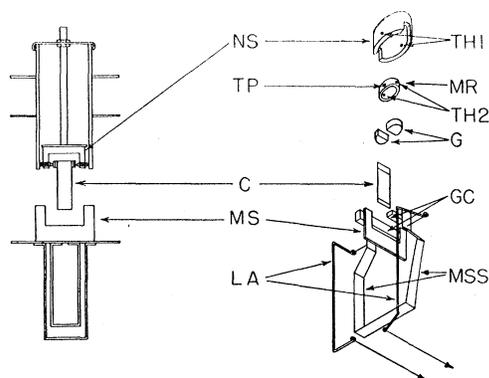
FIG. 3. Schematic diagram of thin-crystal mount. NS=fixed nickel support, TP=tungsten point seat, C=crystal, MS=U-shaped metal stop, LA=lever-arm arrangement, TH1=threaded holes for tungsten points, MR=molybdenum ring, TH2=threaded holes for clamping screws, G=graphite half-disks, GC=graphite contacts, MSS=molybdenum strip springs.

The method of supporting thin crystals is indicated in Fig. 3. The crystal was clamped at the upper end between two graphite half-disks. These half-disks were held in a molybdenum ring by means of pressure applied by screws against the graphite half-disks through metal shims. The molybdenum ring in turn was held in the upper framework between two tungsten points. The molybdenum ring, graphite half-disks, screws, and crystal were balanced so that this assembly was free to swing about a pivot line through the tungsten points, and when at rest the crystal hung parallel to a "plumb-bob" line. The crystal was heated by means of electron bombardment. During the heating, no connection was made to the bottom of the crystal so that it hung vertically while hot. For the lifetime measurements, magnetically controlled graphite contacts could be brought against 2 mm of the lower end of the crystal. Three millimeters of the length at the upper end of the crystal and two millimeters at the lower end were ground to provide ohmic contacts. The lower contact arrangement consisted of two graphite contacts. A large contact could be brought up against a U-shaped metal stop. The position of this stop was adjusted during assembly so that when the crystal was hanging freely on a "plumb-bob" line, the surface of the stop against which the large contact rested, was in the same plane as the surface of the crystal on the side of the large contact. When this large contact was in place, a smaller graphite contact could be brought against the opposite side of the crystal, between the sides of the U-shaped stop. Both the large and small graphite contacts were connected to large molybdenum-strip springs by means of small molybdenum-coil springs. These coil springs insured that the seating of the large graphite contact was flat against the metal stop and that the seating of the small graphite contact was flat against the surface of the crystal. A weight was hung between the sides of the molybdenum-strip spring to give a more positive action to the closing of these lower contacts.

The lower graphite contacts could be pulled away from the crystal by means of a lever arm arrangement and magnetic controls. These contacts were in the retracted position during bakeout of the vacuum system, during heating of the crystal by electron bombardment, and during argon-ion bombardment. All leads connected electrically to the sample during ion bombardment were shielded from sputtering by glass or quartz tubing. A quartz plate, 0.5 mm thick, closed the lower end of the quartz tube to prevent sputtering of the molybdenum ring at the upper end of the crystal and to prevent any of the electron beam, used for heating the crystal, from passing to the metal and graphite at the upper end of the crystal. The crystal hung through a 3×8 mm slot cut in this quartz plate. Although accurate determinations of the bulk lifetimes of the thin crystals after the experiments were impossible, the largest net changes in mean lifetime

between the value at the start of the experiment and at its end occurred during the process of obtaining a vacuum, thus indicating that the high-temperature outgassing of the thin crystals produced no appreciable changes in bulk lifetimes.

III. PROCEDURE

1. Preparation of Crystals

With the exception of crystal No. 1, all samples were cut so that their (100) faces were parallel to the cut faces of the sample, to within one-quarter of one degree. The faces of crystal No. 1 were about two degrees from the (100) plane. The shapes of the crystals were rectangular parallelepipeds. When the desired orientations were obtained, the surfaces of the crystals were mechanically ground on glass using American Optical Company "Centriforce Abrasives," the final abrasive grade on glass being M-305. The surfaces of the crystals were then polished on wax using a MgO abrasive. After flat mirror-like surfaces were obtained, the crystals were given a CP-4 etch. This etch was followed in the case of two crystals by an HF etch. The etches were followed by several rinses in doubly distilled water. It was necessary to have ground ends on the crystals for ohmic contact. This was accomplished in the case of the thick crystals by clamping the crystal with Teflon pads against ground ends of the crystal during the etching process. All the metal parts of the holder for etching were covered with paraffin during the etch. After preparation of the crystal, minimum contact to the etched surfaces was realized by using another holder which gripped the crystal at only three points made of polyethylene. A rinse in a concentrated aqueous cyanide (KCN) solution followed the etching of the crystal.[8] The final rinsing of the crystal was in water doubly distilled in Pyrex glass.

All surfaces of the thin crystals were first etched with CP-4 solution after mechanical preparation. One side of these crystals was then covered with a layer of polystyrene, and all but three millimeters of the length of the crystal on one end and two millimeters on the other end, of the second side were covered with polystyrene. The exposed ends were ground lightly using abrasive paper. After all loose abrasive was removed, the polystyrene was removed in a toluene filled extractor. This process was repeated to obtain ground ends on the other side of the crystal. When all of the polystyrene was finally removed, the thin crystals were given the aqueous cyanide solution rinse, followed by rinses in doubly-distilled water. Following mechanical and chemical preparations of the sample, contact with the crystal was made only by Teflon-tipped tweezers and lens tissue.

2. Cleaning of Crystals in Vacuum

The conditions and method of producing a clean germanium surface have been discussed elsewhere.[4,5,9] Since the reasons for the cleaning procedure used in this laboratory and the stability of the clean surface have been outlined, only the conditions for ion bombardment and anneal used in these lifetime experiments will be summarized. For ion-bombardment of the thick crystals, exposures of approximately five minutes duration in a self-maintained discharge of argon were used. The argon was pumped continuously through the main system during the bombardment. The discharge was not started by electronic excitation but by allowing the pressure of argon to increase in the experimental tube to the point where the discharge began. The ion current to the crystal was then controlled by regulating the pressure of argon in the tube. The crystal was at a potential of 500 volts above the surrounding cage of the crystal mount, and the ion current to the crystal was about 100 microamperes. After the ion bombardment the thick crystals were annealed by heating with an alternating conduction current at temperatures above 500°C for varying lengths of time. It was found that a heating of 15 to 20 hours, followed by a slow reduction in the heating current (over at least one hour), was required to obtain the lowest values of surface recombination velocity after ion bombardment. The thin crystal was ion-bombarded using a controlled discharge of argon produced by electron beams. The current density during ion bombardment was about 100 μa per square centimeter, and the bombarding voltages used were 500 v and 600 v. This controlled discharge had the advantage of being carried out at an argon pressure appreciably less than that required for the self-maintained discharge. The thin crystal, however, could be and was bombarded in a self-maintained discharge. The resulting surface recombination velocity after anneal was not significantly different in the two cases.

IV. RESULTS

The results were obtained from five crystals, three thick and two thin. The crystals are identified according to resistivity, and type, and thickness in the case of thin crystals. The order of presentation of the results parallels that for the investigation for one crystal.

1. Changes in s with Initial Evacuation of the Experimental Tube

The process of pumping the experimental tube brought about rapid increases in the value of surface recombination velocity. This effect was followed closely in the case of the two thin crystals. After one hour of pumping with the fore pump, the value of s for a 37

[9] Farnsworth, Schlier, George, and Burger, J. Appl. Phys. **26**, 252 (1955); **29**, 1150 (1958).

ohm-cm, n-type sample (thickness 0.023 cm), increased from an initial value of 14 cm/sec to 40 cm/sec. Further reduction in pressure to a value of 5×10^{-6} mm Hg resulted in an increase in s to 178 cm/sec. Similar large changes in s were observed on the second thin crystal (65.4 ohm-cm, thickness 0.027 cm), to be referred to below as crystal No. 2. In this case the increase in s was observed to have started within one minute after the forepump was turned on. After a pressure of 6×10^{-6} mm Hg had been obtained, the surface recombination velocity had increased from its initial value of 0 (within the accuracy of measurement) to a value of 85 cm/sec. These two thin crystals had been given an initial etch with CP-4. Increases in s were also observed due to evacuation of the experimental tube for two thick crystals (both about 42 ohm-cm, p type) which had been given an HF etch following the CP-4 etch. These measurements were made before bakeout of the vacuum system, so that no heating of the crystals was involved. This increase in s with evacuation of the experimental tube was most certainly due to the removal of some physically adsorbed gases or vapors from the surfaces of the crystals. Subsequent increases in s resulting from the heating of the crystal during the bakeout of the vacuum system suggest that this physically adsorbed layer is H_2O, but the hypothesis could not be verified.

2. Oxygen Adsorption on Oxide-Covered Surfaces at Room Temperature

Changes in the value of s resulting from adsorption at room temperature on oxide-covered surfaces were zero to within the limit of observable change (about 10 cm/sec). The crystals considered in these measurements had been outgassed in vacuum but no other attempt to clean the surface had been made. Crystal 2, which had received a CP-4 etch initially, was heated in vacuum at temperatures above 500°C for 20 hours before these oxygen adsorption studies were made. The residual pressure in the experimental tube was 3×10^{-9} mm Hg before exposure to oxygen for 20 minutes at pressures above 5×10^{-6} mm Hg. The highest pressure during this exposure was 1.2×10^{-4} mm Hg and was maintained for a period of 6 minutes. The two 42 ohm-cm, p-type, thick crystals which had an HF etch following the CP-4 etch were outgassed in vacuum for over 100 hours at temperatures above 500°C. The residual pressure in the experimental tube was 3×10^{-9} mm Hg and the crystals were sufficiently outgassed (before these adsorption measurements) so that this pressure was the same with the crystals at a temperature of 600°C.

3. Effects of Argon-Ion Bombardment and Anneal

Measurements to determine the effects of argon-ion bombardment and annealing on the value of s were made on one thick and one thin crystal, numbers 1 and 2, respectively, in Table I. The energy of the

TABLE I. Summary of results after cleaning by ion bombardment.

Item	Crystal number 1	2
(1) resistivity (ohm-cm); type	37, n	65.4, intrinsic
(2) bulk lifetime (μsec)	207	
(3) initial surface treatment	CP-4, KCN	CP-4, KCN
(4) thickness of sample (cm)	0.25	0.027
(5) s value after argon-ion bombardment (cm/sec)	5000	6700
(6) s value after anneal above 550°C (cm/sec)	250	460
(7) change in s value due to exposure of cleaned surface to oxygen at room temperature (cm/sec)	0	0
highest pressure of oxygen used (mm Hg)	7×10^{-6}	5×10^{-5}
(8) s value after heating and annealing an ion-bombarded crystal in oxygen at 10^{-6} mm Hg (cm/sec)	10^4	

bombarding ions was 500 ev for both crystals. The current to crystal 1 during ion bombardment was 100 μa, and the crystal was subjected to a series of bombardments and anneals. The surface recombination velocity was always high after ion bombardment, about 5000 cm/sec. This result is consistent with the observation of Law and Garrett.[1] Subsequent heating of the crystal in vacuum at temperatures of 500°C and above produced a decrease in the value of s. This decrease depended on the temperature and duration of heating, and on the rate of subsequent cooling. In other experiments in this laboratory on electron diffraction and work function, using ion-bombardment cleaning of germanium surfaces, short annealing times of the order of 1 hour at 550°C proved sufficient to establish equilibrium conditions. In the case of these lifetime measurements, equilibrium conditions were obtained only after the crystal was heated above 500°C for at least 15 hours in vacuum, following ion bombardment. It was also necessary to reduce the temperature slowly, over a period of at least one hour, to insure reproducible results after the long heating period. Radiation quenching of the crystal caused a decrease in mean lifetime, corresponding to an increase in s, assuming the change in lifetime was caused by a surface effect. The value of s for crystal 1 following the long anneal, and after the cumulative time of ion bombardment had reached one hour, was 250 cm/sec. This value, however, was relative to an assumed value of s of 50 cm/sec for a surface etched with CP-4, and should not be considered as absolute.

The procedure of long anneals was followed in the studies of the effects of ion-bombardment cleaning on crystal 2. This crystal received a cumulative bombardment in a controlled discharge of argon for 56 minutes. The ion current to the crystal was 200 μa. The value of s after ion bombardment was about 6700 cm/sec, and after anneal it was 460 cm/sec. This crystal was also bombarded using a self-maintained discharge for a cumulative time of 18 minutes, at the same ion energies and currents. The resulting value of s after anneal in this case was the same as that following ion bombardment in the controlled discharge, and anneal. The

pressure of argon in the tube was more than an order of magnitude greater in the case of the self-maintained discharge than that in the controlled discharge.

After ion bombardment, crystal 1 was heated and annealed in the presence of oxygen, at a pressure of about 10^{-6} mm Hg, to determine possible effects of residual amounts of oxygen in the experimental tube during the vacuum-annealing process. The change in s for an equivalent heating and annealing in vacuum would have been a *decrease* of more than 4000 cm/sec. Due to heating in oxygen at the increased pressure, the value of s *increased* from the ion-bombarded value of 5000 cm/sec to about 10^4 cm/sec, as indicated in item 8 of Table I. It was decreased again by heating in vacuum. Hence, the decrease of s with vacuum heating after ion bombardment was not due to an effect of oxygen but to annealing out of defects caused by the ion bombardment.

4. Oxygen Adsorption on Clean Surfaces at Room Temperature

Adsorption of oxygen on the surfaces cleaned by ion bombardment and annealing produced no measurable changes in s (less than 7 cm/sec). These studies were made first on crystal 1 after a stable value of s was obtained following ion bombardment and anneal. This crystal had been outgassed at temperatures above 500°C for more than 380 hours prior to the adsorption measurements. The crystal had been ion bombarded for a total time of 50 minutes. Total exposure to oxygen (pressure $\times$ time) was 3×10^{-4} mm Hg-min. The highest pressure was 7×10^{-6} mm Hg for a period of 40 minutes. Measurements of lifetime were made in the presence of oxygen at the increased pressure and also after the residual pressure was again below 5×10^{-9} mm Hg. At no time during these measurements was a change in lifetime observed. The total exposure was more than 50 times greater than that required to adsorb 90% of a monolayer of oxygen, as indicated by low-energy electron diffraction measurements.[4] This absence of an effect on s due to oxygen exposure of cleaned germanium surfaces at room temperature was checked with crystal 2. Here, a higher pressure of 5×10^{-5} mm Hg was used for a period of 15 minutes. The total exposure to oxygen was 8.3×10^{-4} mm Hg-min. As in the case of crystal 1, no measurable change in s was observed.

5. Exposure to Oxygen at Elevated Temperatures

Figure 4 shows the results of exposure to oxygen at an estimated temperature of about 100°C, following ion-bombardment cleaning. The crystal was heated by conduction during these exposures and three sets of data were obtained with two heating currents and two pressures of oxygen. The curve is a plot of observed mean lifetime *versus* the product of pressure and time of exposure to oxygen, on a logarithmic scale. These and

other data taken during these investigations show a decrease in mean lifetime of at least 10 microseconds, caused by an exposure to oxygen at a temperature of approximately 100°C. Assuming that this treatment results in a change in the surface only, these decreases in mean lifetime correspond to an increase in s of at least 20 cm/sec. On closer study, this phenomenon showed an erratic behavior which suggested that the parameter of pressure$\times$time is not the important one, but rather the time and number of repeated exposures to oxygen at an elevated temperature following the first exposure. This same behavior was observed when the cleaned surfaces of crystal 2 were exposed at higher pressures of oxygen while the crystal was warm. The first exposure to oxygen in this case was 3 minutes at a pressure of 10^{-6} mm Hg. The temperature of the crystal was maintained by an oven at 100°C. Using the parameter of pressure$\times$time and considering the results presented in Fig. 4, this exposure should have been sufficient to produce a clearly measurable decrease in the mean lifetime. The decrease, after this treatment, was small and just outside the limits of accuracy of the measurements. Two subsequent exposures following the primary exposure by about 6 hours and 16 hours, respectively, at temperatures of 100°C and 150°C for longer periods of time (40 minutes each) caused a total decrease in mean lifetime of 5 microseconds for crystal 2. This corresponds to an increase in s of 140 cm/sec, again assuming that this is entirely a surface effect. Heating the crystal for about one hour in vacuum at temperatures above 500°C followed by a slow decrease in heating power caused the value of s to return to its clean-surface value.

6. Effects of Outgassing Crystals in Vacuum

As mentioned above, the value of s increased as a result of baking the experimental tube at temperatures of about 350°C. The net effect of outgassing the crystals *prior* to the bombardment and annealing procedure, at temperatures above 500°C, was to produce further increases in the surface recombination velocity. These increases were found to terminate and an approximately stable value was obtained after appreciable high-temperature outgassing. The value of s for crystal 2 after 35 hours of heating in vacuum above 500°C was 420 cm/sec. This value is close to 460 cm/sec for the clean surface on that crystal (Table I). Evidence from low-energy electron diffraction studies of germanium surfaces in this laboratory indicate that heating alone is not sufficient to remove the oxide layer on the crystal remaining after the CP-4 etch.[9]

V. DISCUSSION AND CONCLUSIONS

The surface recombination velocity at a clean germanium surface is about one order of magnitude greater than that at a surface in air subsequent to a CP-4 etch. This difference in s is apparently not primarily a result
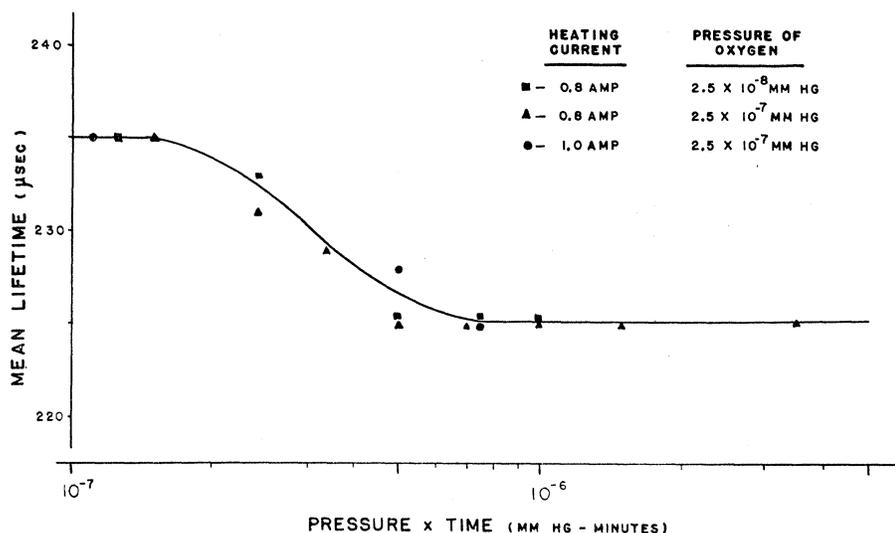
FIG. 4. Mean lifetime vs oxygen exposure at approximately 100°C.

of the oxide layer left by the etch, but is due to a physically adsorbed gas or vapor. Oxygen-exposure studies on outgassed crystals covered with an oxide layer and similar oxygen studies on clean surfaces suggest that this gas is not oxygen. Although it is clear that the structure of adsorbed oxygen on clean germanium surfaces is markedly different from that of the oxide layer left by CP-4 etching,[9] this difference has little or no effect on the surface recombination process. Comparison of the results of Stevenson and Keyes[3] with the experiments described above suggests that water vapor, and not oxygen, is the active element for the changes in s observed with the Brattain-Bardeen cycle. This comparison further suggests that the initial increases in s with evacuation of the experimental tube are a result of the removal of water vapor from the surface.

It is difficult to understand the insensitivity of the surface recombination velocity to adsorption of oxygen at room temperature on the basis of the model developed by Stevenson and Keyes.[3] Since the results of work function and photoelectric yield on clean germanium surfaces suggest that the surfaces are degenerate or nearly so,[5] the insensitivity of s to room-temperature adsorption of oxygen would require the energy level of the recombination centers to lie extremely close to one of the band edges, according to the Stevenson-Keyes theory. If these levels lie at less than kT away from one of the band edges, the Fermi level must cut the surface at a distance greater than kT from the band edges, and the surface is then not degenerate. Any shift in the Fermi level at the surface resulting from oxygen adsorption must also leave the Fermi level greater than kT from the band edge to ensure a constant value of s in this case. Less strenuous limitations can be realized if the Stevenson-Keyes assumption of equal recombination-center capture probabilities for holes, c_p, and for

electrons, c_n, is dropped, as was done by Many et al.[10] Such a modification of the theory would allow the clean surface to be degenerate and still have an s value that is insensitive to oxygen adsorption. Since the clean surface is p type,[11] a shift of the Stevenson-Keyes curve[3] for the relative s value versus surface potential could cause the region of constant nonzero s of this curve to extend over the valence band. Such a shift in the curve would mean that $c_p<c_n$. Finally, it is possible that some other more basic assumption made in the development of the Stevenson-Keyes theory (e.g., constancy of recombination center density) may not be valid in the case of clean germanium surfaces and the theory therefore may not be directly applicable. Some results obtained by Law and Garrett[1] should be mentioned. They found a sensitivity of s to room-temperature adsorption of oxygen for their surface in contrast with the present studies showing no change in s resulting from room-temperature adsorption. The value of s for the surface studied by Law and Garrett was higher than the values obtained for clean surfaces here. This may indicate that their surface was not well annealed after ion bombardment and that oxygen adsorption on a bombardment-damaged surface can affect the surface recombination processes. This view is supported by a comparison of the necessary conditions for well-annealed clean surfaces presented above, and the annealing conditions (420°C for 10 minutes followed by radiation quenching) in the experiment of Law and Garrett.

Finally, the apparent increases in s upon exposure of a clean surface to oxygen at elevated temperatures are probably not simply a result of an enhanced oxygen adsorption. The erratic behavior of this phenomenon

[10] Many, Harnik, and Margoninski, Semiconductor Surface Physics (University of Pennsylvania Press, Philadelphia, 1957), p. 85.
[11] P. Handler, Semiconductor Surface Physics (University of Pennsylvania Press, Philadelphia, 1957), p. 23.

makes it doubtful that this is entirely a surface effect. Similar apparent increases in s resulting from heating germanium in air at 70°–100°C have been reported by Buck and Brattain.[12] In their experiment these effects were also erratic. The present results suggest that the oxygen content in the air was the active agent associated with their observed results.

[12] T. M. Buck and W. H. Brattain, J. Electrochem. Soc. 102, 636 (1955).

Low-Temperature Heat Capacity of Pure and Reduced Rutile*

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(Received July 14, 1958)

The heat capacity of pure and reduced rutile has been measured between 1 and 20°K. Below 4°K, C for pure rutile is proportional to T^3 with a Debye θ equal to 758°K. Upon reduction a large additional contribution appears which is independent of temperature below 13°K. This is probably due to electrons which do not become degenerate above 1°K because of their very high effective mass (300–500 times the free-electron mass).

I. INTRODUCTION

AN electronic contribution to heat capacity has been observed for many metals at low temperatures since its original discovery by Keesom and Kok.[1] Recently such a contribution has also been found in impure semiconductors.[2] Except in superconductors below their transition points, this term is found to be proportional to the absolute temperature T, in agreement with the Pauli-Sommerfeld degenerate electron gas theory.[3] According to this theory the coefficient of this term is proportional to the density of electronic states at the Fermi level, which in turn is proportional to the electron effective mass. Since Breckenridge and Hosler[4] had reported that the electrons in reduced rutile (TiO$_2$) had a high effective mass (30–100 times the free-electron mass) we expected to find a large non-lattice heat capacity in this material at low temperatures. We did indeed find that its heat capacity is very large below 4°K but to a first approximation it is independent of T.

II. EXPERIMENTAL

The first sample was a single crystal boule of rutile[5] weighing 65 g; later we also used 200 g of single crystal

* This work was supported by Signal Corp Contract.
[1] W. H. Keesom and J. A. Kok, Physica 1, 770 (1933).
[2] N. Pearlman and P. H. Keesom, Phys. Rev. 88, 398 (1952).
[3] A. Sommerfeld, Z. Physik 47, 1 (1928).
[4] R. G. Breckenridge and W. R. Hosler, Phys. Rev. 91, 793 (1953).
[5] These samples were kindly provided by Mr. W. C. Clark of the Linde Air Products Company.

granules. The material as received was transparent, but slightly yellow. After the heat capacity was measured at low temperatures the crystal was reduced by the Linde Air Products Laboratory in an argon atmosphere at 1200°C. Later reductions were done in our department in a hydrogen atmosphere at 900°C. This temperature was also used for reoxidations in an oxygen atmosphere. All gases used were commercially pure and passed through a liquid nitrogen trap to remove oil and water vapor. Reduction rendered the material opaque, with a bluish color which deepened with increasing degree of reduction. On reoxidation it regained its yellowish color, but was less transparent than originally. The material was weighed before and after each treatment and the weight loss used as an estimate of the degree of reduction. This correlation is probably not very accurate for the granules, however, because of the difficulty in handling them. A transverse slice taken from the boule showed uniform coloration, indicating that reduction was uniform throughout.

Thermometer and constantan heater wires were secured to the surface of the boule with Glyptal lacquer and the heat capacity measurements carried out in the manner described previously.[2] Phosphor-bronze wire was used as thermometer in the liquid helium range and lead wire at hydrogen temperatures. Corrections were made for the heat capacities of the wires and the Glyptal. After remounting, following reductions and oxidations, the vacuum can surrounding the boule was pumped for several days at room temperature. The heat capacity of the granules was measured in a calorim-