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Electronic Surface States and the Cleaned Germanium Surface*

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The large *p*-type surface conductivity and field-induced surface conductivity of the cleaned germanium surface have been measured over the temperature range 77°–300°K. It is found that the surface conductivity and the field-induced surface conductivity are almost independent of temperature, varying by a factor of two over the temperature range investigated. The effect of oxygen, atomic hydrogen, and water vapor on the surface conductivity has also been observed. A qualitative two-dimensional band model is presented which correlates most of the experimental results. In this model, which is somewhat similar to the three-dimensional band model of graphite, there is a two-dimensional surface state band at the surface which overlaps in energy a two-dimensional valence band just beneath the surface. The states which form the surface state band are assumed to be perturbed out of the conduction band. The filling of these surface states with electrons out of the valence band gives rise to the observed *p*-type conductivity associated with the cleaned germanium surface.

The states perturbed out of the conduction band are shown to be associated with the unfilled orbitals of the germanium surface atoms. A second system, where a similar two-dimensional matrix of unfilled orbitals is found, is in the dislocations associated with medium-angle grain boundaries. It is shown that the transport properties of these grain boundaries are similar in magnitude and temperature dependence to that observed for the clean germanium surface. The same model presented for the surface can be used to explain the transport properties of grain boundaries.

1. INTRODUCTION

IN recent years Farnsworth and colleagues[1] have shown that an atomically clean single-crystal germanium surface can be produced and maintained under ultra high vacuum conditions. The clean surface is produced by first sputtering with argon ions and then annealing at 600°C in ultra high vacuum. The cleanness and regularity of the surface lattice thus produced was confirmed by their use of low-energy electron diffraction techniques. This pioneering work has stimulated the study of the clean germanium surface and a number of investigators have measured the work function, photoelectric threshold,[2] contact potential,[3] surface transport properties,[4–6] and surface recombination velocity.[7–9] Others[10–12] have studied its chemical properties, such as sticking coefficients, oxidation, heats of adsorption, and oxidation kinetics. The picture of the germanium surface which can be deduced from this work is still hazy in detail, but has the following general features. The surface properties of a semiconductor are three dimensional in nature. We will denote the actual surface as the surface region and the portion below the surface as the space-charge region. The work function, photoelectric threshold, contact potential, and the surface transport measurements all indicate that a large density of surface states exists in the surface region. The surface transport properties indicate that these states are acceptor in nature. The exact density of surface states has not been determined but a lower limit of 10^{13} surface states/cm^2 has been estimated.[4] The photoelectric threshold and the work function have been

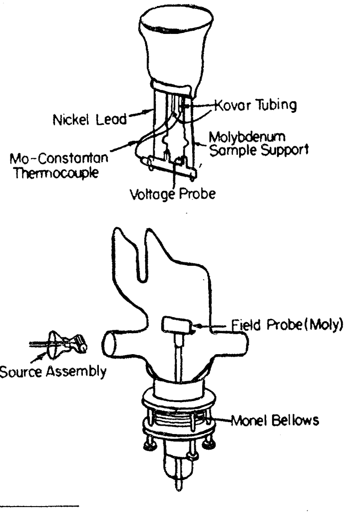

FIG. 1. The experimental tube used for measurement of the surface conductivity and the field-induced surface conductivity.

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[*] This research was supported by the Office of Naval Research.

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[1] R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. **30**, 917 (1959); Farnsworth, Schlier, George, and Burger, J. Appl. Phys. **26**, 252 (1955); R. E. Schlier and H. E. Farnsworth, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957); Farnsworth, Schlier, George, and Burger, J. Appl. Phys. **29**, 1150 (1958).

[2] J. A. Dillon, Jr., and H. E. Farnsworth, J. Appl. Phys. **28**, 174 (1957).

[3] F. Allen and A. B. Fowler, J. Phys. Chem. Solids **3**, 107 (1957); A. B. Fowler, J. Appl. Phys. **30**, 556 (1959).

[4] P. Handler, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957).

[5] R. A. Missman and P. Handler, J. Phys. Chem. Solids **3**, 109 (1959).

[6] G. Heiland and P. Handler, J. Appl. Phys. **30**, 446 (1959).

[7] J. T. Law and C. G. B. Garrett, J. Appl. Phys. **27**, 656 (1956).

[8] S. Wang and G. Wallis, J. Appl. Phys. **30**, 235 (1959).

[9] H. H. Madden and H. E. Farnsworth, Phys. Rev. **112**, 793 (1958).

[10] S. P. Wolsky, Phys. Rev. **108**, 1131 (1957); J. Appl. Phys. **29**, 1132 (1958).

[11] Green, Kafalas, and Robinson, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957).

[12] Rosenberg, Robinson, and Gatos, J. Appl. Phys. **27**, 771 (1958).

found to be approximately equal[2] and this means that the edge of the valence band and Fermi energy are coincident at the surface, independent of the value of the Fermi energy in the bulk of the crystal. The magnitude of the conductivity associated with the surface is found to be between 100–200 μmho/square and the main purpose of the experimental part of this paper is to measure its temperature dependence.

The object of this research on the germanium surface is the understanding of the energy level diagram of the electronic surface states. Tamm[13] and others[14–17] have shown on the basis of static one-dimensional models that surface states may exist at the semiconductor surface. The energies of these surface states lie in the forbidden zone and their wave functions are localized at the surface. The localization arises from the fact that the energy of the surface state is in the forbidden zone and the wave function is exponentially damped going into the crystal. It is also exponentially damped outside the crystal due to the presence of a potential of the nature of an image force. More recently Koutecky[18] has investigated the surface states of a semi-infinite crystal. He assumes a perturbing potential due to the surface which penetrates the crystal which is only a function of the distance from the surface, but otherwise unspecified. His results indicate that localized surface states will appear not only at the surface but also beneath it. The wave functions of these subsurface states have maximum amplitude, not at the surface, but below it. If the perturbation is positive, volume states will be occupied first, followed by subsurface states and finally by surface states. Koutecky points out that the filling of these states will result in a uniform distribution of charge for a filled band, since the volume states have lower amplitudes near the surface. Thus if only one band is considered no space-charge region or excess conductivity should result. Thus a space-charge region of the type assumed for the clean germanium surface can only arise from the proximity of conduction band states to the valence band at the surface. Shockley[17] does consider both the valence and conduction bands in his treatment of diamond-type lattices. In his generalization to three dimensions he suggests that the existence of the surface will allow a band of surface states to exist in the forbidden energy zone. Half of the states have been taken from the valence band and half from the conduction band. Thus the band is half full and should be conducting.

At the present time the experimental data do not allow one to determine whether the observed surface states are of the type first suggested by Tamm or Koutecky or of the type suggested by Shockley. A model will be presented in the latter part of the paper which seems to follow the model presented by Koutecky. In the model, it is assumed that the perturbing potential in the surface layer is negative so that the surface states in the valence band are pushed to lower energies and surface states in the conduction band are lowered in energy so that they overlap the valence band. The band structure at the surface is then similar to the model found for graphite. Localization of charge at the surface then arises, not from the fact that the states are in a forbidden energy zone but from the peculiar filling of the overlapping bands.

The present paper will discuss the experimental methods used to measure the temperature dependence of the surface conductivity associated with a clean germanium surface, and the results obtained. In Sec. 4 a qualitative model of the band structure of the clean germanium surface which is in fair agreement with the experimental data will be presented. It will be shown that grain boundaries [which are similar to the clean surface in that they have a large number of unfilled orbitals] have similar conduction properties.

2. EXPERIMENTAL PROCEDURE

Sample Preparation

Eagle-Picher germanium crystals were oriented by x-ray diffraction so that the (100) direction was normal to the surface of interest. Individual samples were cut out of wafers which had been sliced off either a 20 or 40 ohm-cm *n*-type crystal. These samples were then manually wet-lapped or ground on emery paper to the desired pre-etch thickness. They were then etched in *CP*4 until their thickness was about 0.025 cm. The overall sample dimensions after etching were about 2.0 cm ×0.30 cm×0.025 cm. Two sample geometries were employed in the measurements. The early samples were rectangular. Later samples were similar in shape, but possessed two projections along one edge of the sample which served as voltage probes (Fig. 1). These voltage probes were about 0.20 cm wide and about 0.40 cm long, and were separated by about 1.0 cm.

Experimental Tubes

Figure 1 illustrates the press seals and envelopes employed in the experiment. The glass was of the type which could be sealed to tungsten or Kovar. The sample supports were molybdenum strips, 0.002 in. thick, or 0.016-in. molybdenum wires as shown in Fig. 1. These supports, which were spotwelded to the nickel leads, served as the current leads. The voltage probes were 0.005-in. U-shaped molybdenum wires which slipped over the elongations of the sample. Initially, a tungsten-molybdenum thermocouple was sealed directly into the glass. Later, a molybdenum-constantan thermocouple was used because of its greater emf. The thermocouple wires were brazed into Kovar lead-through

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[13] I. Tamm, Physik. Z. Sowjetunion **1**, 733 (1932).

[14] S. Rijanow, Z. Physik **89**, 806 (1934).

[15] A. Maue, Z. Physik **94**, 717 (1935).

[16] E. T. Goodwin, Proc. Cambridge Phil. Soc. **35**, 205, 221, 232 (1939).

[17] W. Shockley, Phys. Rev. **56**, 317 (1939).

[18] J. Koutecky, Phys. Rev. **108**, 13 (1957).

tubes (Fig. 1). A thin ceramic tube was first used to electrically insulate the thermocouple from the sample, but was later replaced with a thin Linde sapphire tube.

The envelopes were all similar in design. The field plate, which was Kovar or molybdenum, was positioned by flexing a Monel bellows using three positioning screws. The final envelope had two housings containing ion source assemblies. These ion sources consisted of cylindrical tungsten grids surrounding coaxial tungsten filaments (Fig. 1).

Vacuum System

The complete vacuum system is illustrated in Fig. 2. The system was a modification of the ultra-high vacuum system developed by Alpert. The sample tube was mounted next to the ion gauge and between two Bayard-Alpert vacuum valves as shown in Fig. 2. A three-stage diffusion pump evacuated the system through a corrugated copper trap which acted as a getter for backstreaming diffusion pump oil. Valve 2 (Fig. 2) was connected to the ambient gas manifold through a cold trap and stopcock. The ambient gases which were used in the experiment were spectroscopically pure Linde argon, oxygen, and hydrogen. The water vapor used in the experiment was de-ionized water which had been degassed by alternately melting, freezing, and pumping. The ambient gas manifold was evacuated with a second oil diffusion pump.

The system was baked-out by placing a furnace over the vacuum manifold valves, copper trap, and cold trap. The temperature was then raised to 350°–375°C for about twelve hours. A Brown electric pyrometer connected to an iron-constantan thermocouple regulated the temperature during this time.

After bake-out, the ionization gauge was outgassed between fifteen minutes and an hour. The vacua attained were between 5×10^{-9} and 5×10^{-10} mm Hg without the use of getters.

Procedure for Cleaning the Germanium Surface by Means of Argon Bombardment

The samples were cleaned by a modification of the ion bombardment technique developed by Farnsworth *et al.*[1]

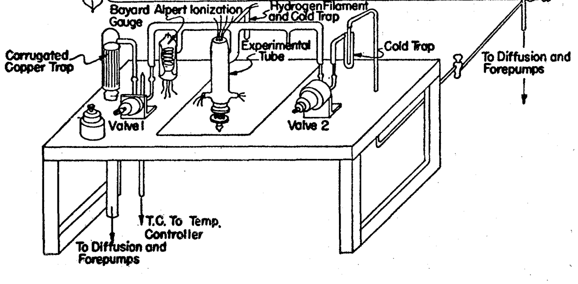

FIG. 2. The experimental vacuum system.

The sample was outgassed for about twelve hours between 500° and 600°C. If, after this outgassing, the pressure in the system did not return to about 5×10^{-9} mm Hg, the system was given a second bake-out, and the sample was outgassed again. After the sample was annealed, argon was admitted through the cold trap to the experimental tube to a pressure of about 5×10^{-3} to 5×10^{-2} mm Hg. The sample was heated to around 300°C by passing an alternating current through the outer leads, and biased between -400 and -500 v dc. The field probe, which had been moved away from the sample, was biased about $+50$ v dc. Under these conditions, a spontaneous glow discharge occurred. The discharge collapsed if the pressure was reduced below the values cited above. The total current measured was about 500 to 1000 μa. However, only a small fraction of this total current was ion current. For the first five or ten minutes, no effect could be observed. After this time, the walls of the experimental tube began to darken, indicating the presence of sputtered germanium. This delayed effect was probably associated with the removal of the oxide layer. Wolsky has found that the sputtering efficiency for germanium oxide is at most one third of that observed for the clean surface. Heating the sample seemed to improve the efficiency of sputtering. It is probable that the sputtering efficiency is decreased with increasing numbers of embedded argon atoms, and that heating the sample drives off many of these embedded argon atoms. After bombardment, the argon was pumped out, and the sample was heated between four and twelve hours at 600°C. When the sample temperature was first increased, a sudden increase in pressure was observed. This gas is assumed to be the residual argon which has been trapped in the surface.

For some of the samples, a visual inspection of the surface revealed a whitish-grey film. Great care had been taken to exclude all traces of oxygen from the system. The static nature of the bombardment process and the high affinity of germanium for oxygen insured that any impurity oxygen introduced with the argon would be gettered by the extensive surface of germanium deposited on the walls. It was therefore concluded that the film was not an oxide. Moreover, continued bombardment did not remove the film, as it should have removed an oxide, yet germanium continued to be sputtered onto the walls of the tube. Another explanation was therefore sought. Wehner[19] has pointed out that sputtered material may be returned to the target during a glow discharge. An x-ray spectrographic analysis of the film revealed only the characteristic germanium peak. It was concluded that the film was germanium which had been back scattered at the relatively high pressures involved during the

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[19] G. K. Wehner, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7.

argon bombardment, although this cannot be stated with certainty.

Consequently, a new experimental tube was designed (Fig. 1) to include two ion guns so that it might be possible to bombard the sample at much lower pressures. The ion guns were symmetrically placed so as to achieve a uniform bombardment. The argon pressure was now reduced to about 5×10^{-4} mm Hg. The sample was heated to about 600°C during the bombardment, and biased at -500 v dc. With the grids biased at about $+250$ v dc, an ion current of 50 μa could be obtained. No glow was observed under these conditions. The usual delay was observed before the walls began to darken. It was noted that darkening was not uniform, but appeared in four spots, roughly 45° from the normal to the surface, on the sides of the tube opposite the surfaces of the sample. Wehner[20] has observed that sputtering is preferential in the close packed direction. The close-packed direction in germanium is the [111] direction, which is 54.7° from the [100] direction. The observed spots correspond to the preferentially sputtered material and indicate the existence of a clean surface during the bombardment. The observed spots indicate that a regular lattice is being sputtered. If the surface were not clean, a thick film with a periodic structure, which has its direction of closest packing parallel to that of the germanium crystal must be present. This possibility seems slight since the oxide-covered surfaces, observed by Farnsworth,[1] are amorphous.

After bombardment, the argon was pumped out, and the sample was allowed to anneal at its bombardment temperature. An investigation of the surface revealed no traces of a film.

Experimental Apparatus

The experimental apparatus is illustrated in Fig. 3. The dc current was provided by dry cell batteries arranged so that they could be placed in opposition. Four batteries were employed to provide either 45 v or 3 v. The dc voltage across the sample and the voltage across a 1000-ohm precision resistor for measurement of the current, were measured with a Leeds and Northrup portable potentiometer or, alternatively, a Brown strip chart recorder. The temperature of the sample was determined by measuring the emf developed between a junction at the sample and a junction at 0°C with a second potentiometer or recorder. The field voltage was supplied by a Hewlitt-Packard sinusoidal signal generator. The field-induced surface conductivity signal was amplified by a Tektronix No. 122 difference amplifier, and was measured by a General Radio wave analyzer, or was filtered by a Spencer-Kennedy Laboratories, Inc. variable electronic filter and measured with a Hewlitt-Packard vacuum tube voltmeter. The field-induced signal was simultaneously displayed on a Dumont oscilloscope. The field voltage could be measured on the same instrument which measured the field-induced voltage by tapping off a fraction of the voltage across a series of precision resistors. Since it was not possible to align the field plate so that it was perfectly parallel to the sample, two balance condensers shown in Fig. 3 were provided to assist in eliminating the unbalance resulting from the difference in capacitive coupling in each arm of the bridge.

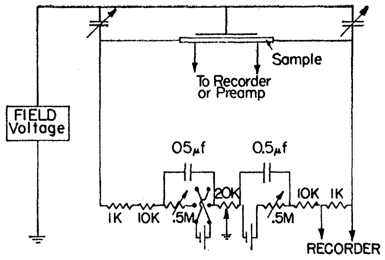

FIG. 3. The bridge used for measuring the field-induced surface conductivity.

When the field plate was in position, the capacity of this condenser was $\sim$1.0 $\mu\mu$f. An alternating field voltage was applied to the field plate by use of a signal generator. This voltage applied to the field plate was about 175 v. Measurements were made at 300 cps. The bridge circuit was balanced while the batteries were in opposition. The unbalance was of the order of 1.0 microvolt. When the dc current was turned on, the magnitude of the field effect voltage in most measurements was at least twice and perhaps 20 times the unbalance. The sign of the carrier at the surface could be determined by letting the field voltage act as the sweeping field on an oscilloscope, and feeding the field effect voltage in as the vertical input. A positive slope indicated conduction by holes, since a positive sweep would increase the resistance of the sample.

The cooling of the sample after high-temperature anneal could be automatically controlled by setting a clock-timer switch. This switch controlled a variable speed motor which slowly turned a variac output down to zero. This took place over periods of $\frac{1}{2}$ to $3\frac{1}{2}$ hours. The field plate was moved away from the sample during all heating operations. The temperature of the sample was originally estimated by measuring the resistance at high temperatures. After that, the original current and the redness of the sample were used.

Experimental Procedure

After the sample was cleaned and annealed, a Dewar flask was slipped around the experimental tube. Voltage, current, temperature, balance, field effect voltage, and field voltage were measured at room temperature. Liquid nitrogen was then slowly poured into the Dewar flask, and the measurements were repeated at a number of different temperatures down to 77°K. For temperatures above room temperature, a small electric furnace was slipped around the tube.

After the measurements on the clean surface as a function of temperature were completed, the sample

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[20] G. K. Wehner, Phys. Rev. **102**, 690 (1956).

was allowed to come back to room temperature, and the ambient gas was admitted. This gas was bled into the sample tube by slowly opening the Alpert valve. The leak rate of the valve was very small, and continuously variable, so that the rate at which the gas was bled into the tube could be closely controlled. Measurements were made at different times during the admission.

After the ambient gas admission had been completed, the gas was pumped out, and the measurements as a function of temperature were repeated. The sample was then allowed to return to room temperature, and the capacitance between it and the field plate was measured with a Brown impedance bridge.

3. RESULTS

Effect of Ambients

In an earlier paper[4] it was shown that oxygen would reduce the large *p*-type conductivity found on a cleaned germanium surface. However the minimum was not observed. In this paper we have tried a number of ambients on the surface in order to swing the bands through the minimum of conductivity. However we have not been successful on the (100) surfaces investigated. As Forman[21] has pointed out, it is only possible to observe the minimum on the (111) surface if one uses an ambient of oxygen followed by water vapor. Nonetheless it will be assumed in this paper that the treatment of the surface first by oxygen and then followed by water vapor brings the bands very close to the flat band condition. The error involved in this assumption is not large and will not affect any of the gross features of the model presented in Sec. 4.

Figure 4 shows the effect of oxygen and then water vapor on the conductivity of a cleaned germanium surface. The conductivity of the sample when the surface has been cleaned is called σ_c. As oxygen is added the conductivity of the sample increases to a maximum called $\sigma_{\max}$. With an increase in oxygen pressure beyond 10^{-7}–10^{-6} mm Hg the conductivity decreases to a point called $\sigma(O_2)$. This is not a stable point, but slowly decreases with time, the change being of the order of 10 μmho/square in a few days. This slow change is probably associated with the logarithmic oxidation of the surface observed by Green.[11] After the oxygen was pumped out water vapor was admitted and the surface conductivity was reduced an additional 25 μmho/square to a point called $\sigma(H_2O)$. This point is assumed to be the flat band condition for the sample. Some of the water vapor is loosely bound and may be removed by pumping.

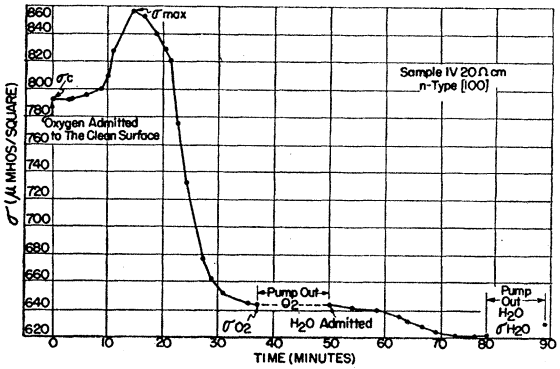

FIG. 4. The effect of oxygen and then water vapor on the conductivity of a cleaned germanium surface.

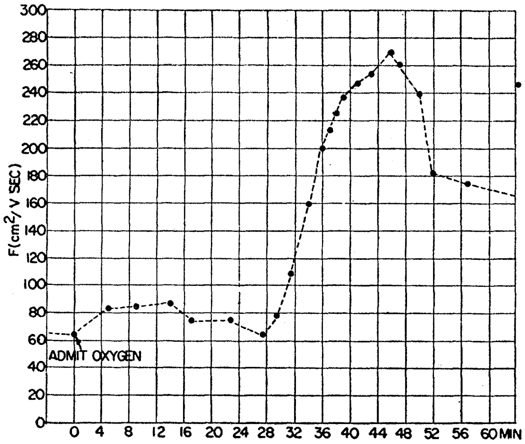

FIG. 5. The effect of oxygen on *F*, the field-induced surface conductivity per unit charge.

The magnitude of the observed changes may vary from sample to sample and from run to run due to variations in surface roughness. A factor which is independent of the actual geometry is the ratio $R=[\sigma_c-\sigma(O_2)]/(\sigma_{\max}-\sigma_c)$. This ratio is found to be quite reproducible and equal to 2.0±0.3 for a cleaned surface. The values reported previously[4] were about 1.6. This ratio seems to be the best indication of the cleanness of the surface, if one assumes that reproducibility of results is a criterion of cleanness. If the sample is just heated to 600°C without being sputtered, this ratio will vary from values as large as ten to as small as four, but will rarely fall below four. After just one argon bombardment and anneal this ratio is always close to two and definitely below four. These observations are in agreement with the data of the low-energy electron diffraction studies of Farnsworth.[1] In those studies it was shown that the diffraction pattern of the clean surface could not be obtained even though the sample had been heated close to its melting point in ultra high vacuum.

In the region between $\sigma_{\max}$ and $\sigma(O_2)$ certain unexplained effects may be observed if the oxygen is admitted in short intense bursts. The conductivity decreases with the burst and then slowly relaxes back to an intermediate value as if some of the oxygen were returning to the gas phase. However, once the point $\sigma(O_2)$ is reached the conductivity cannot be changed by pumping.

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[21] R. Forman, Bull. Am. Phys. Soc. Ser. II, 4, 26 (1959).

The surface conductivity of these experiments is definitely not associated with the diffusion of impurities or vacancies into a thin region beneath the surface. If the pressure of the oxygen admitted to the sample is high enough, the observed conductivity can be reduced in a second to the point $\sigma(O_2)$ and this rules out the possibility of diffusion of oxygen into the sample at room temperatures. The resistivity of the sample at the point $\sigma(O_2)$ or $\sigma(H_2O)$ is very close to the value it had as put into the tube. The variation may be nil or as large as ±30–50%. On a number of occasions it was noted that if the sample was heated above ~750°C, an additional conductance was present which could not be removed by annealing at lower temperatures.

The effect of oxygen on F, the field-induced surface conductivity per unit charge, is shown for a different run in Fig. 5. The value of F for the clean surface may vary from 50–200 cm^2/v sec. The relative changes, however, are much more constant. The ratio of the maximum of F to its value at the clean surface is always in the vicinity of 4 to 5.

The maximum in F always occurs approximately some 60 to 80 μmhos after the maximum in the conductivity.

Figure 6 shows the change in conductivity of a cleaned surface upon the admission of water vapor. The water vapor acts as a simple donor. The magnitude of the change is larger than that observed for the combination of oxygen and water vapor but not out of the range of the observed variations. The important result which is obtained from these ambient measurements, including the hydrogen data of Heiland,[6] is that there is a large p-type conductivity associated with the clean surface which is removed by the addition of gases such as oxygen and water vapor.

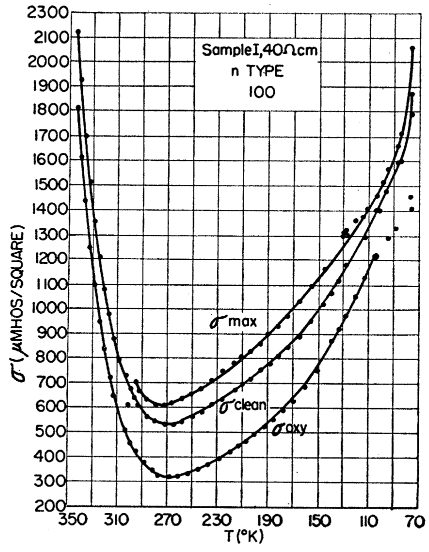

FIG. 7. The temperature dependence of the conductivity of the sample for three different conditions of the surface. σ_c = clean surface, $\sigma_{\max}$ = the sample at the maximum of the surface conductivity, $\sigma(O_2)$ = the surface covered with oxygen.

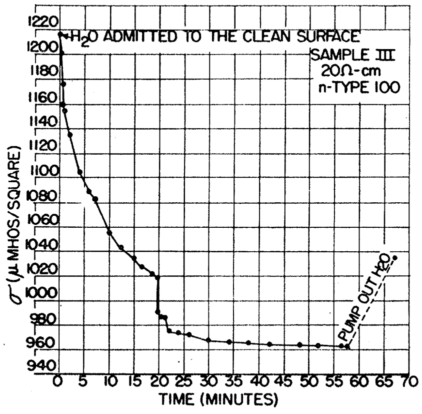

FIG. 6. The effect of water vapor on the conductivity of a cleaned germanium surface.

The Temperature Dependence of the Surface Conductivity

Figure 7 shows the temperature dependence of the conductivity of the sample for three different conditions of the surface as a function of the temperature. To measure $\sigma_{\max}$ *vs* temperature, oxygen was admitted until at a point some five to ten micromhos later the true $\sigma_{\max}$ was reached. The oxygen was then pumped out and the sample observed for fifteen to twenty minutes. No changes in conductivity were noticed during this interval. Liquid nitrogen was then poured into the Dewar surrounding the sample tube and the measurement of $\sigma_{\max}$ *vs* temperature was made at a number of temperatures between 77°K and room temperatures. To measure $\sigma(O_2)$ *vs* temperature, the sample was warmed to room temperatures and oxygen at a pressure greater than one mm Hg was introduced into the sample tube. After approximately one hour the oxygen was pumped out and $\sigma(O_2)$ was measured as a function of temperature. Figure 8 shows the difference between the σ_c and $\sigma(O_2)$ curves for five different temperature runs of the type shown in Fig. 7. These curves represent the temperature dependence of the surface conductivity. While the magnitude of $\sigma_c - \sigma(O_2)$ varies from cleaning to cleaning, the results indicate that the conductivity associated with the surface is roughly independent of the temperature. The spread of the experimental results is probably due to errors in measurement of the true sample temperature. An error of a few degrees from the σ_c run to the $\sigma(O_2)$ run could account for the observed

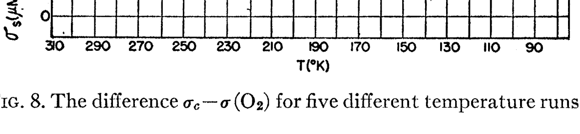

FIG. 8. The difference $\sigma_c - \sigma(O_2)$ for five different temperature runs.

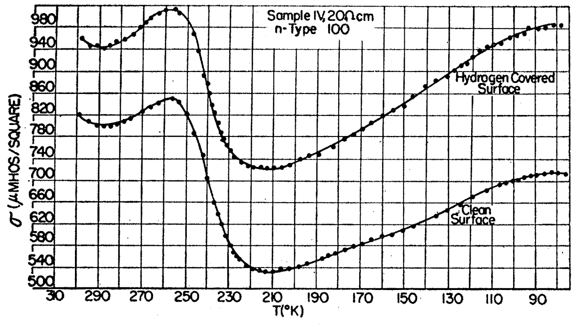

FIG. 9. The temperature dependence of the conductivity of the sample before and after coverage with atomic hydrogen.

spread. As was mentioned above, the minimum in the conductivity was not observed in this work. At the point $\sigma(O_2)$, the region of space charge is still *p*-type, and remains so at all temperatures. From the change in conductivity due to the adsorption of water vapor, at room temperatures it can be assumed that the region of space charge is at least some twenty micromhos from the flat band condition. Under these conditions one should see *p*-type field effect mobilities at all the temperatures investigated. Even though the surface is not at the flat band condition, the data definitely indicate that there is a temperature-independent conductivity associated with the cleaned (100) surface.

Figure 9 shows the temperature dependence of the conductivity of the sample before and after coverage with atomic hydrogen. As pointed out by Heiland[6] atomic hydrogen increases the *p*-type surface conductivity of a cleaned surface, indicating that it acts as an acceptor. Eisinger[22] has shown that atomic hydrogen increases the photoelectric threshold of a cleaned silicon surface and this is consistent with observed conductivity data for germanium.

The apparent electronegativity of atomic hydrogen on germanium, silicon and metals such as tungsten[22] is not well understood. One possible explanation is that the surface atoms of these solids are much more electronegative than the values usually assigned to the isolated atoms, by virtue of their position at the surface. If this were so, hydrogen bonding between the proton and the surface atoms could occur. The addition of the neutral hydrogen atoms at a site would give stability to additional electrons at neighboring sites and would explain the observed increases in work function for semiconductors and metals. The excess conductance induced by the hydrogen is also temperature independent. The dip in total conductivity at 200°K is probably due to the presence of a small number of deep traps in the bulk of the sample.

Figure 10 shows the observed field-induced surface conductivity per unit charge for each of the three curves shown in Fig. 7.

F at σ_c and F at $\sigma_{\max}$ do not vary much with temperature, about a factor of two over the range of temperature investigated. However, the F at $\sigma(O_2)$ changes markedly over the same temperature range and indicates a different region of space charge for this latter case.

4. BAND STRUCTURE OF THE CLEAN GERMANIUM SURFACE

A model of the clean germanium surface must correlate the following facts:

1. The field-induced surface conductivity per unit charge, F, is positive, indicating that

$$|(dP/dE_F)\mu_{ps}| > |(dN/dE_F)\mu_{ns}|, \qquad (1)$$

where F is defined as

$$F=\frac{d\sigma}{dQ}=\frac{(dP/dE_F)\mu_{ps}+(dN/dE_F)\mu_{ns}}{(dP/dE_F)-(dN/dE_F)}, \qquad (2)$$

P = number of holes per cm² in the region of space charge, N = number of electrons per cm² in surface states, μ_{ps} = mobility of holes in the region of space charge, μ_{ns} = mobility of electrons in surface states, $d\sigma$ = change in sample conductivity due to the applied field, and dQ = additional charge induced into sample due to the applied field. The effect of the applied electric field on the semiconductor surface is a displacement of the Fermi energy relative to the electrostatic potential at the surface.

2. The magnitude of F is approximately 100 cm²/v sec for a clean surface and is roughly independent of temperature over the range 77°–300°K.

3. The conductivity associated with the clean surface is

$$\sigma_s = q(P\mu_{ps}+N\mu_{ns}) \simeq 100\text{–}200\ \mu\text{mhos}. \qquad (3)$$

σ_s is roughly independent of temperature, changing by a factor of two over the temperature range 77°–300°K.

4. The quantity $H \simeq 600$–1000 cm²/v sec, where H is defined[23] as

$$H=\frac{R_T\sigma_T{}^2-R_V\sigma_V{}^2}{\sigma_s}=\frac{(P\mu_{ps}{}^2-N\mu_{ns}{}^2)}{\sigma_s/q}, \qquad (4)$$

R_T = total Hall coefficient for volume and surface when the surface is clean in cm²/coul, R_V = Hall coefficient of sample when the bands are flat out to the surface region in cm²/coul, σ_T = sum of the volume and surface conductivities in mhos/square, and σ_V = conductivity of the sample in mhos/square when the bands are flat out to the surface region. If μ_{ns} were zero, H would equal the Hall mobility of the holes in the region of space charge. Since the data are still so rough, no distinction will be made between Hall mobilities and conductivity mobilities.

5. For near intrinsic germanium the number of

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[22] J. Eisinger, J. Chem. Phys. **30**, 927 (1959); **29**, 1154 (1958).

[23] R. Petritz, Phys. Rev. **110**, 1254 (1958); J. N. Zemel and R. Petritz, Phys. Rev. **110**, 1263 (1958).

holes in the region of space charge must always equal the number of electrons in surface states to maintain charge neutrality,

$$N = P. \tag{5}$$

6. The surface germanium atoms have one or more unfilled orbitals which may act as electron acceptors.

7. Perturbation of valence-band states alone cannot give rise to a surface conductivity.[18] Surface conductivity may arise from the mixing of valence-band and conduction-band states to form a half-filled surface band in the manner described by Shockley or by the perturbation of conduction-band states such that they have energies close to or coincident with valence-band states. It is implicitly assumed that no impurities are present.

8. The work function and photoelectric threshold are approximately equal.[2]

9. The distribution of states in the valence band at the surface must be different from the distribution of states in the volume. For if one uses the volume distribution of states to determine the shape of the space-charge region[24–26] one finds that the holes are constrained to move in a potential well less than 20 A wide. This width contradicts the assumption of a normal distribution of states. The uncertainty principle requires that the lowest states be somewhat removed from the edge of the valence band for this width.

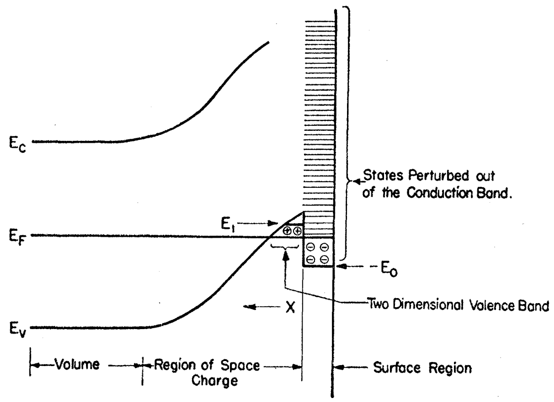

FIG. 11. A schematic representation of the band structure of the clean germanium surface. E_0 is the bottom or edge of the electron surface-state band. E_1 is the edge or top of the quantized hole band.

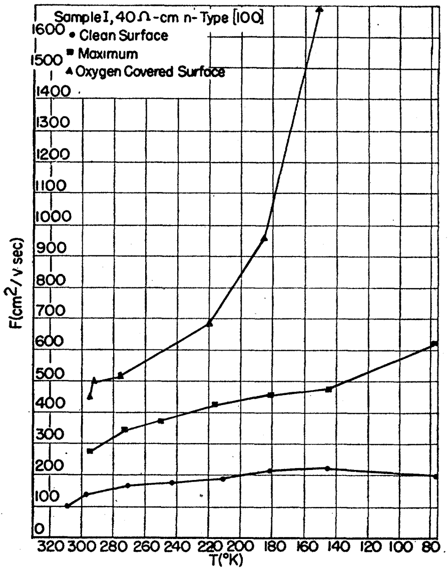

FIG. 10. The temperature dependence of the field-induced surface conductivity per unit charge for the three conditions of the surface shown in Fig. 7.

Rather than attempt to determine the actual band structure, a model similar to the band structure of graphite[27] will be assumed with the additional assumption that the bands are two dimensional and circular. It will be shown that the properties of such a model are in good agreement with the experimental data. Figure 11 shows a schematic representation of the band structure of the clean germanium surface. The bottom of the surface-state band is E_0. It is assumed that these states have been perturbed out of the conduction band and that they overlap the valence band. The number of electrons in this surface band is

$$N = N_0(E_F - E_0), \tag{6}$$

where N_0 is the density of states per electron volt per cm^2. It is independent of the energy for two-dimensional bands and is given by

$$N_0 = 4\pi m^*/h^2, \tag{7}$$

where h is Planck's constant and m^* is an effective mass parameter. It is assumed that these electrons have a finite mobility. It is assumed that the wave functions of the states perturbed out of the conduction band have maxima centered about the surface atoms. E_1 is the highest energy or edge of the two-dimensional hole band. The wave functions of the two-dimensional hole band are assumed to be displaced inward. The holes move in a potential well of approximately 50 A in width. The number of holes in this band is given by

$$P = P_0(E_1 - E_F), \tag{8}$$

where P_0 is the density of states per electron volt per cm^2 and is a constant of the form of N_0 in Eq. (7).

This type of band structure for the holes in the valence band can be shown to be reasonable in the following way. The holes are constrained to move in a potential well set up by the electric field of the electrons in the surface band. The magnitude of this electric field is of the order of 10^5 v/cm. If the electric field is

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[24] R. H. Kingston and S. F. Neustadter, J. Appl. Phys. **26**, 718 (1955).

[25] C. G. B. Garrett and W. H. Brattain, Phys. Rev. **99**, 376 (1955).

[26] R. Seiwatz and M. Green, J. Appl. Phys. **29**, 1034 (1953).

[27] D. E. Soule and J. W. McClure, J. Phys. Chem. Solids **8**, 29 (1959).

assumed constant, then the holes move in a linear potential well. That is, linear inside the crystal for $x>0$ and infinite for $x\leqslant 0$ outside the crystal surface. The solution of the Schrödinger equation is[28]

$$\psi=A[J_{\frac{1}{3}}(t)+J_{-\frac{1}{3}}(t)], \tag{9}$$

where the boundary conditions are $\psi=0$ for $x=0$ and $x=\infty$. The J's are Bessel functions of order $\frac{1}{3}$. A and t are functions of energy and position. The energy levels are found from the boundary condition $\psi=0$ at $x=0$. For a linear potential well where the electric field is 10^5 v/cm, the energy levels are separated by ~ 0.1 ev or $4kT$ at room temperatures. The holes are assumed to be perfectly free in the directions parallel to the surface and this gives rise to a two-dimensional band extending downward from E_1. It is assumed that all other two-dimensional bands associated with higher energy states in the direction normal to the surface may be neglected. If the holes shield each other to an appreciable extent, the effective electric field will be smaller and the separation of energy levels will be somewhat less.

The motion of the holes and electrons parallel to the surface may not be perfectly free. With 10^{12} charges/cm^2 the electrons are 100 A apart while the depth of the well is only 50 A. Thus the potential in which the holes move might not be a function of only the depth into the crystal but also depend on the position of the holes with respect to electron charge at the surface. This problem is more difficult to treat and no attempt will be made in this paper. The model presented in this paper can be considered as a limiting case of the actual situation.

Equations (6) and (8) assume that both the hole and electron bands are strongly degenerate. The experimental values of the surface conductivity indicate, together with Eq. (5), that N and P are of the order of 10^{12}/cm^2. This requires that N_0 and P_0 be less than 4×10^{13} states/ev for Eqs. (6) and (8) to hold over the temperature range investigated. If N_0 and P_0 are greater than 4×10^{13} states/ev, then N and P are given by

$$N=N_0kT\ln\{1+\exp[(E_F-E_0)/kT]\}, \tag{10a}$$

and

$$P=P_0kT\ln\{1+\exp[(E_1-E_F)/kT]\}. \tag{10b}$$

In this case, however, electrical neutrality requires that $N_0=P_0$ and that $E_1-E_0=2(E_1-E_F)$. Also N and P must decrease as the temperature is lowered. In the remainder of this section it will be assumed that the strongly degenerate case is applicable.

In this model it is assumed that any surface states associated with the valence band have been perturbed to lower energies and are completely filled at all times. The surface germanium atom on a (111) surface has three bonds to the crystal below it and one free orbital with one electron in it. This neutral atom can be considered as having seven electrons about it compared to an atom in the volume which has eight. The energy necessary to ionize one of the seven electrons of the surface atom should be large and its state should lie several electron volts below the conduction band, since this ionization results in a separation of charge. However, if the germanium surface atom captures an eighth electron in a state perturbed out of the conduction band it then has a stable octet of electrons in its outer shell. The ionization of this electron to the conduction band does not result in the separation of charge and therefore its energy state should lie much closer to the conduction band. Considerations similar to those described above should hold for surfaces other than the (111).

It is expected that the mobility of the holes and electrons at the surface will be relatively temperature independent. Both carriers move in narrow potential wells and the mode of scattering consists of collisions with the surface rather than collisions with the lattice in the form of phonons. Thus the usual T^{-1} dependence found for three-dimensional degenerate bands should be absent. Also the type of scattering at the surface is restricted due to the quantization of the momentum in the direction normal to the surface. Since the levels of the second band of states lie more than a few kT above the edge of the first band of states, a hole or an electron will not be able to gain enough energy in colliding with the surface to change the magnitude of its momentum normal to the surface. Thus the quantization rules out the possibility of diffuse scattering at the surface. However, the scattering need not be specular either, but may be represented by an intermediate case. The carrier may change its direction parallel to the surface, but the angle of incidence must equal the angle of reflection on collision with the surface. Thus one should observe mobilities greater than those predicted for diffuse scattering[29] but somewhat less than those predicted for specular scattering.

The dominant characteristic of this model is its temperature independence. Thus all measurements of the transport properties of holes and electrons in these bands should show temperature independence.

Using Eqs. (2), (6), (8), F can be written

$$F=(\mu_{ps}-a\mu_{ns})/(1+a), \tag{11}$$

where

$$dP/dE_F=-P_0,\quad dN/dE_F=N_0,\quad\text{and}\quad N_0/P_0=a.$$

Equation (4) for H may be rewritten using Eqs. (3) and (5):

$$H=(\mu_{ps}{}^2-\mu_{ns}{}^2)/(\mu_{ps}+\mu_{ns})=\mu_{ps}-\mu_{ns}. \tag{12}$$

Equations (11) and (12) may be solved for μ_{ps} and μ_{ns}:

$$\mu_{ps}=[a(H-F)-F]/(a-1), \tag{13}$$

$$\mu_{ns}=[H-(1+a)F]/(a-1), \tag{14}$$

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[28] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 182.

[29] J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).

F is obtained from Fig. 10 and H from the room temperature data of Missman and Handler.[5] If μ_{ns} is assumed equal to zero, then Eqs. (11) and (12) may be used to determine a, the ratio of the density of states in the electron band to the density of states in the two-dimensional valence band.

$$a = N_0/P_0 = H/F - 1 = 5. \qquad (15)$$

For strongly degenerate bands $N_0 \leqslant 4\times 10^{13}$ and therefore $P_0 \lesssim 10^{13}$ states/cm^2 ev. Equation (7) then implies that $m^*/m < 0.1$ for both the holes and the electrons (m is the free electron mass). If N_0 and P_0 are not independent of the energy these values may be interpreted as the effective density of states at the Fermi energy. In this type of model, it is very difficult to determine the total number of surface states present. Theory indicates that the number of surface states should roughly equal the number of surface atoms. However, the exact number may be ascertained only if they lie at a discrete energy in the vicinity of the Fermi energy.

If μ_{ns} is finite, then the limits on a are

$$H/F > a > 1. \qquad (16)$$

If a is assumed to have a value of two, then $\mu_{ps} = 900$ cm^2/v sec and $\mu_{ns} = 300$ cm^2/v sec, where $F = 100$ and $H = 600$.

A measurement of the transverse magnetoresistance gives an additional equation[23] of the form

$$M = \mu_{ps}^2 + \mu_{ns}^2 - \mu_{ps}\mu_{ns}. \qquad (17)$$

Equations (11), (12), and (17) should then determine a, μ_{ps}, and μ_{ns} exactly.

It may be worth noting that the present model may be used to explain the conductivity of medium-angle grain boundaries of the type investigated by Reed,[30] Matare,[31] and Tweet.[32] These grain boundaries which contain large numbers of dislocations will also contain large numbers of unfilled orbitals of the type suggested by Shockley,[33] and investigated by Reed.[34] If the distance between dislocations is small, such that the electronic wave functions on adjacent dislocations overlap, then the physical situation will closely resemble the clean surface. In this case the conduction properties of the grain boundary should be similar to that of the clean surface. In fact Reed, Weinreich, and Matare[28] have observed a temperature-independent p-type conductivity over the temperature range 2°–300°K in a large number of bicrystals containing a single grain boundary. The magnitude of the observed conductivity is of the order of 100–300 μmho/square, in good agreement with values shown in Fig. 8. The conductivity is definitely not associated with impurities.

Tweet[32] has also measured the Hall coefficient for a number of grain boundaries in gold-doped germanium. In one of his samples a temperature-independent conductivity was observed in the range where the gold levels were completely de-ionized. In this sample the magnitude of the conductivity was similar to that observed for the clean surface. Also the product of Tweet's reduced Hall coefficient times his reduced conductivity gives a quantity similar to the quantity H defined in Eq. (11). Tweet's value of H in this temperature range has approximately the same value as reported by Missman and Handler for the cleaned germanium surface at room temperatures.

Matare reports that the application of a field normal to the grain boundary gives changes in conductivity which are independent of temperature over the range 2°–300°K. The fact that no freeze out of carriers is observed at temperatures as low as 2°K indicates that the acceptor-type levels of the grain boundary must be coincident with the valence band edge or overlap it as is shown in Fig. 11.

The model presented here is in fair agreement with all the experimental data published thus far. However the low values of the measured surface recombination are still not well understood. In these experimental papers it has been assumed that the electrons in the bulk and at the surface are in thermal equilibrium. However the barrier for the flow of electrons to the surface is ~0.3 ev and the diffusion of electrons may very well be the rate limiting step. Thus in the data of Law and Garrett[7] there is no change in surface recombination velocity with the initial admission of oxygen. The change in the barrier height does not become appreciable until the conductivity is well below its cleaned-surface value. At this point Law and Garrett do observe a large increase in surface recombination velocity.

No attempt is made in the present paper to describe the energy level diagram of the surface in the presence of oxygen.

The model presented is by no means unique. It is possible, for example, for states to be perturbed out of the conduction band and valence band to form a similar set of overlapping bands in energy and space somewhere in the forbidden band. In this model the macroscopic electrostatic potential may be the same throughout the volume and the bulk. This model is similar to the type predicted by Shockley[17] except that two distinct bands, rather than one, are formed.

5. CONCLUSION

The surface conductivity and the field-induced surface conductivity per unit charge are shown to be almost independent of temperature over the range 77°–300°K. A model of the clean germanium surface is presented which assumes that the band structure at the surface is similar in gross detail to that of graphite,

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[30] Reed, Weinreich, and Matare, Phys. Rev. **113**, 454 (1959).

[31] H. F. Matare, J. Appl. Phys. **30**, 581 (1959).

[32] A. G. Tweet, Phys. Rev. **99**, 1182 (1955).

[33] W. Shockley, Phys. Rev. **91**, 228 (1953).

[34] W. T. Reed, Jr., Phil. Mag. 7, **45**, 775, 1119 (1954); 7, **46**, 111 (1955).

except that the bands are two dimensional in nature and separated in space. The electron-band or surface states are perturbed out of the conduction band to form a surface-state band which overlaps the valence band in energy.

The filling of these surface states with electrons out of the valence band gives rise to the observed p-type surface conductivity. The states perturbed out of the conduction band are most likely associated with the unfilled orbitals of the germanium surface atoms. These same types of unfilled orbitals are found in the dislocations associated with grain boundaries, and the similarity in conduction properties between the clean surface and medium-angle grain boundaries is shown.

The data are still very crude and it is hoped that greater accuracy will be obtained in the future.

6. ACKNOWLEDGMENTS

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Slow Electrons in Polar Crystals: Self-Energy, Mass, and Mobility*

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The parameters for the Feynman model of a polaron are evaluated numerically for various values of the electron lattice interaction α, in the usual idealization of the problem of a slow electron in a polar crystal. The self-energy and effective mass thus obtained are compared with earlier polaron theories, indicating the superiority of the Feynman model for a wide range of α. The polaron size and the effect of the continuum approximation are estimated, and it is concluded that the alkali halides, at least, may be in the border region for the validity of this approximation. The problem of calculating polaron mobility as determined by scattering with longitudinal optical mode phonons is analyzed and previous theories are critically reviewed. A new theory based on the Feynman model is developed in which the Boltzmann equation is used with resonance scattering considered as the fundamental scattering process. A comparison with previous theories shows some improvements and stresses still doubtful points. A comparison with various experiments suggests the possible inadequacy of the usual idealization.

I. INTRODUCTION

We consider the behavior of a slow electron in the conduction band of a polar crystal in which the interaction between the electron and the longitudinal optical modes of lattice vibration is too strong to be treated by perturbation theory, i.e., we consider the single entity of an electron and its associated cloud of virtual phonons, the polaron. We idealize the problem in the usual way by (1) neglecting all but the longitudinal modes, (2) treating the latter as a vibrating continuum, (3) assuming that the lattice frequencies all equal the same constant ω, (4) assuming that the electrons in all filled bands follow the electron in the conduction band inertialessly, and (5) by replacing the periodic potential by an effective mass m, which we call the *bare* electron mass (to be distinguished from m_e, the mass of an electron in free space). Thus, we assume the system to have the Hamiltonian

$$H=\mathbf{p}^2/2m+\sum_k \mathcal{V}_k(\tau_k e^{i\mathbf{k}\cdot\mathbf{r}}+\tau_k{}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}})+\sum_k \hbar\omega\tau_k{}^\dagger\tau_k,$$

where

$$\begin{aligned}\mathcal{V}_k&=\hbar\omega(4\pi\alpha/V)^{\frac{1}{2}}(\hbar/2m\omega)^{\frac{1}{4}}k^{-1}\equiv\mathcal{V}/k,\\ \alpha&=(e^2/2\hbar\omega)(2m\omega/\hbar)^{\frac{1}{2}}(\epsilon_\infty{}^{-1}-\epsilon_0{}^{-1}).\end{aligned}\tag{1.1}$$

The problem of fundamental theoretical interest is to find a theory capable of giving the very low-lying states of this system (those of a slow polaron without free phonons) or at least capable of determining the properties of a free, slowly moving polaron characterized by these states: the polaron self-energy, effective mass, charge distribution, etc. A problem of more direct experimental interest is to apply such a theory to the behavior of the polaron in interaction with external fields and thermal phonons, e.g., to calculate the polaron mobility or the cyclotron resonance response.

Calculations of the second kind share all the difficulties found in self-energy and effective mass calculations, so that a theory which is incapable of reasonably accurate results for the properties of a slow, freely

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