Surface Conductivity of Cleaved Silicon Surfaces*

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The experimental results of Palmer, Morrison, and Dauenbaugh on the conductivity of cleaved surfaces of silicon are reinterpreted in terms of a large density of states below the center of the forbidden energy gap. This new interpretation shows that the conductivity measurements and the work function and photoelectric threshold measurements are not in disagreement. If a Shockley-type band of surface states is present at the surface, it is possible to estimate an upper bound for the mobility of its carriers. The value of the mobility is found to be less than 0.01 cm²/volt sec.

I

IN recent years a number of very interesting and exciting experiments on cleaved silicon surfaces have been performed. Allen and Gobeli[1–3] have measured the work function and photoelectric threshold of silicon (111) surfaces freshly cleaved in a vacuum of 10^{-10} mm Hg. They find that both the work function and especially the photoelectric threshold depend upon the bulk doping of the crystal and may vary by tenths of electron volts as one proceeds from highly doped *n*-type to highly doped *p*-type crystals. Their results indicate that there is a large density of states in the forbidden energy gap. The density of states is approximately equal to the number of surface atoms. The exact density present depends upon the model chosen with the lower bound being close to 2×10^{14} states/cm² ev. The neutral point of these surface states is found to be $\sim$0.23 ev below the center of the gap. The neutral point is the energy at which the Fermi level would intersect the surface such that there would be neither an excess of positive nor negative charge trapped at the surface. Earlier work on silicon surfaces cleaned by argon bombardment followed by annealing also suggested the existence of surface states whose neutral point lay below the center of the gap.[4]

As a result of field effect and surface channel experiments on cleaved silicon surfaces, Palmer, Morrison, and Dauenbaugh[5] recently concluded that the neutral point of the dominant surface states lay near the center of the gap. The purpose of this paper is to show that the experiments of PMD [Palmer, Morrison, and Dauenbaugh] can be equally well understood in terms of the surface states of Allen and Gobeli. Since the results of PMD are largely negative in character (no large change in conductances), it will be shown that their data indicate that the neutral point of the states lies within $\pm$0.25 ev of the center of the gap. Because of the resistivity of the samples used, no further definition of the neutral point is possible.

In order to show that the data of PMD can be interpreted equally well by surface states below the center of the forbidden gap, for example, it will be necessary to discuss the data in terms of the resistivity of the silicon crystals used in their experiments. Careful analysis of the data will show that the results of their field-effect experiments cannot be explained by any model and are therefore subject to question.

II

PMD performed four experiments, two channel-conductance experiments and two field-effect experiments. The channel experiments consisted of constructing an *npn* structure by diffusing phosphorus into an 80 ohm-cm *p*-type silicon crystal and a *pnp* structure by diffusing boron into a 20 ohm-cm *n*-type silicon crystal. These structures were cleaved so that the new surface intersected the two junctions. If a channel [inversion layer] were formed, e.g., a *p*-type surface region on an *n*-type crystal, it would have been possible to measure the conductance of the channel caused by the cleavage. In neither the *npn* nor the *pnp* experiment was the conductivity of the channel greater than 10^{-8} mho/square. The field-effect experiments consisted of cleaving homogeneous *n*- and *p*-type crystals where the cleaved-off part of the sample was used as a field plate. The field-effect measurements showed a slightly *n*-type surface on both *p*- and *n*-type bulk material. The field-effect mobility was estimated to be about 50 cm²/volt sec. They also found that the surface conductance and the field-effect mobility were extremely insensitive to oxygen even up to atmospheric pressure.

III

These results can be best understood by reference to Figs. 1 and 2. Figure 1 shows the configuration of the energy bands at the surface for both *n*- and *p*-type silicon when the neutral point of the surface state band lies at the center of the forbidden gap. The configuration of the energy bands will be identical for a discrete state of very high density located at the center of the

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[1] F. G. Allen and G. W. Gobeli, Bull. Am. Phys. Soc. **6**, 421 (1961).
[2] G. W. Gobeli and F. G. Allen, Bull. Am. Phys. Soc. **6**, 421 (1961).
[3] G. W. Gobeli and F. G. Allen, J. Phys. Chem. Solids **14**, 23 (1960).
[4] J. A. Dillon and H. E. Farnsworth, J. Appl. Phys. **29**, 1195 (1958).
[5] D. R. Palmer, S. R. Morrison, and C. E. Dauenbaugh, Phys. Rev. Letters, **6**, 170 (1961).

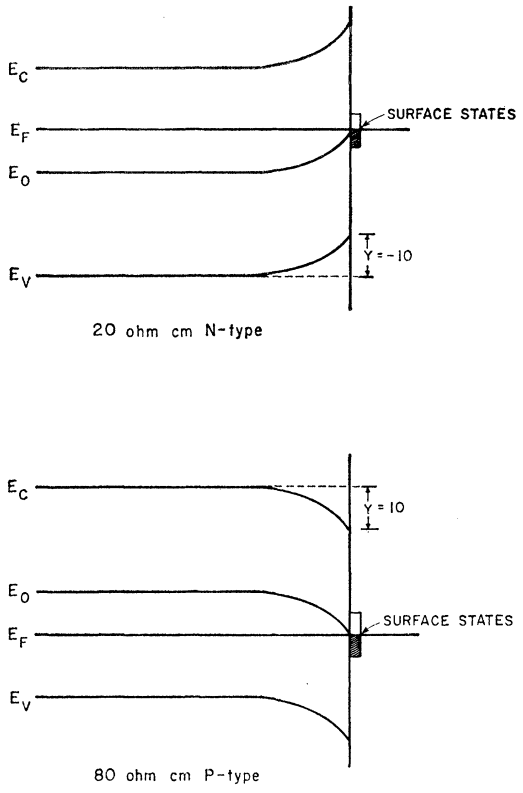

FIG. 1. Configuration of the energy bands at the surface with the neutral point of the surface states at the center of the forbidden-energy gap.

gap. In drawing this figure it was assumed that the n-type silicon was 20 ohm-cm and that the p-type silicon was 80 ohm-cm. The temperature was taken to be 295°K. Thus the Fermi level lies $\sim$0.25 ev above the center of the forbidden gap for the n-type sample and approximately an equal amount below the center of the forbidden gap for the p-type sample. Because of the high density of states, the differences in potential between the volume and the surface [the amount of band bending] are equal in magnitude but of opposite sign.

Figure 2 shows the surface conductivity of the n- and p-type samples as a function of the difference in potential between the volume and the surface. The surface conductivity is defined as

$$\sigma = q(P\mu_{ps} + N\mu_{ns}), \tag{1}$$

where q is the electronic charge and P and N are the surface excess of carriers per cm^2 of holes and electrons, respectively. For the exact definition of quantities like P and N the reader is referred to the article of Garrett and Brattain.[6] P and N are functions of a dimensionless parameter defined as

$$Y = q(\psi_s - \psi_0)/kT, \tag{2}$$

where $\psi_s - \psi_0$ is the potential difference between the volume and the surface, k is Boltzmann's constant, and T is the absolute temperature. In drawing Fig. 2, it was assumed that the electron and hole mobilities in the region of space charge are equal to their volume values. In an n-type sample, N is negative when Y is negative [bands bent up]. Also, for small negative values of Y, the absolute magnitude of N is much greater than P and consequently σ is negative. The negative values of σ in n-type samples, as the bands are bent up, result from the fact that the rate of removal of electrons from the region of space charge is much greater than the addition of holes. The negative charge at the surface is compensated by fixed donor atoms rather than by mobile holes for small negative values of Y. Fig. 2 shows that Y must be less than -26 in order to obtain positive values of σ. A similar argument explains the negative values of σ for the p-type sample. The difference in the two curves arises from the fact that the electron mobility is almost three times greater than the hole mobility. The values of P and N as a function of Y were obtained from the published graphs of Kingston and Neustadter.[7]

The field-effect mobility is defined as

$$\mu_{FE} = C(Y)d\sigma/dY, \tag{3}$$

where C is a function of Y, but does not change sign. Therefore the sign of the slope of the σ vs Y curves of Fig. 2 will indicate whether the holes or electrons are the majority carrier in the region of space charge. In the region where σ has a minimum, μ_{FE} is zero and has no simple relation to the mobility of the carriers. For other values of Y, μ_{FE} represents a lower bound for the mobility of the carriers when surface states are present and may be equal to the true mobility if no surface states are present. Fig. 2 shows that the n-type sample will have an n-type field effect mobility

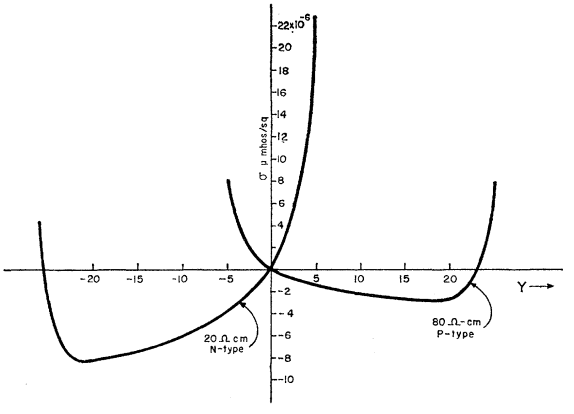

FIG. 2. Excess conductivity of the region of space charge as a function of the difference in potential between the volume and the surface for n- and p-type silicon at 295°K.

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

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

for all Y greater than -21 and a p-type field-effect mobility for Y less than -21. The p-type crystal will have a p-type field-effect mobility for Y less than 20 and an n-type field-effect mobility for Y greater than 20. Reference to Fig. 1 shows that Y is equal to $+10$ for the p-type sample and therefore the sign of the field effect must be p type in contradiction to the data of PMD. For the n-type sample Y is equal to -10 and the field-effect mobility is n-type in agreement with the data.

The negative results of the channel experiments are in agreement with this model since $|Y|$ would have to be greater than 25 before a channel could be easily observed on either the *pnp* or *npn* structure.

IV

Figure 3 shows the configuration of the energy bands at the surface for an n- and p-type crystal when the neutral point of the band of surface states is approximately 0.23 ev below the center of the forbidden gap. For the n-type sample, Y is equal to -19; for the p-type sample, Y is equal to one. Reference to Fig. 2 shows that it would be possible to have an n-type field-effect mobility at the surface of the n-type crystal. Since Fig. 2 was drawn using the bulk values of the mobilities, the true minimum in σ will lie at more negative values of Y. This change in the minimum is due to the reduction in the mobility of the holes which are drawn into the region of space charge. These holes move in a very narrow potential well and undergo diffuse scattering at the surface in addition to conventional volume scattering. Although the number of holes is determined by Y, their contribution to the conductivity is determined by the width of the region of space charge. The electron mobility is unchanged at these values of Y, since we are only counting the number of electrons removed.

The value of Y for the p-type sample is about one, indicating a p-type field-effect mobility. As with the previous model of Fig. 1, this is in contradiction to the data of PMD.

The p-type sample with Y equal to one will not form a channel across an *npn* structure, so the final problem which remains is to examine why the n-type sample will not form a conductive p-type layer across the *npn* structure. The maximum value of the conductivity of the holes in the region of space charge is about 2×10^{-8} mho/square at $Y=-19$. This value was computed using the bulk value of the hole mobilities. If one takes into account diffuse scattering at the surface, the above value of σ should be reduced by an order of magnitude and PMD would not have been able to detect this conductivity. If the surface band of states were to lie somewhat closer to the center of the gap it would be impossible to detect the channel. It would be necessary for the center of the surface band of states to lie at least 0.30 ev below the center of the gap in order to simply detect the presence of the channel. There are two ways to overcome this difficulty: the first would require the use of intrinsic silicon; the second would achieve the same result by heating the sample to above room temperatures. This latter method would bring the Fermi level closer to the center of the

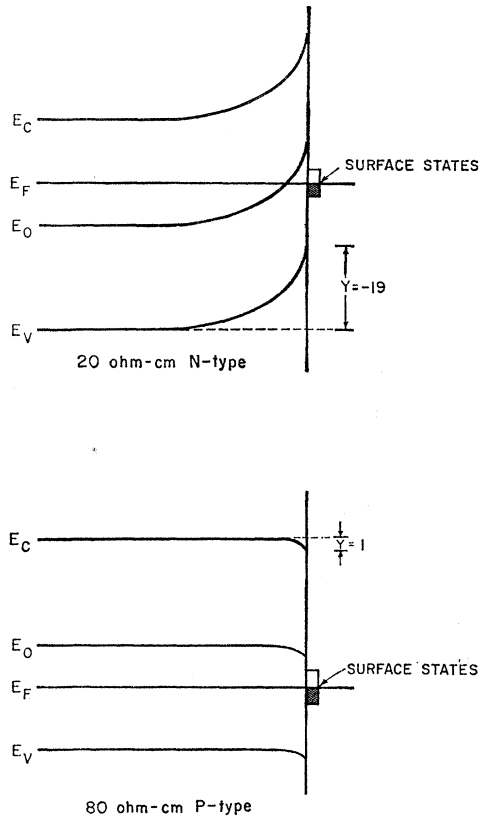

FIG. 3. Configuration of the energy bands at the surface with the neutral point of the surface states 0.23 ev below the center of the forbidden-energy gap.

TABLE I. Comparison of experimental results with predictions of the two models.

Sample type	Type of experiment	Result	Agreement with the model of surface states at the center of the gap	Agreement with the model of surface states 0.23 ev below the center of the gap
p	Field effect	n-type field effect mobility	No	No
n	Field effect	n-type field effect mobility	Yes	Yes
p	Cleavage across an *npn*	No observed channel	Yes	Yes
n	Cleavage across a *pnp*	No observed channel	Yes	Yes

gap, and increase the equilibrium density of holes in the volume, relative to the number of electrons.

Table I shows the agreement of the experimental data with the predictions of the two models. Both models describe the data equally well. Since the results of the work function and photoelectric-threshold data can be explained only by surface states whose neutral point lies below the center of the forbidden gap, it seems much more reasonable to choose this model to explain the data of PMD.

There remains the question: Why is it that neither model can explain the n-type field-effect mobility observed on the p-type sample? The answer lies in the number of very difficult problems which need to be surmounted before a reliable field-effect experiment may be performed on a cleaved surface. Banbury reported,[8] contrary to all other work,[9–11] an n-type field-effect mobility for the cleaved germanium surface which was insensitive to the admission of oxygen. His spurious results can be explained by the presence of capacitive coupling between his very large field-effect plate and parts of the sample surface which were uncleaved. It is possible that PMD may have had the same difficulty. PMD might argue that the same experimental apparatus was used for their silicon as for their germanium experiments.[9] For germanium they found results that were in good agreement with the model of a large p-type space-charge region.[10] Unfortunately one cannot compare the two experiments since spurious effects which may be dominant in the silicon experiment are probably negligible in the germanium experiment. In the germanium-cleavage experiment, the surface layer had a conductivity one to two orders of magnitude greater than the volume conductivity and therefore a major fraction of the current passed through the surface of interest. For the silicon cleavage experiment, the situation is different: The surface conductivities of the cleaved and uncleaved portions are of about the same order of magnitude and could contribute equally to the field-effect mobility. Examination of Fig. 1 of reference 9 will show that there will be appreciable capacitive coupling of the field plate to noncleaved portions of the surface.

Using the model of the surface shown in Fig. 3, it is also possible to explain why no large changes in conductivity were observed when oxygen was admitted to the homogeneous cleaved crystals of PMD. If one assumes that oxygen tends to make V approach zero [the flat band condition], then it is obvious that one should see almost no change for the p-type sample shown in Fig. 3. For the n-type sample the addition of oxygen would cause V to be reduced in absolute magnitude perhaps by half. Reference to Fig. 2 shows that a change in the magnitude of V by about ten units would increase the conductivity per square of the specimen by only one or two micromhos, which is probably too small to be detectable in the PMD experiments. This would be especially true if one used the results of oxygen admission on cleaved germanium samples as a guide.[9] Cleaved germanium surfaces show large decreases in conductance when exposed to oxygen, whereas in the model discussed here one should look for small increases in n-type samples.

It should be pointed out that the reasoning used above to show that the neutral point of the surface states lies below the center of the gap could equally well explain the experimental results of PMD by having the neutral point 0.23 ev above the center of the gap with an inversion of the roles played by holes and electrons. We see that, for the samples used, the neutral point of the surface states is indeterminate to ± 0.23 ev. However, these samples do offer the opportunity of observing the conductivity carriers in surfaces states directly and this point will be discussed in the next section.

V

It has been pointed out by Shockley[12] that the surfaces of diamond-type crystals should have a band of localized states in the forbidden gap. The number of states is approximately equal to twice the number of surface atoms, since for each surface atom one state has been removed from the valence band and one state from the conduction band. This surface-state band will be approximately half-filled by the electrons forced out of the valence band. In the ideal case this statement would imply that the surface is conductive. The filling of this surface band would also depend upon its position relative to the Fermi level. However, the change in charge due to bending of the energy bands at the surface will be relatively small compared to the number of electrons already present. The magnitude of the charge trapped in the surface due to bending of the energy bands is usually of the order of 10^{11} to $10^{13}/\text{cm}^2$ and this represents only 10^{-4} to 10^{-2} of the charge already present in the surface band. Thus if the surface state band gives rise to a conductivity, the number of carriers can be considered equal to the number of surface atoms.

The experiments of PMD now afford the opportunity to estimate an upper bound for the conductivity of charge in surface states. Reference to Fig. 3 shows that if a p-type silicon sample of the proper resistivity is chosen there will be no region of space charge or any additional conductivity associated with it. In the ideal case any additional conductivity which would be observed upon cleavage would be associated with the surface states. The cleavage experiments of PMD on p-type silicon nearly fulfill these requirements. They

[8] G. A. Barnes and P. C. Banbury, J. Phys. Chem. Solids **8**, 111 (1959).
[9] D. R. Palmer, S. R. Morrison, and C. E. Dauenbaugh, J. Phys. Chem. Solids **14**, 27 (1960).
[10] P. Handler and W. Portnoy, Phys. Rev. **116**, 516 (1959).
[11] R. Forman, Phys. Rev. **117**, 698 (1960).
[12] W. Shockley, Phys. Rev. **56**, 317 (1939).

found essentially no change in conductivity in their homogeneous crystal-cleavage experiments with the admission of oxygen. This result must be contrasted with the large change in work function upon oxygen admission which is observed by Gobeli and Allen.[3] The magnitude of the work function change is approximately 0.5 to 0.6 ev and certainly indicates that a chemical reaction has taken place with an appreciable amount of electron transfer. One would also assume that the nature of the silicon-oxygen surface would be such that any conductive mechanisms which might take place would be orders of magnitude smaller than that expected for the clean cleaved-silicon surface. Since PMD would have been able to see changes greater than one micromho/square, an upper limit may be set on the mobility of the electrons in the surface band of states.

$$\mu_{ss}=\sigma_s/qN_s<0.01 \text{ cm}^2/\text{vsec}, \quad (4)$$

where q is the electronic charge, σ_s is the conductivity per square and N_s is the density of atoms on a (111) surface. If there are no peculiar effects due to the nature of the junctions, the cleavage experiments on the *npn* structure allow one to set the upper bound of μ_{ss} two orders of magnitude lower since PMD claimed they could detect a conductance of 10^{-8} mho. Using this value for σ_s the upper bound for μ_{ss} is less than 10^{-4} cm^2/volt sec.

These extremely low values of the surface state mobility may arise from experimental artifacts. However, if experimental difficulties are excluded, it suggests that the overlap of the nonbonding orbitals of adjacent-surface atoms is very small. Thus if a Shockley-type band were to exist it would have to be very narrow. These results have great theoretical significance but the experiments will have to be repeated with this problem in mind before any conclusions can be reached. As an alternative explanation it may be assumed that the states which have been removed from the valence band do not coalesce with those removed from the conduction band. In this model the lower band would be full while the upper band would be empty. No conduction would be expected. This splitting of the surface states into two sets may arise by adjacent surface atoms bonding to each other directly or through the lattice. The resolution of these problems calls for additional experimental work.

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Electron Spin Resonance in Antimony

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Electron spin resonance of conduction electrons in antimony has been investigated at 34.3 kMc/sec and 1.5°K. The results were consistent with the theory of Cohen and Blount for the g factor of conduction electrons in Bi and Sb. The principal axes of the g tensor coincided with those of the tilted-ellipsoidal Fermi surface. The parameters of the electron spin resonance were determined to be $g_1=3.4$, $g_2=29.5$, $g_3=3$. Resonance was also observed from transitions that involved both an orbital transition and a Zeeman transition.

I. INTRODUCTION

THE g factor of conduction electrons in antimony was shown by Cohen and Blount to be large for orientations of an antimony crystal in a magnetic field when the spin-orbit coupling was large compared to the band gap.[1] This theory was followed by the observation of a large g factor for one orientation of antimony.[2] The present paper reports an experimental study of electron spin resonance in antimony with the purpose of presenting values of the parameters of the g factor for antimony.

When an antimony crystal is in a magnetic field, there may be four different electronic transitions between energy levels caused by Landau and Zeeman splitting. The transitions are shown in Fig. 1 where

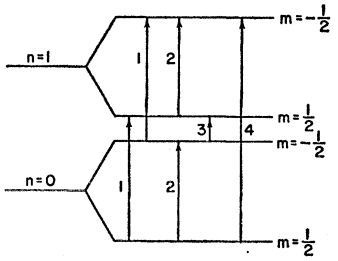

FIG. 1. Energy level diagram showing the Zeeman splitting of Landau levels $n=0$, 1 for conduction electrons in antimony.

[1] M. Cohen and E. I. Blount, Phil. Mag. **5**, 115 (1960).
[2] G. E. Smith, J. K. Galt, and F. R. Merritt, Phys. Rev. Letters 4, 276 (1960).