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Field Effect on an Illuminated Ge Surface and Investigation of the Surface Recombination Process

SHYH WANG AND GEORGE WALLIS
Sylvania Electric Products, Incorporated, Woburn, Massachusetts

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Surface conductance, photoconductance, and field effect were measured in the Brattain-Bardeen ambient cycle on germanium surfaces etched with CP-4. From the surface-conductance measurement, values of surface potential were deduced, and from the photoconductance measurement, relative changes of surface recombination velocity were obtained. By analyzing the change of surface recombination velocity as a function of surface potential, dominant recombination centers with discrete levels were found near the center of the gap with a ratio of hole to electron capture probabilities of 9. The energy levels of these centers were found to be consistent with the field-effect data. In addition, the effect of a normal ac field upon an illuminated sample was examined. The results can be interpreted as a superposition of the changes in the photoconductance and the surface conductance due to the field-induced change in surface potential. This effect can be used to determine the value of trap energy and the ratio of capture probabilities to a greater degree of accuracy than can the surface recombination velocity. Possible other applications of the effect are discussed.

INTRODUCTION

RECENT work by Stevenson and Keyes[1] and by Many and co-workers[2] has established the applicability of Shockley and Read's model of the carrier recombination process[3] to germanium surfaces. By measuring simultaneously the surface conductance and surface recombination velocity, Many *et al.* deduced the energy levels and the ratios of capture probabilities of the recombination centers. The surface potential was changed by the application of a high electric field normal to the germanium surface.[4]

We too have investigated the surface recombination velocity as a function of surface potential on germanium surfaces, and we have confirmed some of the results obtained by Many *et al.* In addition, we have studied the effect of a small ac field applied normal to the surface of an illuminated filament. This will be referred to as the field effect under illumination and is interpreted as a superposition of the changes in photoconductance and surface conductance as a result of the field-induced change in surface potential.

We modified the surface potential by the Brattain-Bardeen ambient cycle.[5] In addition to the measurements of (1) surface conductance, (2) photoconductance, and (3) small-signal ac field-effect conductance, we also measured the ac field-effect conductance under illumination.

From (1) and (2), the surface recombination velocity was plotted as a function of the surface potential. A theoretical fit to the plot gave the energy level and the ratio of the capture probabilities of the recombination centers. The sign of the field effect indicated whether the surface was *n* or *p* type, and its magnitude measured the small change in surface potential due to the applied field. Using the results obtained from (1), (2) and (3), the field effect under illumination was calculated as a function of surface potential and compared with the experimental results.

REVIEW OF SURFACE RECOMBINATION PROCESS

According to Shockley and Read's theory of recombination through traps,[3] the rate of recombination depends upon the state of occupancy of these traps. On a semiconductor surface the occupancy of the traps and hence the surface recombination velocity are controlled by the surface potential. Many *et al.*[2] have applied Shockley and Read's formula to a semiconductor and expressed the surface recombination velocity, v_s, as

$$v_s=\frac{N_t(c_nc_p)^{\frac{1}{2}}(n_0+p_0)/2n_i}{\cosh[(E_t-E_i-q\varphi_0)/kT]+\cosh[q(\varphi_s-\varphi_0)/kT]},\tag{1}$$

where $\varphi_0=(kT/2q)\ln(c_p/c_n)$, c_p and c_n are the capture probabilities per state per unit time for holes and electrons, respectively, p_0 and n_0 are the bulk hole and electron concentration, respectively, n_i is the intrinsic carrier concentration and N_t is the number of states per unit area. E_t-E_i is the difference between the trap energy and the intrinsic Fermi level at the surface and is measured in electron volts. The quantity $q\varphi_s/kT$ is defined as $Y-\ln(p_0/n_i)$, where kTY/q is the surface potential in volts. The energy level diagram is shown in Fig. 1.

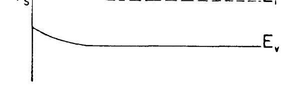

FIG. 1. Energy level diagram of germanium surface.

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[1] D. T. Stevenson and R. J. Keyes, Physica **20**, 1041 (1954).

[2] Many, Harnik, and Margoninski, paper presented at the Semiconductor Surface Conference, Philadelphia, 1956 (to be published).

[3] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

[4] Similar work was done by H. K. Henisch and W. N. Reynolds, Proc. Phys. Soc. (London) **B68**, 353 (1955); P. C. Banbury and J. D. Nixon, Proc. Phys. Soc. (London) **B69**, 487 (1956).

[5] W. H. Brattain and J. Bardeen, Bell System Tech. J. **32**, 1 (1953).

Equation (1) predicts that v_s has a maximum value at $\varphi_s=\varphi_0$. A plot of v_s as a function of φ_s gives the values of $|E_t-E_i-q\varphi_0|$ and c_p/c_n. Equation (1) applies only if one assumes a single trap or a pair of traps having the same φ_0 and spaced symmetrically around $q\varphi_0/kT$. A detailed fitting to Eq. (1) is required to check these assumptions.

MEASUREMENT OF v_s BY PHOTORESPONSE

The conventional way of measuring v_s is by the photodecay method.[1] A simpler and more accurate way is to measure the relative photoresponse. When a germanium slab of thickness a is uniformly illuminated at one face by nonpenetrating light, the steady state photoconductance (excess conductance under illumination) is given by[6]

$$G_L=\frac{KL[\cosh(a/L)-1+\beta\sinh(a/L)]}{v_s[(1+\beta^2)\sinh(a/L)+2\beta\cosh(a/L)]}, \qquad (2)$$

where $L=(D\tau)^{\frac{1}{2}}$, $\beta=D/Lv_s$, $D=(n_0+p_0)D_nD_p/(n_0D_n+p_0D_p)$, and K is a proportionality constant. If the bulk lifetime, τ, is sufficiently long, such that $a/L<1$, then Eq. (2) can be reduced to

$$G_L=K[1/\tau+2v_s/a]^{-1}. \qquad (3)$$

By substituting v_s from Eq. (1) into Eq. (3), the photoconductance can be expressed as

$$G_L=\frac{K\tau\{C+\cosh[q(\varphi_s-\varphi_0)/kT]\}}{C+B+\cosh[q(\varphi_s-\varphi_0)/kT]}, \qquad (4)$$

where

$$C=\cosh[(E_t-E_i-q\varphi_0)/kT], \qquad (5)$$

$$B=(C+1)[\tau-(\tau_{\text{eff}})_{\min}]/(\tau_{\text{eff}})_{\min}, \qquad (6)$$

$$1/(\tau_{\text{eff}})_{\min}=1/\tau+2(v_s)_{\max}/a, \qquad (7)$$

and

$$(v_s)_{\max}=N_t(c_nc_p)^{\frac{1}{2}}(n_0+p_0)/2n_i(C+1). \qquad (8)$$

The term $(\tau_{\text{eff}})_{\min}$ is determined experimentally by the photodecay method. In Eq. (4), C and φ_0 are the only parameters and can be evaluated from a fit to the experimental curve of G_L *versus* φ_s.

FIELD EFFECT UNDER ILLUMINATION

Application of an electric field normal to a dark semiconductor surface changes φ_s and hence, the surface conductance on account of the induced surface charge. This is known as the field effect.[7-9]

When a semiconductor slab is under illumination, the field changes not only the surface conductance, G_s, but the photoconductance, G_L, as well. The effect upon the latter is due to a change in v_s as a result of the field-induced change in φ_s.[10] In the following discussion the applied ac field is assumed to be a small perturbation of the original surface potential.

The relationship between the dark surface conductance, G_s, and φ_s has been derived by Garrett and Brattain.[11] For a small change in φ_s, the corresponding change in G_s is given by

$$(\Delta G_s)_{\text{F.E.}}=(\partial G_s/\partial\varphi_s)\Delta\varphi_s. \qquad (9)$$

In the above equation, $(\partial G_s/\partial\varphi_s)$ is a function of E_f and φ_s and can be derived by differentiating Eq. (22) in Garrett and Brattain's paper.[12] The change in photoconductance due to a field-induced change in φ_s can be written as

$$(\Delta G_L)_{\text{F.E.}}=(\partial G_L/\partial\varphi_s)\Delta\varphi_s. \qquad (10)$$

The total change in conductance of a sample under illumination due to a normal field is primarily the sum of the above effects,

$$(\Delta G)_{\text{F.E.}}=(\Delta G_s)_{\text{F.E.}}+(\Delta G_L)_{\text{F.E.}}. \qquad (11)$$

However, the term $(\Delta G_s)_{\text{F.E.}}$ in Eq. (11) might be different from that in Eq. (9) on account of the added surface carriers created by light. For sufficiently weak illumination, this effect is small. The same conclusion applies to $\Delta\varphi_s$ is Eqs. (9) and (10). Experimentally, the dark field-effect conductance, $(\Delta G_s)_{\text{F.E.}}$, and the field-effect conductance under illumination, $(\Delta G)_{\text{F.E.}}$, were measured, and $(\Delta G_L)_{\text{F.E.}}$ was obtained by subtracting the former from the latter.

The expression,

$$\frac{(\Delta G_L)_{\text{F.E.}}}{G_L}=\frac{B\sinh[q(\varphi_s-\varphi_0)/kT]}{\{C+B+\cosh[q(\varphi_s-\varphi_0)/kT]\}\{C+\cosh[q(\varphi_s-\varphi_0)/kT]\}}\frac{q\Delta\varphi_s}{2kT}, \qquad (12)$$

contains three parameters C, φ_0, and $\Delta\varphi_s$.[13] The quantities C and φ_0 are obtained from the photoconductance measurement. The quantity $\Delta\varphi_s$ is evaluated from Eq. (9) by measuring the dark field-effect conductance. The right-hand side of Eq. (12) is then calculated as a function of φ_s and compared with the measured value of $(\Delta G_L)_{\text{F.E.}}/G_L$.

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[6] This expression, valid for small signals only, is obtained by integrating over the sample the solution of W. van Roosbroek's one dimensional, ambipolar transport equation [Phys. Rev. **91**, 282 (1953)]. Similar expressions have been obtained by H. M. Bath and M. Cutler, Phys. Rev. **100**, 1259(A) (1955), and by L. H. Hall, Phys. Rev. **97**, 1471 (1955).

[7] W. Shockley and G. L. Pearson, Phys. Rev. **74**, 232 (1948).

[8] C. G. E. Low, Proc. Phys. Soc. (London) **B68**, 10 (1955).

[9] W. L. Brown, Phys. Rev. **100**, 590 (1955).

[10] Essentially the same interpretation of the field effect under illumination was given recently by W. H. Brattain and C. G. B. Garrett, Bell System Tech. J. **35**, 1019 (1956).

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

[12] See the Appendix of the present paper.

[13] The factor $\frac{1}{2}$ in Eq. (12) arises because the ac field is applied to only one surface.

EXPERIMENTAL PROCEDURES AND RESULTS

A germanium slab, 0.04 cm thick, was cut from an *n*-type single crystal of resistivity 35 ohm-cm and bulk lifetime 800 microseconds. The surface orientation was close to the (110) plane. The slab had side legs used as potential probes in the surface conductance measurement. The sample was etched in CP-4, and the leads were soldered to the copper-plated ends. The first run was made several hours after etching.

During the experiment, φ_s was altered by changing the ambient gas as in the Brattain-Bardeen cycle,[5] (ozone, dry oxygen, dry and wet nitrogen). The sample was put in a double-walled glass tube permitting water to circulate from a constant temperature bath regulated at 29°C, which also controlled the temperature of the gas. In addition, the circulating water served to filter out the penetrating radiation. A big block of another sample, cut from the same crystal, was used as a thermometer, and any conductance change of the test sample due to temperature drifts was corrected. The temperature drift during a run was within ±0.05°C. The conductance value was measured to five significant figures.

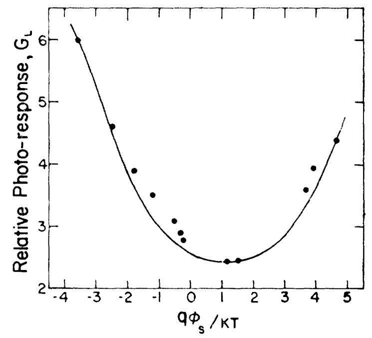

FIG. 2. Photoconductance, G_L, *versus* $q\varphi_s/kT$. Solid curve represents fit of Eq. (4) to experimental points with $C=8$, $q\varphi_0/kT=1.1$

In the measurement of the field effect under illumination, light was shone steadily at one surface, and an ac field was applied to the other surface. The same light source was used in the photoconductance measurement but was chopped at 60 cps. The photoconductance method of measuring the effective lifetime was periodically checked against the photodecay method. For the field-effect measurement, a 32-cps sinusoidal voltage source was used to assure that the surface and the bulk semiconductor were in equilibrium with the applied field, and a peak field strength of 3×10^3 volts/cm was employed. The same measuring circuit was used as the one described in Low's paper.[8]

The following four measurements were made in rapid succession: (1) the surface conductance, G_s; (2) the small-signal field effect, $(\Delta G_s)_{\text{F.E.}}$; (3) the photoconductance, G_L; and (4) the field effect under illumination, $(\Delta G)_{\text{F.E.}}$. The value of φ_s was determined from a measurement of the increase in G_s with respect to its minimum value. In evaluating φ_s, the bulk mobility was used because Schrieffer's correction for the surface mobility[14] is not important within our experimental range of φ_s. In the calculations, we used the following experimental values: $n_0=4.53\times10^{13}$ cm^{-3}, $p_0=1.67\times10^{13}$ cm^{-3}, $\tau=800$ μsec and $(v_s)_{\max}=55$ cm/sec.

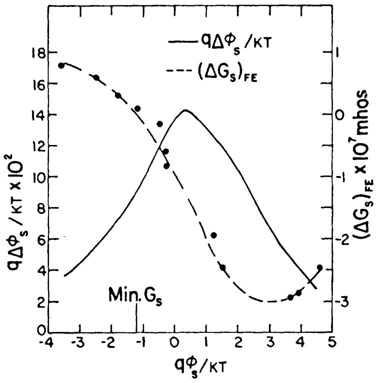

FIG. 3. Field-effect conductance, $(\Delta G_s)_{\text{F.E.}}$, *versus* $q\varphi_s/kT$ (dotted curve). $q\Delta\varphi_s/kT$ *versus* $q\varphi_s/kT$ (solid curve) which was calculated from the dotted curve.

In Fig. 2, experimental values of G_L for a typical run at 29°C are plotted against φ_s. The best fit of Eq. (4) to the experimental curve is obtained with $C=8$ and $q\varphi_0/kT=1.1$. This value of φ_0 corresponds to $c_p/c_n=9$.

In Fig. 3, the experimental value of $(\Delta G_s)_{\text{F.E.}}$ is plotted against φ_s (dashed curve). Using Eq. (9), $\Delta\varphi_s$ was calculated for various values of φ_s from the $(\Delta G_s)_{\text{F.E.}}$ plot and is shown as a solid curve. By substituting the values of $\Delta\varphi_s$ from Fig. 3 and the experimental values of C and φ_0 into Eq. (12), $(\Delta G_L)_{\text{F.E.}}/G_L$ was calculated as a function of φ_s and is shown as solid curve in Fig. 4. The dots represent the experimental values of $(\Delta G_L)_{\text{F.E.}}/G_L$. The agreement between experiment and theory is gratifying.

Measurements were also made on another *n*-type single crystal (35 ohm-cm, $\tau=1700$ microseconds) and on a *p*-type single crystal (18 ohm-cm, $\tau=220$ microseconds). The experiment was repeated several times for each sample. Although the value of maximum surface recombination velocity changed slightly from one run to the next, substantially the same values of C and φ_0 were obtained.

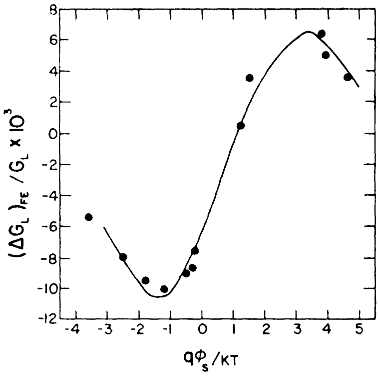

FIG. 4. $(\Delta G_L)_{\text{F.E.}}/G_L$ *versus* $q\varphi_s/kT$. The theoretical curve (solid) was calculated fom Eq. (12), using $C=8$, $q\varphi_0/kT=1.1$ and $q\Delta\varphi_s/kT$ from Fig. 3.

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

DISCUSSION OF EXPERIMENTAL METHOD

The validity of the experimental method depends on the intensity of the illumination. Illumination of a semiconductor surface upsets the equilibrium carrier concentration at the surface and consequently, may change φ_s. Since φ_s was determined in the dark, it may not correspond to the φ_s at which the photoconductance and the field effect under illumination were measured. Apart from possible changes in φ_s, the added carrier concentration also affects the field effect such that the terms $\Delta\varphi_s$ and $(\Delta G_s)_{\text{F.E.}}$ in Eq. (9) are different from the corresponding terms in Eqs. (10) and (11). The light intensity must be adjusted so that the above changes are negligible. To this end, two criteria were used: (1) Photoconductance measurements were made using different light intensities. Since the same values of φ_0 and C were obtained, the light intensity was sufficiently low to have a negligible effect on φ_s. (2) Using Garrett and Brattain's analysis,[11] the quasi-Fermi levels were calculated for the observed photoconductance. Then, $\Delta\varphi_s$ and $(\Delta G_s)_{\text{F.E.}}$ were calculated for a dark and an illuminated sample. The results showed a maximum difference of ten percent between the two cases. Hence, the carrier concentration, generated by illumination, did not seriously affect the field effect measurement.

A comparison of $(\Delta G_L)_{\text{F.E.}}/G_L$ with G_L follows. In the region where v_s dominates τ_{eff}, i.e., B is much larger than C and $\cosh[q(\varphi_s-\varphi_0)/kT]$, Eq. (12) for a single-trap model can be reduced to

$$\frac{(\Delta G_L)_{\text{F.E.}}}{G_L}=\frac{\sinh[q(\varphi_s-\varphi_0)/kT]}{C+\cosh[q(\varphi_s-\varphi_0)/kT]}\frac{q\Delta\varphi_s}{2kT}. \tag{13}$$

Since the quantity $q\Delta\varphi_s/kT$ is independently determined from the field effect, the interpretation of the $(\Delta G_L)_{\text{F.E.}}/G_L$ curve depends only upon C and φ_0 but not upon N_t. On the other hand, the interpretation of the v_s curve depends critically on the assumption that N_t remains constant. Therefore, certain conclusions can be reached by comparing the behavior of the G_L and the $(\Delta G_L)_{\text{F.E.}}/G_L$ curve. (1) If the two curves can be fitted to their respective expressions, then one can conclude that the single-trap model is valid and N_t, E_t, and φ_0 remain invariant. (2) If the $(\Delta G_L)_{\text{F.E.}}/G_L$ curve, but not the G_L curve, can be fitted, then the single-trap model is still valid, E_t and φ_0 remain constant but N_t changes. (3) If neither curve can be fitted, then no unique interpretation is possible. Either the single-trap model is not valid or it is valid but E_t or φ_0 changes.

In general, it is preferable to determine the parameters C and φ_0 from the $(\Delta G_L)_{\text{F.E.}}/G_L$ curve rather than from the G_L curve because the former is more sensitive to these parameters. In particular, the point $\varphi_s=\varphi_0$ is sharply defined. In another application, one may use $(\Delta G)_{\text{F.E.}}/G_L$ as a measure of $\Delta\varphi_s/kT$ and φ_s provided B, C, and φ_0 are known for a given surface. Thus, $(\Delta G_L)_{\text{F.E.}}/G_L$ should give the same information about $\Delta\varphi_s$ as the conventional small-signal field effect, but should be superior in two respects: (1) The measurements can be preformed in a region of φ_s where $(\Delta G_L)_{\text{F.E.}}$ is an order of magnitude larger than $(\Delta G_s)_{\text{F.E.}}$; (2) The signal does not depend upon surface mobility. The effect, for instance, can be used to advantage in the study of the frequency behavior of the surface states.

DISCUSSION OF EXPERIMENTAL RESULTS

Most of the experimental uncertainty is in the determination of φ_s near the minimum surface conductance where small conductance changes correspond to large changes in φ_s. In this region the field-effect measurement is very sensitive to φ_s and served as a qualitative check on the surface conductance measurement. In view of the experimental uncertainties, the fits in Figs. 2 and 4 are considered to be gratifying. Therefore, within our experimental range of φ_s, the surface recombination process is predominantly controlled by traps with $c_p/c_n=9$ and $E_t-E_i=0.028\pm0.069$ ev. We have two possible choices of the sign owing to the nature of the hyperbolic cosine function in Eq. (5), and from the measurements we cannot deduce whether $E_t-E_i=0.097$ ev or/and -0.041 ev.

Information about fast surface states can be obtained from the field-effect data.[15,16] It is generally assumed that the fast surface states act as recombination centers. Therefore, a check was made whether the above recombination centers are consistent with the field-effect data. To this end, the rate of change of charge in the fast surface states, $\Delta Q_{ss}/\Delta\varphi_s$, as well as the change of charge, Q_{ss}, were deduced from the curves in Fig. 3 and are shown as dots and as dashed curve, respectively, in Fig. 5. The fit to the $\Delta Q_{ss}/\Delta\varphi_s$ points, shown as solid curve in Fig. 5, was calculated on the assumption of two pairs of traps: one pair corresponding to the recombination centers with $E_t-E_i=(1.1\pm2.8)kT$ and density 4×10^{10} cm^{-2}, and another pair of traps with $N_1\exp[-q(E_{t1}-E_i)/kT]=2.2\times10^8$ cm^{-2} and $N_2\exp[q(E_{t2}-E_i)/kT]=7.4\times10^8$ cm^{-2}. Judging from the fact that no appreciable deviation from the Boltzmann distribution was observed, $E_{t1}-E_i>6kT$ and $E_{t2}-E_i<-5kT$. In view of the experimental uncertainties, the fit is considered to be satisfactory.

The recombination center which was established in this work appears to be the same as the one found by Many *et al.*[2] on two samples, ($c_p/c_n=30$, $E_t-E_i=0.11$ ev). Although different techniques were employed in the two investigations, the results are in reasonable agreement. Notice that a ratio of 30 to 9 in c_p/c_n corresponds to a difference of 0.015 ev in $q\varphi_0$. Our value

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[15] H. C. Montogomery and W. L. Brown, Phys. Rev. **103**, 865 (1956).

[16] Bardeen, Coovert, Morrison, Schrieffer, and Sun, Phys. Rev. **104**, 47 (1956).

of $c_p/c_n=9$ is probably more accurate because it was obtained from both the G_L and the $(\Delta G_L)_{\text{F.E.}}$ measurements.

Garrett and Brattain[17] have interpreted their field-effect and photoconductivity data in terms of a continuous distribution of fast surface states. In their analysis, φ_s was determined by extrapolating graphically the truncated data on each separate set of the above measurements in conjunction with the field effect under illumination. The validity of such a procedure rests on the assumption that the fast-state distribution is unaffected by the gas changes in the Brattain-Bardeen cycle. It has been observed experimentally that the assumption may be violated in certain cases, as will be discussed later. Garrett and Brattain have reported a ratio of hole to electron probabilities of 150. Uncertainties in the measurement of φ_s are presumably responsible for the spread in the reported values of φ_0, although differences in sample preparation and orientation may to a lesser extent contribute to the discrepancies.

There appears to be good agreement between our field-effect data and those of Montgomery and Brown[15] as indicated by the similarity in the shape of their Q_{ss} *versus* φ_s curve and ours. The energy levels of the discrete surface states near the center of the gap are $E_t-E_i=(1\pm2)kT$ according to Montgomery and Brown as compared to our value of $(1.1\pm2.8)kT$ Our Q_{ss} curve is different from the corresponding curve by Bardeen *et al.*[16] At least in part, the discrepancy may be due to the use of the Schrieffer correction[14] by Bardeen *et al.*, which was not taken into consideration by Montgomery and Brown and by us.

The surface states at $(E_t-E_i)>6kT$ and at $(E_t-E_i)<-5kT$ which we deduced from our field-effect measurements may be compared with surface states deduced in a similar way by Montgomery and Brown at $E_t-E_i=(1\pm7)kT$ and by Bardeen *et al.* at $E_t-E_i=-5kT$ to $-6kT$. The same surface states have been calculated from channel measurements by Statz *et al.*,[18,19] at $E_t-E_i=-5.5kT$ and at $E_t-E_i=5$ to $7kT$. Apparently, the same states have also been deduced from their surface recombination studies by Many *et al.*,[2] at $E_t-E_i=-9kT$. In our measurements of surface recombination velocity, however, the range of φ_s was limited to the observation of traps near the center of the gap.

In some of our measurements, there was a difference between the point where $(\Delta G_L)_{\text{F.E.}}$ was zero and the point where G_L was a minimum. Possibly, a difference in the φ_s values of the two surfaces is responsible for the discrepancy. $(\Delta G_L)_{\text{F.E.}}$ measures only the properties of the surface to which the field is applied while G_L measures the combined properties of both surfaces. Also, the ambient gas might change the trap density and thus affect the G_L curve but not the $(\Delta G_L)_{\text{F.E.}}/G_L$ curve. We have observed experimentally that both of these effects occur occasionally. On one sample we measured the field effect simultaneously on both surfaces and found that during a Brattain-Bardeen cycle the two signals did not change at the same rate. During a run shortly after etching, we obtained a G_L curve which could not be analyzed meaningfully whereas the simultaneously measured $(\Delta G_L)_{\text{F.E.}}/G_L$ curve was behaving as expected. This was interpreted as a clear-cut indication that the trap density had changed during the run.

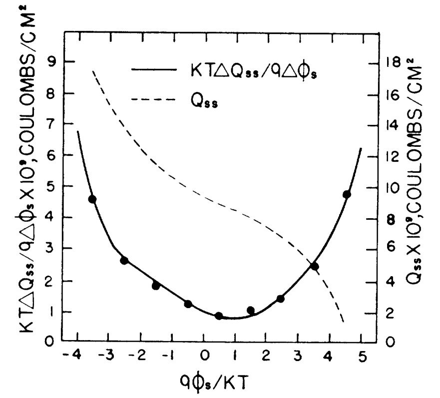

FIG. 5. Rate of change of charge in surface states, $kT\Delta Q_{ss}/q\Delta\varphi_s$, *versus* $q\varphi_s/kT$. The dots were derived from the experimental data shown in Fig. 3. The solid curve was calculated by assuming a distribution of fast surface states as discussed in the text. The dashed curve represents the changes in charge in the fast surface states, Q_{ss}.

An attempt was made to extend the range of φ_s by employing high humidity ambients and discharge in oxygen over prolonged periods of time. However, under such severe ambient conditions, the surface conductance measurement became erratic. The effect of baking in air at 85°C was also examined. Although the value of $(v_s)_{\max}$ was increased by a factor of two after seventy hours of baking, the same values for $q\varphi_0/kT$ and C were observed. Therefore, it appears that baking does not introduce new recombination traps but simply increases the density of the original traps.

CONCLUSIONS

In the investigation of photoconductance as a function of φ_s, a detailed comparison between theory and experiment has been made. Over a range in φ_s of $8kT$, surface recombination centers have been identified which have a ratio of hole to electron capture probabilities of 9 and $|E_t-E_i-0.028|=0.069$ ev. Moreover, it has been found that aging at room temperature and baking at 85°C in air only changes the trap density but does not introduce new types of traps.

From the field-effect data, the charge in the fast

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[17] C. G. B. Garrett and W. H. Brattain, Bell System Tech. J. **35**, 1041 (1956).

[18] Statz, de Mars, Davies, and Adams, Bull. Am. Phys. Soc. Ser. II, **1**, 322 (1956).

[19] Statz, de Mars, Davies, and Adams, Phys. Rev. **101**, 1272 (1956).

surface states was plotted as a function of surface potential. The plot can be fitted by two pairs of surface state groups. One group corresponds to the above recombination centers and the other group, having a larger density of states, is at least $5kT$ above and below the intrinsic Fermi level. Within our experimental range of φ_s, the latter group seems to have a negligible effect upon the surface recombination process.

The effect of a small ac field applied normal to the surface of an illuminated sample has been examined. The results can be interpreted as a superposition of (1) a change of surface conductance and (2) a change of photoconductance as a result of the field-induced change in φ_s. Good agreement between theory and experiment has been obtained. The effect can be used as an additional tool to investigate the surface recombination centers.

APPENDIX

Garrett and Brattain[11] expressed the surface conductance as

$$G_s = q(\mu_p \Gamma_p + \mu_n \Gamma_n),$$

where Γ_p and Γ_n are the surface excesses of holes and electrons. For a small change in φ_s,

$$\Delta G_s = (\partial G_s/\partial Y)\Delta Y = -[\epsilon\epsilon_0 kTn_i/8\pi]^{\frac{1}{2}} F^{-1} \times [\mu_p \lambda(e^{-Y}-1) + \mu_n \lambda^{-1}(e^{Y}-1)]\Delta Y,$$

where

$$F = \pm[\lambda(e^{-Y}-1) + \lambda^{-1}(e^{Y}-1) + (\lambda - \lambda^{-1})Y]^{\frac{1}{2}},$$

$$Y = q\varphi_s/kT + \ln\lambda, \quad \text{and} \quad \lambda = p_0/n_i.$$

If one knows λ, $(\partial G_s/\partial Y)$ can be calculated as a function of φ_s.

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R-Center Production in Alkali Halides

G. R. Cole* and R. J. Friauf
University of Kansas, Lawrence, Kansas

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The suggestion that both the R_1 and R_2 bands in colored KCl crystals may be due to transitions of the F_2 center is considered. Formation mechanisms in support of this view are presented which are consistent with (1) the behavior of the R and M bands during F-light irradiation, (2) the observed decrease of the R bands and increase of the M band produced by heating, and (3) the photoconductivities measured for the R_1 and R_2 bands.

HERMAN, Wallis, and Wallis[1] have shown that the intensity ratio of the R_1 to R_2 bands in colored potassium chloride is essentially constant over a wide range of conditions. They point out that if, as is currently accepted,[2,3] the R_1 band is due to a transition of the F_2^+ center and the R_2 band is due to a transition of the F_2 center, prolonged F-light irradiation and consequent production of conduction electrons would tend to increase the intensity of the R_2 band and decrease that of the R_1 band. Furthermore their theoretical calculations indicate that the center composed of two electrons trapped by two adjacent negative-ion vacancies, called an F_2 center, might well be responsible for *both* R bands.[4] This suggestion is supported by a more detailed consideration of formation mechanisms.

The most direct mechanisms by which an F_2^+ center could be formed by conduction electrons freed from F centers[5] involve clusters containing two negative-ion vacancies. The possibilities appear to be: (1) an electron is captured by two adjacent negative-ion vacancies, but such trapping centers should be very rare in the lattice. (2) An electron is captured by a neutral vacancy pair plus a negative-ion vacancy, but this forms an M center. (3) An electron is captured by a neutral vacancy quartet, followed by expulsion of a positive-ion vacancy, again forming an M center. Following either (2) or (3), the M center could trap another electron and expel another positive-ion vacancy, thus forming an F_2 center. Positive ion vacancy expulsion processes have been suggested by Seitz[2,3] as a mechanism of F-center production when x-ray photoelectrons are trapped by neutral vacancy pairs.

This mechanism of M- and F_2-center formation is in accord with the observed initial increase of the M band

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* Present address: Savannah River Laboratory, E. I. du Pont de Nemours Company, Aiken, South Carolina.

[1] Herman, Wallis, and Wallis, Phys. Rev. **103**, 87 (1956).

[2] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[3] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[4] At the Color Center Symposium held at Argonne National Laboratory October 31–November 2, 1956, J. Lambe and W. D. Compton described a temporary bleaching of the R_1 band in NaCl at 77°K by intense illumination in this band; the illumination did not affect the R_2 band, thus indicating that two different centers may be responsible for these transitions. Nonetheless the remarks in this paper still seem pertinent to the attempt to understand the optical and thermal transformations of these centers and their photoconductive properties.

[5] That such mechanisms are responsible for R- and M-band production, rather than transport of vacancy clusters to F centers, is indicated by the work of M. Ueta and W. Känzig, Phys. Rev. **94**, 1390 (1954), concerning the influence of plastic strain on R- and M-band formation.