Surface Effects in Electron-Irradiated Ge at 80°K*

WALTER E. SPEAR†
Purdue University, Lafayette, Indiana
(Received June 23, 1958)

Photoconductivity, surface conductance, Hall and field effect measurements have been made before and after electron irradiations. Before irradiation, both *n*- and *p*-type specimens show a photoconductive shoulder in the range of photon energies between 0.70 and 0.55 ev, which is connected with a surface effect. Irradiation with energies below the threshold for the introduction of volume defects (about 400 kev) quenches the photoconductivity in the shoulder and causes an increase in surface conductance in *n*-type, and a decrease in *p*-type specimens. 4.5-Mev irradiations (a) extend the shoulder to about 0.49 ev and (b) introduce a sharp peak at 0.39 ev. Both features are due to electronic transitions in the surface region. Field effect measurements with steady fields and a superimposed alternating potential indicate that the shoulder is connected with transitions from the valence band into a group of slow surface states lying between 0.70 and 0.58 ev above the valence band. Irradiation below 400 kev increases the surface potential Y until, in *n*-type specimens, the Fermi level passes through a high concentration of fast states within 0.05 ev of the conduction band. 4.5-Mev irradiations decrease Y; transitions to a second group of slow states lying between 0.4 and 0.2 ev above the valence band can now take place.

I. INTRODUCTION

ALTHOUGH volume defects introduced in Ge by electron irradiation have been studied in comparative detail,[1,2] little attention appears to have been given to the effect of irradiation on the Ge surface. In this paper an attempt is made to correlate the results of photoconductivity, surface conductance, Hall and field effect measurements in order to gain some understanding of the surface changes taking place during irradiation. The experiments were all carried out at 80°K and the above parameters were measured as a function of the incident electron flux at a number of widely different electron energies.

The irradiation experiments have been divided into two groups. The first, which will be referred to as "low-energy irradiations," comprises experiments with incident electron energies up to 300 kev.[3] It has been shown[4,5] that the threshold for the introduction of volume defects in Ge lies around 400 kev. Thus low-energy irradiations are unlikely to produce volume defects and should not cause any change in the position of the Fermi level within the specimen. The second group, the "high-energy irradiations," includes experiments with 4.5-Mev electrons; volume defects are now introduced. The photoconductive changes after 4.5-Mev irradiation have been investigated by Stöckmann *et al.*[2,6] who interpreted their results in terms of transitions between volume defect centers and the bands. The present investigation, originally suggested by this work, shows, however, that surface rather than volume effects are responsible for the observed photoconductive changes.

II. EXPERIMENTAL DETAILS

Most experiments were made on Sb-doped *n*-type, and Ga-doped *p*-type material. Specimen resistivities ranged from 10 to 22-ohm-cm at room temperature. The samples were ground to the form of a thin plate with surface area of 6×2 mm; the thicknesses ranged from 80μ to 850μ. After etching in *CP*4, the specimens were fitted with Hall probes, potential and current leads. Throughout the experimental run the specimen was kept in a vacuum of about 5×10^{-6} mm of Hg. All irradiations, as well as electric, magnetic, and optical measurements could be carried out without breaking the vacuum.

The photoconductivity experiments were made with steady illumination, and a dc potentiometer was used to measure the change in conductance. The optical arrangement consisted of a Perkin-Elmer monochromator and a mirror system focusing the light on to the specimen. The complete optical path was enclosed by a light-tight box. In all measurements, the spectral resolution at wavelengths in the 2μ region was about 0.07μ at half-width. A Ge filter was used for measurements beyond the fundamental absorption edge. In the range from 1.1μ to the absorption edge a Si filter was employed.

Field effect measurements were made at various stages during high- and low-energy irradiations. The field was applied by a thin Ge electrode separated from the front surface of the specimen by a 25μ Mylar spacer. The irradiations and some of the photoconductive measurements at wavelengths beyond the absorption edge were made through this electrode. For experiments in conjunction with 25-kev irradiations a 1μ Al foil, stretched above the Ge surface, served as a field electrode.

* Work supported by the U. S. Atomic Energy Commission.
† Now at University of Leicester, Leicester, England.
[1] K. Lark-Horovitz, in *Semiconducting Materials*, edited by H. K. Henisch (Academic Press, Inc., New York, 1951), p. 47.
[2] H. Y. Fan and K. Lark-Horovitz, *International Conference on Fluoresence and Phosphorescence, Garmisch-Partenkirchen, August, 1956* [Friedrich Vieweg und Sohn (to be published)].
[3] Spear, MacKay, Klontz, and Lark-Horovitz, Bull. Am. Phys. Soc. Ser. II, 3, 141 (1958).
[4] W. L. Brown and W. M. Augustiniak, Bull. Am. Phys. Soc. Ser. II, 2, 156 (1957).
[5] J. W. MacKay (private communication).
[6] Stöckmann, Klontz, Fan, and Lark-Horovitz, Phys. Rev. 98, 1535(A) (1955) and private communication.

III. EXPERIMENTAL RESULTS BEFORE IRRADIATION

Figure 1 shows the spectral dependence of the photoconductivity at 80°K for a number of *n*-type specimens of different thicknesses. The photoconductivity $\Delta\sigma$[7] is plotted against the photon energy in ev. All curves were measured at a constant incident light intensity. In every case it was found that the photosensitivity extends beyond the fundamental absorption edge at 0.75 ev; a "shoulder" appears, which extends from 0.70 ev to values between 0.60 and 0.55 ev. The speed of response in this spectral range lies between 3 and 20 sec for the various specimens investigated. During this time $\Delta\sigma$ rises to its final steady value, or decays to zero when the light is turned off.

The curves in Fig. 1 represent a stable state of the Ge specimens. Warming up to room temperature and subsequent cooling to 80°K does not affect the response. Some specimens have been investigated for several weeks, during which time the photoconductivity curves were reproducible within 20%. The comparison in Fig. 1 of specimens of widely different thicknesses shows clearly that in the shoulder region there is a consistent decrease of photoconductivity with thickness. As light in this spectral range is absorbed almost uniformly throughout the specimens, one would expect $\Delta\sigma$ to be independent of thickness if it represented a true volume effect. The results show that this is not the case; they suggest that the observed photosensitivity in the shoulder region may be connected predominantly with electronic transitions near the surface.

This conclusion is supported by the marked effect of surface treatment on $\Delta\sigma$. In Fig. 2, curve 1 refers to a specimen etched in CP4 in the normal way. The same specimen is then immersed in HF for one minute, after which curve 2 is obtained. There is no change on the short-wavelength side of the absorption edge, but in the shoulder region the photoconductivity has been increased by a factor 20. The curves obtained with *p*-type specimens are qualitatively similar to those in Fig. 1, but the corresponding values of $\Delta\sigma$ are smaller by an order of magnitude or more.

IV. LOW-ENERGY IRRADIATIONS

1. Surface Conductance

It is found that irradiation with electron energies in the 5–300 kev range increases the specimen conductance G, in *n*-type, and decreases it in *p*-type specimens. Typical curves of the conductance change ΔG as a function of the incident electron flux ϕ are shown in Fig. 3 for an *n*-type specimen (1 flux unit$\equiv 10^{13}$ electrons cm^{-2}). With the exception of the 5-kev curve, ΔG increases rapidly at first, reaches a maximum and then slowly decreases. The range of 25-kev electrons in Ge is about 2μ and therefore irradiations with energies between 5 and 25 kev will affect only a narrow region near the front surface; 300-kev electrons, however, will

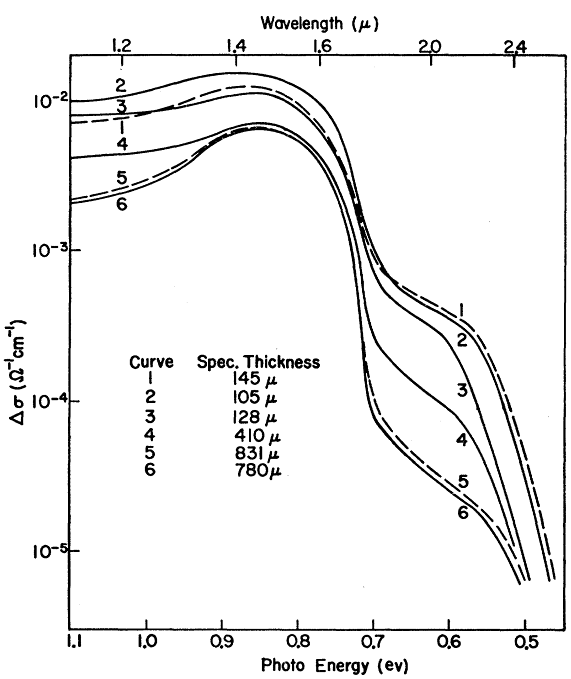

FIG. 1. Photoconductivity at 80°K as a function of the incident photon energy for *n*-type specimens of different thicknesses.

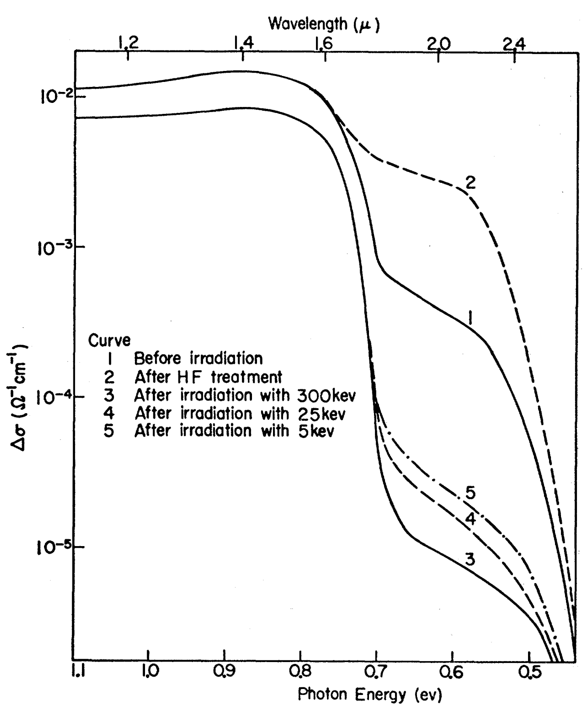

FIG. 2. Photoconductivity *vs* incident photon energy for *n*-type specimens showing the effect of surface treatment (curve 2), and of low-energy irradiations (curves 3–5).

[7] Defined by $\Delta\sigma=\sigma$ (illuminated)—σ (dark).

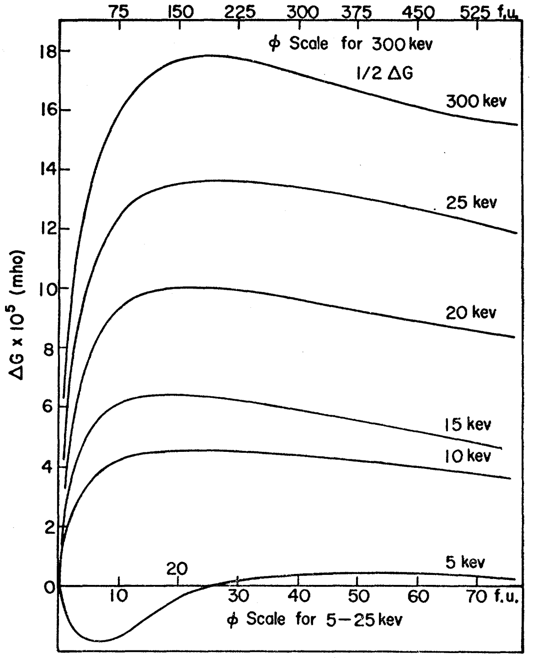

FIG. 3. Surface conductance changes in an n-type specimen as a function of the incident electron flux ϕ, for irradiations in the 5–300-kev range. [1 f.u. (flux unit) $=10^{13}$ electrons cm^{-2}.] Note that the upper ϕ scale refers to the 300-kev curve only.

penetrate the complete specimen. In spite of this, the curves are remarkably similar, which clearly indicates that the observed conductance changes are essentially confined to the surface region. To compare the measurements at different energies, it is assumed in Fig. 3 that at 300 kev the conductance change associated with the front surface is $\frac{1}{2}\Delta G$. For n-type specimens etched in CP4, the maximum values of $\frac{1}{2}\Delta G$ after 300-kev irradiation lie between 1.4 and 1.9×10^{-4} mho/□. The conductance changes are markedly dependent on surface treatment.[5] A comparison of the ΔG values in Fig. 3 shows that 25-kev irradiations are considerably more effective in changing the surface conductance than are 300-kev electrons. It suggests that this type of irradiation effect should be small after 4.5-Mev irradiations with comparable values of ϕ. The conductance changes observed after high-energy experiments can therefore be interpreted predominantly as a volume effect caused by the introduced defect centers.

When the specimen, after low-energy irradiation, is kept at 80°K, the conductance slowly returns towards its original value; in 15 hours a 20% change in ΔG was observed. The recovery can be accelerated if the specimen is warmed to room temperature. On subsequent cooling to 80°K the original conductance is obtained and further irradiations lead to practically the same ΔG *vs* ϕ curves.

With p-type specimens, apart from the change of sign of ΔG, the general character of the curves is similar to that shown in Fig. 3.

2. Photoconductivity

The irradiations have a significant effect on the photoconductivity. In Fig. 2, curves 3, 4, and 5 were obtained after irradiation with 300-, 25-, and 5-kev electrons, respectively. It can be seen that the response in the shoulder region is almost completely quenched. The results shown have been obtained by irradiating until the specimen conductance has reached its maximum value. Under this condition the quenching of $\Delta\sigma$ has always been found to be complete. On warming to room temperature and subsequent cooling to 80°K, the original photoconductivity (curve 1) is restored. The changes in surface conductance and the quenching of the photoconductivity after low-energy irradiations always occur together; the experiments indicate a close connection between these effects.

V. HIGH-ENERGY IRRADIATIONS

4.5-Mev electrons will introduce a practically uniform distribution of defect centers throughout the volume of specimens used in these experiments. It has been shown[1,2] that in an n-type specimen the introduced defects accept electrons from the conduction band. Upon irradiation, the Fermi level will therefore move from its position near the conduction band towards the center of the energy gap, and eventually, the specimen is converted to p-type. The defects might be expected to introduce a volume contribution to the observed photoconductivity in the shoulder region and at longer wavelengths. However, they may also modify the previously observed surface contribution for the following reasons: (a) the shift of the Fermi level and possibly

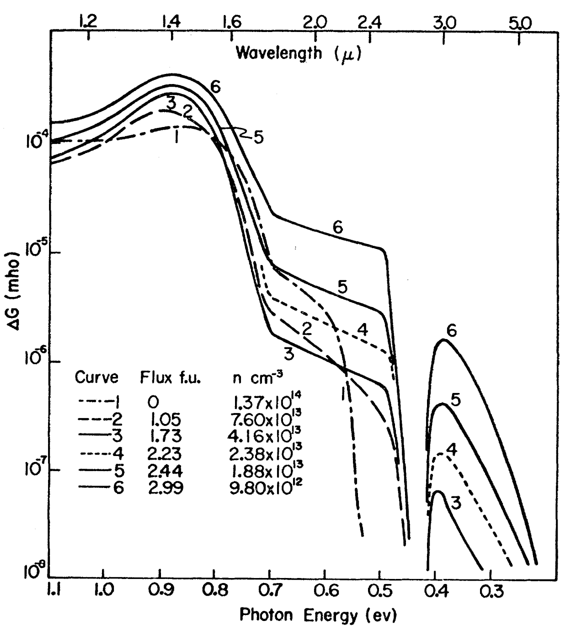

FIG. 4. Photoconductance $\Delta G'$ *vs* photon energy measured after short successive irradiations at 4.5 Mev.

changes in surface potential, will alter the distribution of electrons in surface states; (b) defect centers produced near the surfaces may give rise to transitions not observable with the same type of center in the volume of the specimen; (c) the irradiation may introduce new surface states. It is evident that the first problem consists in distinguishing clearly between the surface photoconductivity and any volume contribution that might be introduced.

The experimental results of Stöckmann *et al.*[2,6] are in general agreement with the more detailed measurements of the spectral dependence of photoconductance[8] given in Figs. 4 and 5. The measurements were made after short successive irradiations, and the specimen was kept at 80°K during the whole experiment. Figure 4 (curve 3) shows clearly two new features: (a) the shoulder extends toward longer wavelengths and possesses now a sharp cutoff near 0.49 ev, and (b) a peak at 0.39 ev appears. With further irradiation, the photoconductance throughout the spectral range increases and reaches a maximum, represented by curve 6. The following stages are shown in Fig. 5. $\Delta G'$ now decreases rapidly (curve 7), and then becomes negative at all wavelengths beyond the absorption edge. Hall effect measurements after each irradiation show that so far, the free carrier concentration has been reduced from 1.37×10^{14} cm^{-3} to about 10^{12} cm^{-3}. The position of the Fermi level has changed from $E_c-\zeta=0.072$ ev to about 0.10 ev. After further irradiation

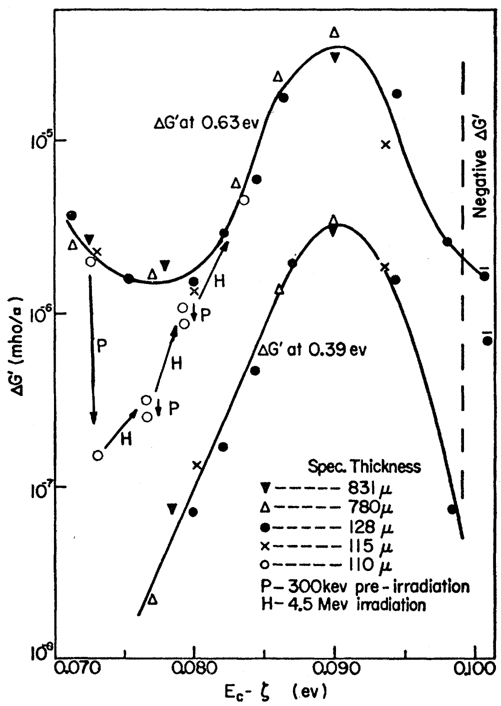

FIG. 6. Values of the photoconductance $\Delta G'$, (normalized to a square surface area) at photon energies 0.63 ev and 0.39 ev are plotted against the position of the Fermi level with respect to the conduction band for *n*-type specimens of widely different thicknesses. The open circles refer to an experiment in which each 4.5-Mev irradiation (*H*) was preceded by a 300-kev irradiation (*P*).

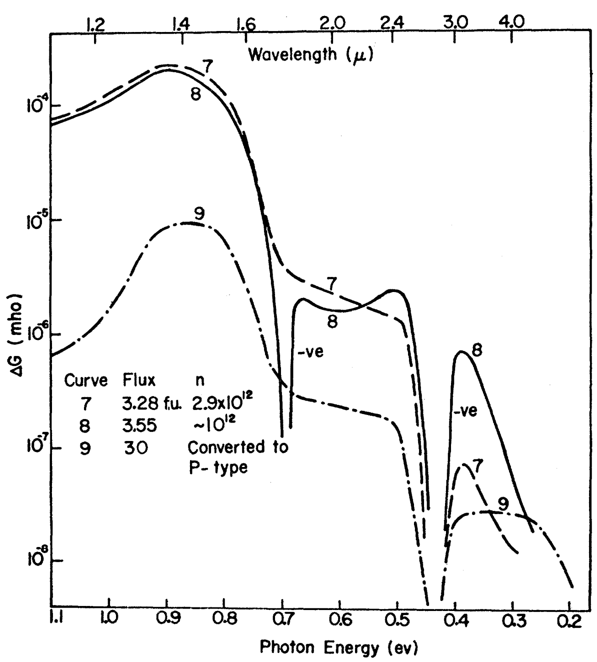

FIG. 5. Continuation of Fig. 4; in curve 8, $\Delta G'$ is negative at wavelengths beyond the fundamental absorption edge.

[8] In these figures, the photoconductance $\Delta G'$, rather than $\Delta\sigma$, is plotted.

the specimen is converted to *p*-type (curve 9). $\Delta G'$ is now positive throughout and the response in the 0.39-ev region extends to about 0.25 ev.

The data obtained for five specimens of widely different thicknesses has been correlated in Fig. 6. The photoconductance at photon energies of 0.63 ev and 0.39 ev is plotted against $E_c-\zeta$. It can be seen that the experimental points for all the specimens fall reasonably well on two common curves. This implies that $\Delta G'$ is essentially independent of specimen thickness, which can only be the case, if it depends predominantly on surface effects. It is therefore concluded that electronic transitions between the defect centers in the volume of the specimen and the bands do not contribute to the observed photoconductance. However, it may be possible that such an effect could be found with specimens of much lower resistivity where the concentration of defects can be made correspondingly larger.

If a similar comparison is carried out at a photon energy of 0.89 ev, the maximum in the fundamental region, two distinct curves are obtained corresponding to thick and thin specimens. $\Delta G'$ is about four times larger for the thick specimens, which shows that in this spectral range, volume effects contribute to the photoconductance.

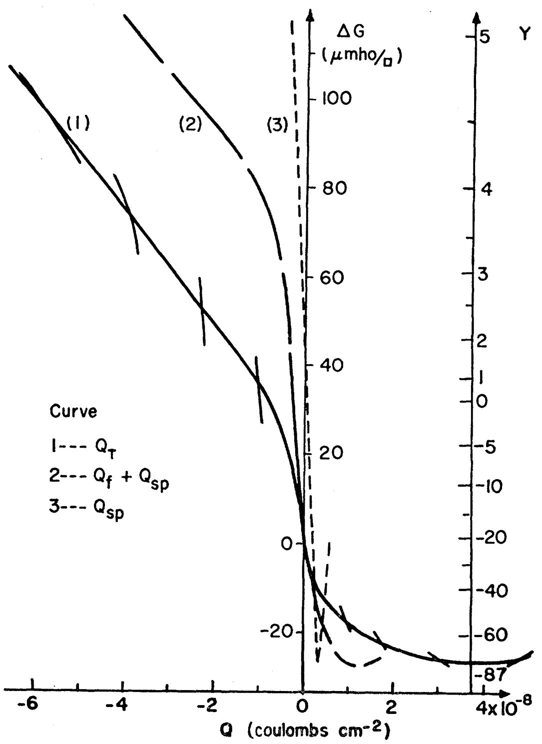

FIG. 7. Results of a field effect experiment on an n-type specimen before irradiation. Curve 1 shows the surface conductance change ΔG produced by a steady field, which induces a total charge Q_T coulombs cm^{-2}. Curve 2 refers to results with a superimposed alternating field. The Y-scale gives calculated values of the surface potential.

VI. FIELD-EFFECT EXPERIMENTS AND DISCUSSION

It was found that the main features of the experimental results could be explained by a model based on the following assumptions: (a) the photoconductivity beyond the fundamental edge is connected with transitions of electrons from the valence band into surface states, and (b) the irradiations produce definite and reproducible changes in surface potential. It is the purpose of the field-effect measurements to provide some experimental support for these assumptions. In view of the photoconductive response times, the experiments will be mainly concerned with a group of surface states, normally referred to as "slow states."[9,10] Their relaxation times fall within the range from about 0.1 sec to many minutes. The experimental method used here is essentially an adaptation of that described by Montgomery and Brown.[11] The main difference lies in the use of a steady field instead of the gaseous ambient medium,[12] to move the surface potential throughout a range of values sufficiently large to include the conduction minimum.

In a series of preliminary experiments the specimen conductance at 80°K was measured as a function of time after applying a steady field across the surface at $t=0$. During the first 10 sec, ΔG decays fairly rapidly; however, at $t=60$ sec, $\Delta G/\Delta t$ was sufficiently small in all cases to ensure that the surface potential determined by the steady field remained practically constant during the recording of the alternating field pattern. No relaxation of the pattern[11] towards its shape in absence of the field could be detected in any of the following experiments. The magnitude of ΔG at $t=60$ sec depends on magnitude and direction of the applied steady field; it amounts to values between 50% and 90% of the conductance change measured at $t\simeq 3$ sec.

Curve 1 in Fig. 7 shows a typical steady field effect curve for an n-type specimen.[13] ΔG is measured 60 sec after applying the field, and Q_T denotes the total induced surface charge per cm^2. It is assumed that at each value of ΔG the group of slow states of interest here is in equilibrium with the bands. The alternating field patterns are shown at a few points along curve 1. The frequencies used ranged from 7 to 300 cps. Except for points close to the conduction minimum, the patterns were found to be frequency-independent. This suggests[14] that the conductance changes they represent are connected with the fast surface states. If the patterns at doints other than $\Delta G=0$, are displaced along a line $\Delta G=$const, they fit together accurately, forming a continuous curve (curve 2). This has been done with considerable accuracy on a large-scale plot of Fig. 7. The procedure is justified because each value of ΔG, determined by curve 1, is related uniquely to a value of the surface potential.

For charge neutrality in the surface region, $Q_T=Q_{sp}+Q_f+Q_s$ must be satisfied; Q_{sp} denotes the charge per cm^2 in the space charge region, Q_f and Q_s refer to the charge in fast and slow states, repectively. The measured conductance changes were related to the surface potential by numerically integrating the solutions of the space charge calculation given by Kingston and Neustadter.[15] Experimentally determined bulk mobility values were used in these calculations. The conductance minimum of curve 2 is the reference point to which the vertical position of the Q_{sp} curve is adjusted.[16] The corresponding values of Y, the surface potential expressed in units of kT/q,[17] are shown along a separate axis. It can be seen that before irradiation a depletion layer of $21kT$ height (0.15 ev) exists at the surface. The three other specimens investigated led to similar results.

[9] S. R. Morrison, in *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, 1957), p. 169.
[10] Statz, deMars, Davis, and Adams, Phys. Rev. **101**, 1272 (1956).
[11] H. C. Montgomery and W. L. Brown, Phys. Rev. **103**, 865 (1956).
[12] W. H. Brattain and J. Bardeen, Bell. System Tech. J. **32**, 1 (1953).
[13] The following refers to results with n-type specimens; p-type specimens are discussed in a separate section.
[14] G. G. E. Low, Proc. Phys. Soc. (London) **B68**, 10 (1955).
[15] R. H. Kingston and S. F. Neustadter, J. Appl. Phys. **26**, 718 (1955).
[16] W. L. Brown, Phys. Rev. **100**, 590 (1955).
[17] $(kT/q)Y$ is defined as the difference in electrostatic potential at the surface and deep in the interior of the Ge.

The number of electrons, n_s and n_f in slow and fast surface states, can now be obtained directly from Fig. 7 as a function of Y. n_s[18] is practically zero between $Y \simeq -40$ and $Y \simeq -10$. It then increases rapidly and reaches an almost constant value at $Y=4.5$. For $Y>1$ the n_s *vs* Y curve can be fitted to a Fermi distribution calculated for a single level of slow surface states of density 2.5×10^{11} cm^{-2}, situated 0.06 ev below the conduction band. This level indicates approximately the extent towards the conduction band of this group of slow surface states. n_f begins to rise steeply at $Y\simeq4$ and exceeds the maximum value of n_s for $Y>4.5$, i.e., when the conduction band approaches the Fermi level to within 0.04 ev. This result implies a considerable concentration of fast surface states near the conduction band. In the range of high-depletion layers, results are less conclusive; this is partly connected with the loss in accuracy caused by the rapidly changing Y. Nevertheless, Fig. 7 indicates the existence of a second group of slow states extending from $Y\simeq-40$ towards the valence band.

In Fig. 8, $(1/kT)dn/dY$ for the slow and fast surface states is plotted against the position of the Fermi level with respect to the valence band at the surface. The ordinate represents approximately the minimum density per unit energy range of the states under consideration.[16] Comparison of the s-curves with Fig. 1 suggests strongly that the photoconductivity in the shoulder region is caused by transitions between the valence band and the group of empty slow surface states between 0.70

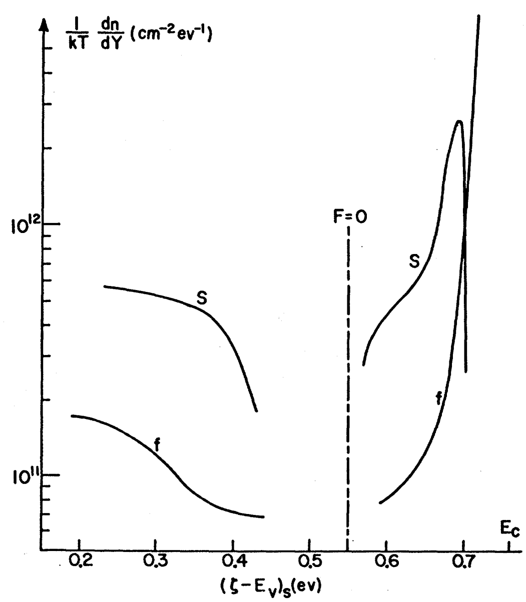

FIG. 8. Plot of $(1/kT)dn/dY$ against the position of the Fermi level with respect to the valence band at the surface. The ordinate represents approximately the density of surface states per unit energy range. Curves s: slow states; curves f: fast states. Line $F=0$: position of Fermi level in absence of field.

[18] qn_s is given by the horizontal distance between curves 1 and 2.

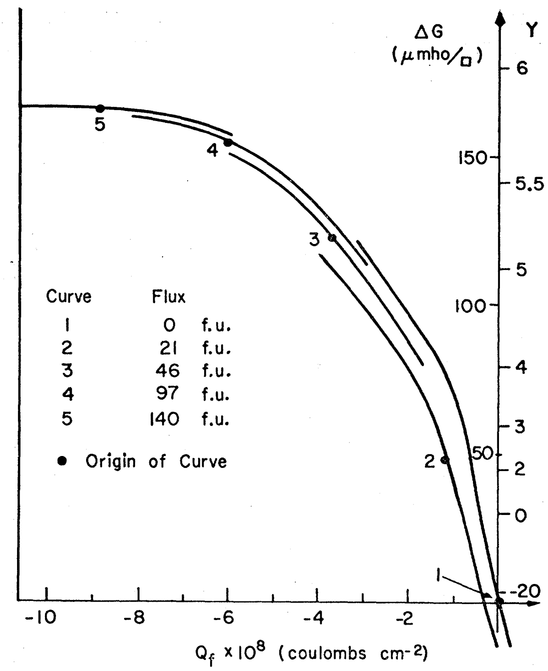

FIG. 9. Field effect measurements on an n-type specimen during successive stages of 300-kev irradiation. The curves represent the response of the fast states.

and about 0.58 ev. The depletion layer which exists before irradiation, essentially confines the generated free holes to the "channel" near the surface. Recombination with free electrons is unlikely in the surface region, and under illumination, the steady state is determined by recombination between trapped electrons and free holes. Under these conditions the lifetime of generated holes may considerably exceed the bulk lifetime. Transitions in the 0.39-ev region are not observed, because these states are occupied; this is indicated by the line $F=0$, denoting the position of the Fermi level in absence of a field. The increase in the density of fast states between 0.2 and 0.3 ev may be connected with the level of fast states, 0.138 ev below the middle of the gap, reported by Statz *et al.*[10]

1. Low-Energy Irradiations

Figure 9 shows field-effect curves for the fast states after successive stages of low-energy irradiation (300 kev). The curves, obtained by the method described above, represent surface changes during the initial stages of irradiation up to the maximum of $\frac{1}{2}\Delta G$ in Fig. 3. Qualitatively similar results are obtained with 25-kev electrons. It can be seen that the initial depletion layer (origin 1) is transformed into an accumulation layer by a comparatively small electron flux (origin 2). The surface potential then increases further and approaches a steady value near $Y=5.7$, i.e., $(E_c-\zeta)_s=0.03$ ev. The reason is that the Fermi level now lies in the region of high density of fast states (Fig. 8), and most of the induced negative charge condenses into these states, instead of increasing the surface conductance. In the case of curves 3 to 5 it was no longer possible to reach the conductance minimum, and their horizontal positions have been located with respect to curve 2. It is believed that the gradual decrease of ΔG beyond the maximum in Fig. 3 is caused by a decrease in mobility. This may be connected with the mechanism discussed by Schrieffer,[19] or possibly with an increased probability of trapping of free electrons by the fast states close to the band.

The results of Fig. 9 also explain the quenching of the photoconductivity (Fig. 2) and its close connection with the surface conductance changes. When the accumulation layer has reached a depth corresponding to origin 5, the group of slow states between 0.70 and 0.58 ev lies below the Fermi level and will be partially filled; the probability of transitions will therefore be lower. In addition, the presence of free electrons at the surface will reduce the lifetimes of any generated holes.

The fact that low-energy irradiation increases Y implies that negative charge must have been removed from the surface. There is a considerable amount of evidence[20] to indicate that many of the slow surface reactions result from chemisorbed oxygen which can act as an acceptor trap. It is therefore likely that the observed changes in Y are caused by interaction of the incident electrons with the negative ions. The subsequent recovery may be connected with a transfer of negative charge across the surface to the chemisorbed layer. If this is correct, the extreme slowness of this process at 80°K indicates that the states introduced by the chemisorbed layer cannot be identified with the photoconductivity.

2. High-Energy Irradiations

Figure 6 shows fairly convincingly that 4.5-Mev irradiation introduces two opposing mechanisms, both of which tend to alter Y. The first, which produces the initial decrease in the $\Delta G'$ curve for 0.63 ev, is almost certainly identical with the mechanism responsible for the quenching after low-energy irradiation; but, as one would expect, the cross section for the interaction between 4.5-Mev electrons and the chemisorbed ions will now be smaller. The second mechanism, is connected with the introduced defect centers; it soon compensates the initial decrease of $\Delta G'$ and leads to the rise in both the 0.63 ev and the 0.39 ev curves. This is clearly shown in Fig. 6 by the experimental points denoted by open circles. Each 4.5-Mev irradiation (H) is preceded by a 300-kev pre-irradiation (P). The latter causes the large initial quenching, which is then rapidly compensated by the introduced defect centers. Field effect experiments indicate that the rising part of the $\Delta G'$ curves coincides with a change in origin to a new, apparently steady value at $Y\simeq -38$.[21] The Fermi level with $F=0$ now lies at $(\zeta - E_v)\simeq 0.32$ ev and therefore passes through the second group of slow states (Fig. 8). Transitions from the valence band to higher lying states in this group should be observed; the appearance of the 0.39-ev peak is therefore connected with states already present before irradiation. After conversion to p-type, with the Fermi level lying closer to the valence band, curve 9 in Fig. 5 indicates that now a wider range of states of the second group contributes to the photoconductivity. The extension of the shoulder region cannot be accounted for by the distribution of slow states in Fig. 8. There exists some independent evidence[22] that 4.5-Mev irradiation introduces volume defect levels in this energy range. It is therefore likely that the extension of the shoulder region is connected with defect centers near the surface, and not with the introduction of new surface states by the irradiation.

The negative response, shown by curve 8 in Fig. 5, appears to be connected with the same transitions as those which give rise to the positive photoconductivity. The reason for the change of sign is most probably the mechanism of recombination. However, the results of field effect experiments in this range of Y are not sufficiently conclusive to provide a more detailed explanation of the negative effect.

3. p-Type Specimens

Field-effect experiments were made on two unirradiated p-type specimens. The results confirm the presence of the second group of slow states and show that, at least in p-type specimens, their density decreases sharply near 0.20 ev. The origin of both curves indicates a p-type accumulation layer of about 0.02-ev height. The explanation of the experimental results is essentially similar to that for n-type specimens. During illumination, transitions from the valence band into slow surface states take place, which increase the concentration of free holes in the p-type "channel". The effect of low-energy irradiations on the surface potential should be in the same direction as for n-type specimens. This leads to a p-type depletion layer which should cause a decrease in surface conductance and also a quenching of the photoconductivity. Both these effects are found experimentally.

VII. CONCLUSIONS

1. The photoconductivity beyond the fundamental absorption edge, which has been found in Ge at 80°K, is caused by transitions of electrons from the valence band into a group of slow surface states lying in a range from about 0.58 to 0.70 ev above the valence band.

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

[20] For example, the article by G. W. Pratt and H. H. Kolm, in *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, 1957), p. 311.

[21] A decrease in Y would be expected as a result of the negatively charged defect centers introduced in the space charge region.

[22] Fan, Kaiser, Klontz, Lark-Horovitz, and Pepper, Phys. Rev. **95**, 1087 (1954).

2. Irradiation of n- and p-type specimens leads to an increase in surface potential which causes the observed changes in surface conductance and quenches the photoconductivity in the shoulder region. With increasing electron energy, the irradiation becomes less effective in producing a change in surface potential.

3. Irradiation with 4.5-Mev electrons introduces volume defects which, however, do not contribute to the photoconductivity beyond the absorption edge. In n-type specimens, the resulting decrease in surface potential now allows transitions to empty states in a second group of slow surface states lying between 0.2 ev and 0.4 ev above the valence band.

4. It is shown experimentally that a considerable concentration of fast surface states exists within 0.05 ev of the conduction band.

ACKNOWLEDGMENTS

The author remembers with gratitude the help and encouragement given by the late Dr. K. Lark-Horovitz. He wishes to thank Dr. J. W. MacKay and Dr. E. E. Klontz for advice and many discussions during his stay at Purdue University, and Dr. H. Y. Fan for comments on the manuscript. Thanks are also due to Mr. J. Raby for help with the irradiations.

PHYSICAL REVIEW VOLUME 112, NUMBER 2 OCTOBER 15, 1958

Semiconductor Surface Potential and Surface States from Field-Induced Changes in Surface Recombination

George C. Dousmanis
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey
(Received March 15, 1957; revised manuscript received May 28, 1958)

Experiments are reported on the effects of ac electric fields and ambients on the surface recombination velocity in germanium and silicon. The variations in surface recombination are detected by changes in the reverse current of large area "back surface" diodes. The experimental method is an improved version of that of Thomas and Rediker and is a convenient means of exploring surface type, stability, time effects at the surface, and effects induced by high ac fields and ambients on the slow surface states. Observation of a maximum of surface recombination in terms of applied field provides a reference point from which the zero-field value of the surface potential can be evaluated, and the dependence of the surface recombination velocity (s) on the surface potential (ϕ_s) can be established. Values of ϕ_s are in the range of ± 0.25 v in Ge and ± 0.5 v in Si. The energies of the main recombination states are at 6 kT to 9 kT from mid-gap in Ge and at $+16\ kT$ or $-16\ kT$ in Si. Information on the surface potential and the surface states obtained by the present technique is in reasonable agreement with that derived from other types of measurements. The present results are independent of uncertainties due to surface mobility. Experimental patterns show directly that the "charge" surface states are also the ones that give rise to surface recombination. The width of the observed curves of s *vs* induced charge (and ϕ_s) depends on bulk resistivity and is smaller for the higher resistivity samples. Such behavior could arise from contributions to s from recombination states distributed in the surface space-charge region.

1. INTRODUCTION

FIELD-INDUCED effects in semiconductor surfaces yield substantial information on the physics of the surface and on its electrical behavior. These effects include changes induced in surface conductivity upon application of an external electric field[1–5] (usually called the field-effect), as well as changes in surface recombination velocity.[6–8] The present work is concerned with the effects of ambients and ac electric fields, in the frequency range of 0.01 to 1000 cps, on the semiconductor surface potential and the corresponding changes in surface recombination velocity.

The electric field is applied normally to the "back" surface of alloy-type germanium and silicon diodes and the effects on the surface recombination velocity are detected by the changes in the diode current.[7,9] This technique is shown to be a very effective one in determining the type of surface (p, n, or intrinsic) that one obtains with a given chemical treatment and ambient atmosphere as well as the extent of stability of the surface potential with time. A new method of approximately determining the zero-field value of the surface potential (ϕ_s) is provided by the observation of a maximum of surface recombination (s) in terms of an applied field E. The experimental curves of s *vs* E and those of s *vs* ϕ_s are discussed and interpreted in terms of the energy levels, distribution, and carrier capture cross sections of the surface states that give rise to recom-

[1] W. Shockley and G. L. Pearson, Phys. Rev. **74**, 232 (1948).
[2] J. Bardeen and S. R. Morrison, Physica **20**, 873 (1954).
[3] W. L. Brown, Phys. Rev. **100**, 590 (1955); H. C. Montgomery and W. L. Brown, Phys. Rev. **103**, 865 (1956).
[4] Bardeen, Coovert, Morrison, Schriefer, and Sun, Phys. Rev. **104**, 47 (1956).
[5] R. H. Kingston, J. Appl. Phys. **27**, 101 (1956).
[6] Henisch, Reynolds, and Tipple, Physica **20**, 1033 (1954).
[7] J. E. Thomas, Jr., and R. H. Rediker, Phys. Rev. **101**, 984 (1956).
[8] Many, Margoniski, Harnik, and Alexander, Phys. Rev. **101**, 1433 (1955); E. Harnik *et al.*, Phys. Rev. **101**, 1434 (1955); A. Many and D. Gerlich, Phys. Rev. **107**, 404 (1957).
[9] G. C. Dousmanis, Bull. Am. Phys. Soc. Ser. II, **2**, 65, 135 (1957); The preliminary results for Ge given in the latter abstract were subject to considerable inaccuracy in the field measurements.