

Field Effect in Germanium at High Frequencies

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Changes in conductivity near the surface of germanium in response to an ac electric field have been investigated at frequencies as high as 50 Mc/sec for both *n*- and *p*-type material, and in wet air, dry oxygen, and ozone ambients. In certain ambients the sign of the field effect changes at a frequency closely related to the reciprocal of the minority carrier lifetime. At higher frequencies the field effect mobility is sometimes substantially larger than bulk mobility of the majority carrier. A model is suggested which is in harmony with most of the experimental observations.

THE change in conductivity near the surface of a semiconductor produced by an electric field normal to its surface is often referred to as the field effect. Investigators have made use of dc, ac, and pulsed fields to explore the time-dependent aspects of the effect, but have often encountered difficulties at high frequencies because of the large displacement currents which flow in supplying charge to the surface region. A method of measuring field effect described by Aigrain and his co-workers¹ is especially suited to high-frequency work, and has been used in the present investigation for determining field effect in germanium at frequencies as high as 50 Mc/sec.

Field-effect mobility is often much less than the bulk mobility of the carriers involved, and this has been attributed to immobilization of part of the carriers in surface states. Variations of field effect with frequency are intimately related to the time constants of the surface states. Previous work²⁻⁵ has shown the existence of slow surface states affecting frequencies in the range from a fraction of a cycle to a few cycles per second, and has also indicated changes in field effect mobility at a frequency corresponding to the reciprocal lifetime of minority carriers.⁴⁻⁶ The present work extends the investigation upward in frequency by four decades. One would expect that at some sufficiently high frequency none of the surface states would have time to communicate with either the conduction or valence band, and the field-effect mobility should be just the bulk mobility for majority carriers.

PROCEDURE

A diagram of the experimental arrangements is shown in Fig. 1. The sample was a rectangular bar of single crystal germanium about $0.5 \times 2 \times 10$ mm, with contacts soldered to the ends, and surfaces suitably prepared as described below. The germanium bar formed one plate of a condenser, whose dielectric was a slab of single

crystal strontium titanate, giving a capacity around $30 \mu\text{f}$. Ten volts ac was applied to the condenser, producing a maximum field of 4×10^4 volts/cm. A smaller voltage of the same frequency and phase was applied from end to end of the germanium sample. Product modulation of the latter voltage by the conductivity changes due to the field effect produced a dc current in the galvanometer proportional to the field effect, as will be shown.

The field effect will be expressed in terms of μ_{fe} , the field-effect mobility.^{7,8} This is ordinarily defined as

$$\mu_{fe} = dG_1/d\Sigma, \quad (1)$$

where G_1 is the conductance of the specimen per square of surface and Σ is the net charge induced by the field per unit area of surface. As thus defined, μ_{fe} is the slope of a field effect pattern of the sort shown in Figs. 2, 3, and 5 of reference 6.

The total conductance is

$$G = G_1 W/L,$$

where W is the width and L the length of the specimen, while

$$\Sigma = C v_B/WL,$$

where C is the total capacity between plate and specimen and v_B the voltage across this capacity. It follows

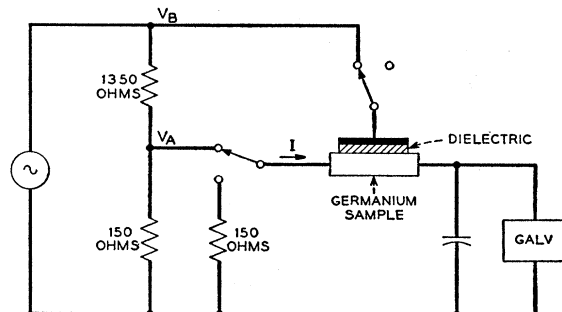


FIG. 1. Experimental arrangements for measuring field-effect mobility.

⁷ This terminology, used by Schrieffer,⁸ seems more descriptive than the term "effective mobility" used by the author in reference 6 for the same quantity.

⁸ J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).

¹ Aigrain, Lagrenaudi, and Liandrat, J. phys. radium **13**, 587-8 (1952).

² Statz, Davis, and deMars, Phys. Rev. **98**, 540 (1955).

³ R. H. Kingston, Phys. Rev. **98**, 1766 (1955).

⁴ G. G. E. Low, Proc. Phys. Soc. (London) **B68**, 10 (1955).

⁵ S. R. Morrison, Phys. Rev. **102**, 1297 (1956).

⁶ H. C. Montgomery and W. L. Brown, Phys. Rev. **103**, 865 (1956).

that

$$\mu_{fe} = (L^2/C)dG/dv_B. \quad (2)$$

The applied voltages shown in Fig. 1 are sinusoidal with root-mean-square values V_A and V_B , and may be written

$$v_A = \sqrt{2}V_A \cos(\omega t - \theta), \quad (3a)$$

$$v_B = \sqrt{2}V_B \cos \omega t, \quad (3b)$$

where θ is the phase angle between the applied voltages. For small changes, the conductivity may similarly be written

$$G = G_0 + \sqrt{2}G_A \cos(\omega t - \theta'), \quad (3c)$$

where θ' is the phase of the field effect with respect to v_B . The longitudinal current through the specimen due to v_A is

$$I = v_A G \\ = \sqrt{2}V_A G_0 \cos(\omega t - \theta) + V_A G_A [\cos(\theta' - \theta) \\ + \cos(2\omega t - \theta' - \theta)], \quad (4)$$

$$I_{dc} = V_A G_A \cos(\theta' - \theta). \quad (5)$$

By an artifice familiar in ac circuit theory, we shall now extend the simple definition (1) of μ_{fe} by regarding it as a complex number, whose magnitude is the ratio of the amplitudes of two sinusoidal quantities, G_1 and Σ , and whose angle denotes the phase relation between the sinusoids. From (2) it follows that the magnitude of μ_{fe} is $(L^2/C)G_A/V_B$ and from (3) its angle is seen to be θ' . From this and (5) it follows that

$$\mu_{fe} \cos(\theta' - \theta) = I_{dc} L^2 / C V_A V_B. \quad (6)$$

This is the basic relation between μ_{fe} and the experimental quantities.

In the circuit of Fig. 1, $\theta \approx 0$, when $\omega C \ll G_0$ (i.e., below a few Mc/sec in these experiments). In this frequency range (6) shows that the measurements give $\mu_{fe} \cos \theta'$, which is the real part of μ_{fe} . The practical upper frequency limit of the method is reached when $\omega C \approx 4G_0$. Near this frequency the displacement current through C due to v_B is comparable to the longitudinal current due to v_A , both current and voltage vary along the specimen, and θ is by no means negligible. In this range one can estimate μ_{fe} by calculating the voltage

and current distribution and integrating their product over the sample. Above this range such calculations become unreliable because they depend critically on symmetry assumptions regarding current distribution which are hard to justify.

Rectification at the end contacts and thermal emf's due to small temperature differences between the ends of the specimen produced spurious dc currents which were not entirely negligible. Corrections were determined by observing the dc currents, in the absence of any field effect, due to v_A alone and to v_B alone. The sum of these was used as a correction, the addition of the currents being justified by the fact that the ac currents due to v_A and v_B are out of phase by 90 degrees (except at the very high frequencies) and the rectification effects follow a square law with current.

The sample was housed in a glass container in which it could be exposed to various gaseous ambients. The "wet air" ambient consisted of stationary air maintained at 50% relative humidity by contact with a saturated solution of $K_2Cr_2O_7$. The "dry O_2 " ambient was commercial tank oxygen flowing through the container at a slow rate. "Ozone" refers to a mixture of ozone and oxygen obtained by irradiating tank oxygen with ultraviolet light before it flowed into the container.

RESULTS

Measurements of μ_{fe} are shown in Fig. 2 for a specimen of p -type germanium at room temperature over the frequency range 300 cycles per second to 2 Mc/sec, in three gaseous ambients. The resistivity was 20 ohm-cm, and all surfaces were etched 2 minutes in CP-4 and rinsed a few minutes in cold distilled water. In wet air there is a strong inversion layer at low frequencies, with μ_{fe} about one-third of bulk mobility for electrons. At 6 kc/sec μ_{fe} becomes positive and increases in the 100-kc/sec range to a value about 50% greater than bulk mobility for holes. The sample lifetime for minority carriers was measured by time decay of photoconductivity after a short pulse of light and found to be 25 microseconds. The corresponding frequency $f = 1/(2\pi \times 25 \times 10^{-6}) = 6400$ is about the inflection point of the curve, and this relation is characteristic of all samples examined. With the ozone ambient there is no inversion layer and μ_{fe} is almost constant with frequency at a value about one-third of bulk mobility for holes. The dry O_2 ambient gives an intermediate condition.

Figure 3 shows measurements of μ_{fe} on another p -type specimen over a wider range of frequencies. To obtain the high-frequency measurements, the field was restricted to a portion near the center of the specimen, and a small capacitor was placed in series with the plate. Both of these measures decrease the galvanometer readings, but substantially increase the upper frequency limit of the method. This specimen had a resistivity of 20 ohm-cm, and the surfaces were etched in a

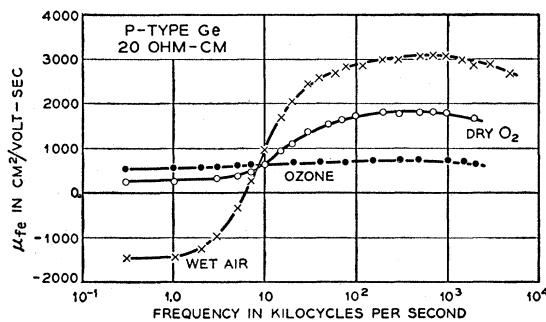


FIG. 2. Field-effect mobility in p -type germanium.

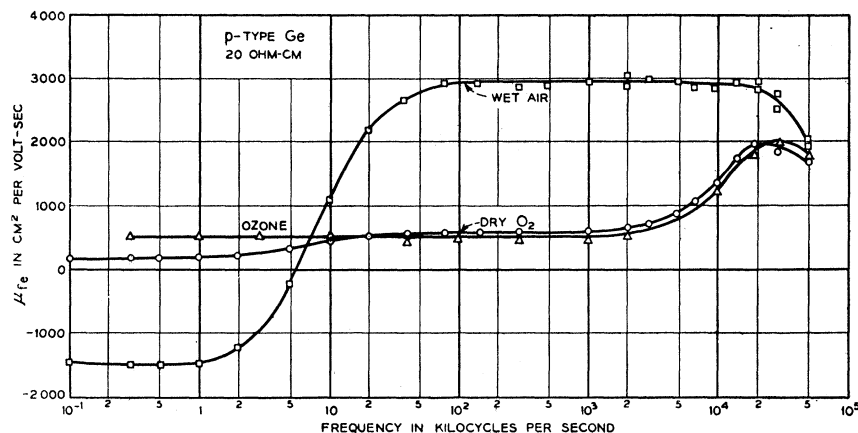


FIG. 3. Field-effect mobility in *p*-type germanium over an extended frequency range.

NaOH—H₂O₂ etch and rinsed in cold distilled water, giving a lifetime of 25 microseconds. In the wet air and ozone ambients the behavior is much like that of the preceding sample. In oxygen the high-frequency value of μ_{fe} is smaller than in the preceding sample, being hardly distinguishable from the ozone value. The cause of this difference is not known. At the highest frequencies the curves for the various ambients come together, giving the first experimental evidence for a field effect process with a time constant in the 10⁻⁸ second range.

Measurements on an *n*-type specimen in several ambients are shown in Fig. 4. The resistivity was 20 ohm cm. For curve *A* the surfaces had been etched one minute in CP-4 and measurements were made in a dry oxygen ambient. The body lifetime of this material was 900 microseconds, and the sample lifetime 175 microseconds in air at 40% relative humidity, probably somewhat less in dry oxygen. Curve *B* was measured in dry oxygen after the back surface of the sample had been sandblasted, reducing the sample lifetime by an order of magnitude, and increasing the transition frequency in about the same ratio. The small decrease in μ_{fe} at high frequencies is probably due to deterioration of the surface by masking with polystyrene cement during sandblasting. Curve *C* was measured with the same surfaces in an ambient of air at 50% relative humidity. Except for reversal with respect to the sign of the field effect, there is considerable similarity in behavior of *p*- and *n*-type material.

Measurements were made on a *p*-type specimen of 22 ohm-cm resistivity whose surfaces were not etched, but had been prepared by dry lapping on successively finer grades of carborundum paper, finishing with 4/0. In this case no inversion layer was observed and μ_{fe} was very small, varying from 150 at 300 cps to 300 at 2 Mc/sec in dry oxygen, and about half those values in wet air. Subsequent etching of the surfaces produced field effects comparable to those in other etched specimens.

In several instances, samples which had been etched

and which exhibited normal field effect were soaked for 5 or 10 minutes in hot ($\approx 80^\circ\text{C}$) deionized water, with the hope that a cleaner, more sensitive surface might result. On the contrary, this treatment usually destroyed the inversion layer at low frequencies, greatly reduced the field effect at high frequencies, and made the sample less sensitive to ambient gasses.

With *p*-type material strong inversion layers at low frequencies and large values of μ_{fe} were obtained with both the CP-4 and the NaOH—H₂O₂ etches. However, the latter seemed to give more dependable results and surfaces which did not deteriorate easily when subjected to various ambient conditions. With *n*-type material only the CP-4 etch has been tried.

Several of the samples have been subjected to the ambient cycle wet air, dry oxygen, ozone, dry oxygen as many as six or eight times with only minor changes in the field effect for a particular ambient.

DISCUSSION

The measurements of μ_{fe} are believed to be accurate to 5 or 10% up to frequencies around 2 Mc/sec, where the reactance of the capacity is comparable to the

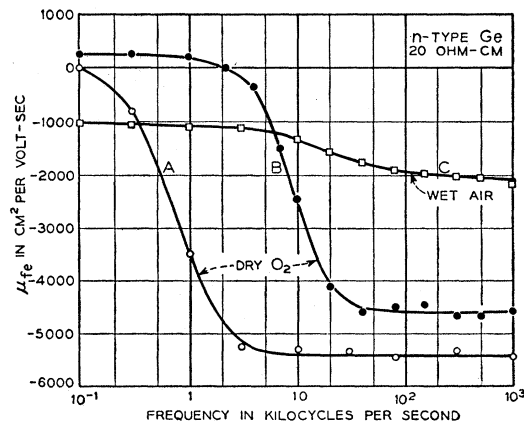


FIG. 4. Field-effect mobility in *n*-type germanium.

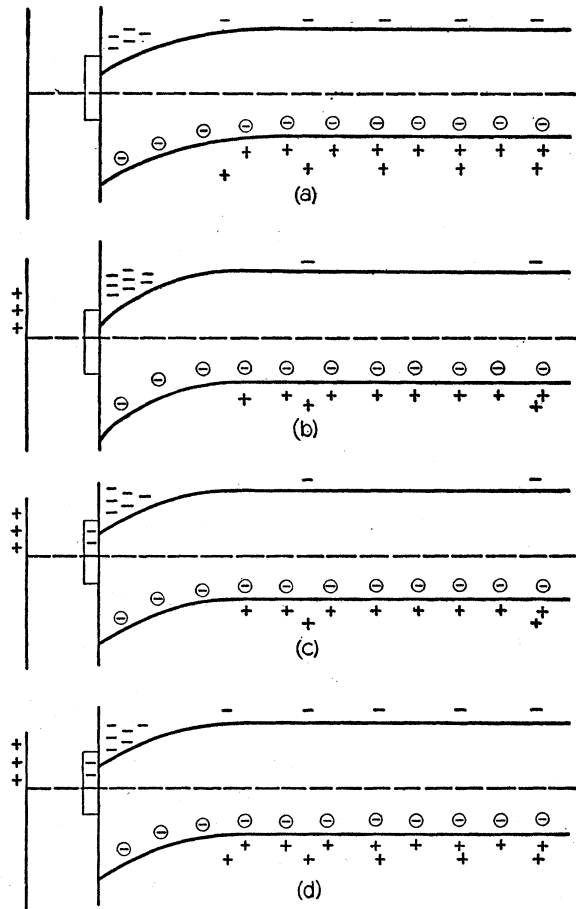


FIG. 5. Energy level diagrams before and after applying a field

longitudinal resistance of the specimen. Analysis of the circuit indicates that corrections to the measured values become substantial at higher frequencies. For example, under the conditions of Fig. 3 it was estimated that the true value of μ_{te} was 14% higher than that shown in the figure at 5 Mc/sec and 54% higher at 15 Mc/sec. If one accepted these corrections at face value the curve for the wet air ambient would rise substantially in this frequency range, and the other curves would rise even more steeply than shown. However, the basis of these corrections is very involved, and they depend critically upon assumptions of symmetry in the specimen and circuit which are hard to substantiate. Consequently the values of μ_{te} above 5 or 10 Mc/sec must be regarded as rather uncertain. The relative values in the different ambients are probably significant even at the highest frequencies, since the capacities in the structure change very little with ambient. Thus one may conclude that at least one of the curves undergoes a substantial change in the region of 15 Mc/sec.

With ambients that produce an inversion layer at low frequencies there is always a large change in μ_{te} at a frequency $f=1/(2\pi\tau)$, where τ is the sample lifetime for minority carriers. An intimation of such a change

was contained in earlier work⁶ which showed phase shift loops in field effect patterns at this frequency, but due to frequency range limitations no quantitative results were obtained above the critical frequency. The present work shows that μ_{te} changes in one sweep from its low-frequency value to a value opposite in sign and substantially in excess of bulk mobility for the majority carrier, and then remains constant for at least one or two decades in frequency.

With the opposite extreme of ambient there is no inversion layer at low frequencies, μ_{te} has the sign appropriate to majority carriers and a magnitude one-quarter to one-half of bulk mobility, and changes only a little through the frequency range including $f=1/(2\pi\tau)$.

Most of the experimental findings can be understood on the basis of the following model and assumptions, suggested by W. L. Brown. Consider a *p*-type semiconductor with an inversion layer at the surface produced by charge in slow surface states. The equilibrium situation with no induced field effect is shown by the band diagram of Fig. 5(a). The bands bend down at the surface because negative charge is required in the space-charge region to neutralize positive charge in slow surface states. (For simplicity, initial charge in slow or fast surface states is not shown in the diagrams, since this is presumed not to change during the discussion.) Now, suppose a steady field is applied in such a direction as to charge the semiconductor negatively. After a very short interval, comparable to the dielectric relaxation time, holes flow out of the body (through the end contacts) leaving a net negative charge. If one could observe field-effect mobility after this very short time, it would be μ_p , bulk mobility for holes, since the changes in charge thus far have involved only holes in the body region. Soon after this, the electrons in the conduction band rearrange themselves by moving toward the surface, establishing space charge neutrality in the interior, but with no change in the total number of conduction electrons.

The situation is now as shown in Fig. 5(b). The concentration of conduction electrons near the surface has increased. These electrons are now out of equilibrium with the valence band and the surface states. It is assumed that equilibrium can be re-established with the fast surface states much more quickly than with the valence band. Thus after some suitable time shorter than the minority carrier lifetime the situation is as shown in Fig. 5(c). Conduction electrons have gone into fast surface states sufficient to establish equilibrium between the conduction band and the fast states. Let α_1 be the ratio of the number of electrons going into fast states to the total number of units of electronic charge induced by the field. The field-effect mobility at this stage is $\mu_p + \alpha_1\mu_n'$, where μ_n' is the mobility of electrons in the space charge region, which may be less than bulk mobility because of the Schrieffer effect.⁸

After a still longer time equilibrium is established between both bands and the fast surface states, through the usual lifetime processes. It is immaterial to the reasoning whether the recombination centers responsible for this change are the same as the fast states or not. This final step gives rise to the situation shown in Fig. 5(d), where everything is in equilibrium except the slow surface states, which are assumed not to have changed. The added charge now consists entirely of electrons near the surface or in the fast surface states. If α_2 is the ratio of the number of electrons in fast states to the total increase in electrons, the field effect mobility at this stage is $-(1-\alpha_2)\mu_n'$.

It seems likely that α_1 and α_2 are the same or nearly equal, although a rigorous demonstration has not been worked out.⁹ If they are indeed equal, it follows that the difference between field effect mobilities at low and high frequencies is $\mu_p + \mu_n'$. If one knows μ_p and μ_n one can, in principle, determine the magnitude of the Schrieffer effect μ_n'/μ_n . For this interpretation to be valid, the inversion layer must be strongly developed, so that the contribution of majority carriers to the field effect is negligible. Since μ_n and μ_p depend on impurity content of the sample and vary rapidly with temperature, a great deal of care would be required to make a satisfactory estimate of μ_n'/μ_n in this way. The data of Fig. 3 cannot be interpreted in this way, since examination of the field-effect pattern at low frequencies reveals that the inversion layer was only partially developed. The data of Figs. 2 and 4 are probably subject to the same limitation, although low-frequency patterns were not recorded for these samples.

The case with an enhancement layer can be analyzed in a similar manner. Assuming a *p*-type specimen, most of the charge in the space-charge region consists of holes in the valence band. If a field is applied in such a direction as to charge the semiconductor positively, holes very quickly flow into the space-charge

region, sufficient to satisfy the charge required by the field. After this short time, comparable to the dielectric relaxation time, the field effect mobility is μ_p' . The holes are now not in equilibrium with the surface states or the conduction band. After a longer time a quasi-equilibrium is established with the fast surface states, and a fraction α' of the added charge is immobilized in the surface states. The field-effect mobility is now $(1-\alpha')\mu_p'$. The time required is presumably of the same order of magnitude as that for quasi-equilibrium between fast states and the conduction band in the inversion layer case, but much shorter than minority carrier lifetime. After a still longer time, comparable to the lifetime, equilibrium is established with the conduction band. This results in a negligible change because the electron density is much smaller than the hole density. Thus in the case with no inversion layer, the field-effect mobility has the sign of the majority carrier, is a fraction of bulk mobility at low frequencies, changes very little at high frequencies, and tends to bulk mobility at very high frequencies.

Generally, the experimental results fit in quite well with this model. Thus, one concludes that at frequencies of the order of a few hundred cycles per second complete equilibrium is established between fast surface states and both the conduction and valence bands. At frequencies in the region of hundreds of kilocycles per second there is quasi-equilibrium between the fast states and the near band. With some reservations as to the reliability of the data above 10 megacycles per second, as discussed earlier, there is at least a suggestion that the time required for quasi-equilibrium between the fast states and one band is of the order of $1/(2\pi \times 15 \times 10^6) = 10^{-8}$ second.

ACKNOWLEDGMENTS

The author is indebted to W. L. Brown for suggesting the model used to explain field effect mobilities substantially in excess of bulk mobility, and to B. A. McLeod who made many of the early measurements in the low- and middle-frequency range.

⁹ C. G. B. Garrett is preparing an analysis of this situation for a forthcoming paper.