Effect of Electric Field on Surface Recombination Velocity in Germanium*

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The surface recombination velocity of *n*-type germanium is found to vary when an electric field is applied normal to the surface of the material. The results are sensitive to the atmosphere around the germanium. The theoretical predictions of the relation between surface recombination velocity and surface potential are qualitatively confirmed by these experiments. In addition, further evidence in favor of the surface-trap explanations for semiconductor excess noise now is found.

INTRODUCTION

As indicated by Stevenson and Keyes,[1] the surface recombination velocity s for minority carriers at a semiconducting surface should be a function of the surface potential ϕ_s.[2] The surface potential may be varied by changing the ambient gas or by applying an external electric field normal to the germanium. A general review of surface effects on semiconductors including the effects of external electric fields has been given by Bardeen and Morrison.[3] An effect of alternating electric field on s is described in the following. Somewhat similar phenomena, but for dc fields, have been reported by Henisch[4] and by Keyes, Sawyer, and Stevenson.[5]

In the work described here, changes in s were inferred from the variation in reverse current of an indium-alloy diode, prepared on a thin wafer of 5.0 ohm-cm *n*-type germanium. As discussed by Webster,[6] the reverse current of such a diode is determined primarily by the surface recombination velocity of the germanium, for usual values of bulk lifetime and resistivity. The indium-alloy side of the wafer was sealed in its own environment, as shown in Fig. 1, and electrically shielded. The opposite side of the wafer was exposed to various ambients. The electric field was applied normal to the exposed surface of the wafer from a close-spaced metal electrode.

EXPERIMENTAL DETAILS AND RESULTS

The metal field electrode was separated from the germanium wafer by a gap of about 0.01 cm. Most of the work described here was performed using the grid from a 416 A microwave triode as the field electrode. As manufactured, this grid is conveniently mounted on a metal disk and has 10^{-3}-cm diameter wires on 2.5×10^{-3}-cm centers; thus it is effectively a plane, permeable electrode. No difference in behavior was found using solid electrodes; the gases used as ambients apparently were carried rapidly into the gap. The diode current was displayed on the vertical axis of an oscilloscope and the electric field on the horizontal axis as indicated in the circuit of Fig. 2. Most of the measurements were made by using 60-cycle voltage on the field electrode. The peak applied field was of the order of $\pm2\times10^4$ volts/cm and the maximum change in diode current indicated was about 0.4 microampere or about 10 percent of the total diode current.

A series of oscillograms taken in various ambients[7] is shown in Fig. 3. An increase in diode current is an upward deflection in the figure and positive voltage on the field electrode is to the right. Photograph (a) was taken with a dry oxygen ambient, which presumably gives a *p*-type surface, and (b), (c), and (d) were taken in oxygen of successively increasing moisture content. (e) through (i) were taken with nitrogen ambient of successively increasing moisture content ranging to

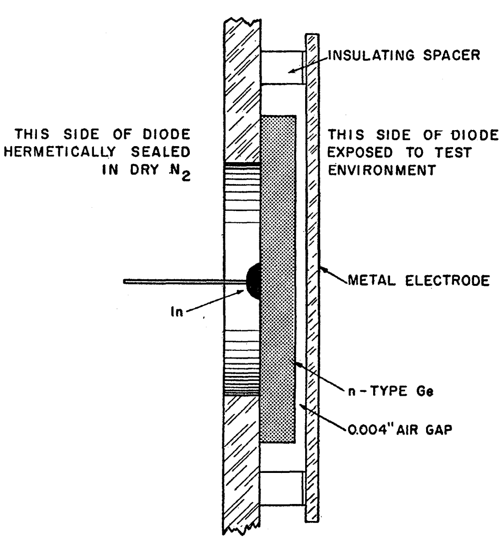

FIG. 1. The experimental arrangement. The indium alloy side of the diode is hermetically sealed from the exposed diode surface.

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

[2] ϕ_s is a measure of the departure in electron volts of the Fermi level at the surface from the "center" of the band gap, the "center" being the location of the Fermi level for material having hole density p equal to electron density n.

[3] J. Bardeen and S. R. Morrison, Physica **20**, 873 (1954).

[4] Henisch, Reynolds, and Tipple, Physica **20**, 1033 (1954).

[5] Keyes, Sawyer, and Stevenson (private communication).

[6] W. M. Webster, Proc. Inst. Radio Engrs. **42**, 914 (1954).

[7] The effects of these ambients on surface potential have been discussed by Bardeen and Morrison (see reference 3).

100 percent relative humidity at (i), presumably giving an n-type surface. The moist oxygen curves were found to overlap the dry nitrogen curves although the extremes indicated by photographs (a) and (i) could only be obtained in oxygen and nitrogen respectively. Since positive voltage on the field electrode corresponds to making the surface more n-type, moving to the right in one photograph is equivalent to moving to the right in the sequence of ambients. Thus the photographs may be fitted together to make a smooth curve.

Exposure of the germanium to light simultaneously with the electric field, in the usual range of ambients, produced curves which were similar to those shown in Fig. 3 but inverted. The amplitude was much larger and increased with the light intensity. Thus the maximum of Fig. 3(e) became a pronounced minimum in the same ambient. However, the curves taken with the light on showed *only* the minimum corresponding to Fig. 3(e) with no maximum corresponding to Fig. 3(a).

Figure 3(a) is noteworthy for another reason. The slope upward to the left, present in dry oxygen, is greatly accentuated by exposure of the germanium to ozone, which would be expected to make the surface even more p-type than the oxygen. In the case of one diode, this exposure to ozone caused the diode current to become much more noisy, so much so that the noise could be easily seen on the oscilloscope (this diode exhibited the best saturation characteristic of all diodes studied). With zero field on the exposed surface and an ac vacuum tube voltmeter substituted for the oscilloscope, the noise voltage rose as much as a factor of six when the exposed surface of the diode was in ozone. At first, it might seem that Fig. 3(a) would imply that s went through a minimum and increased again as the surface became more p-type. An alternative explanation will be given later.

The low-frequency response of the interaction between applied field and diode current was investigated down to 0.015 cps. The maximum response came at 140 cps although the response was constant within 10 percent to 3 cps. At 0.015 cps it was down 70 percent. The low-frequency observations are consistent with the long-time relaxation phenomenon in the field effect reported by Bardeen and Morrison.[3] This low-frequency drop-off explains why no attempt was made here to observe s variations with dc fields.

The behavior outlined above appears to be characteristic of normal, clear germanium surfaces. The full range of variation has been obtained on several diodes and repeatedly on the same diode after re-etching. The same behavior has been found for *CP*4 etched surfaces and anodically etched (in NaOH solution) surfaces. The patterns are only stable and reproducible after the surfaces have been exposed to the air for more than an hour. The only surfaces which did not show the full range of variation of Fig. 3 were those which were visibly dirty and those which were several weeks old. For the dirty surfaces the tendency was usually in the same direction, but the full range could not be covered; in other words, the surfaces appeared to be stabilized at one of the conditions shown in Fig. 3, and wet nitrogen would alter the picture slightly to the right and dry oxygen to the left. For the few old surfaces studied, the behavior was very strange with some indication that nitrogen at 100 percent humidity gave surfaces less n-type than nitrogen at lower humidities. Stevenson[8] has also seen this last type of variation for some surfaces.

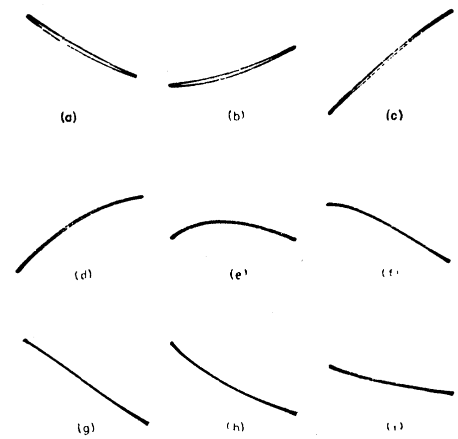

FIG. 3. Effect of electric field on surface recombination velocity.

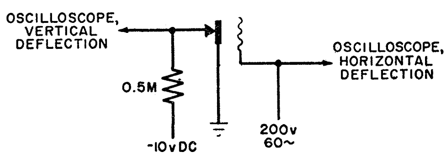

FIG. 2. The measuring circuit.

DISCUSSION

One possible variation of s with ϕ_s is shown in Fig. 4, reproduced from reference 1. It should be remembered that s is defined by the following relation: $J_p = s(p - p_0)$, where J_p is the number of holes recombining per unit surface area per unit time and p and p_0 are the actual and equilibrium hole densities in the *bulk* just inside any surface barrier which may exist. Figure 4 shows the variation if the cross section for recombination-trap interaction with the conduction band is the same as that for interaction with the valence band. The shape of the curves would be somewhat different for different cross section values, but in general, s should be low for strongly n- or p-type surfaces, and high for intermediate values of ϕ_s. The data of Fig. 3, except for photograph (a) which will be discussed later, are clearly consistent with a variation of the type shown in Fig. 4. The absence of a flat top, as in Fig. 3(e), may be understood from the fact that ϕ_s should change most

[8] D. T. Stevenson (private communication).

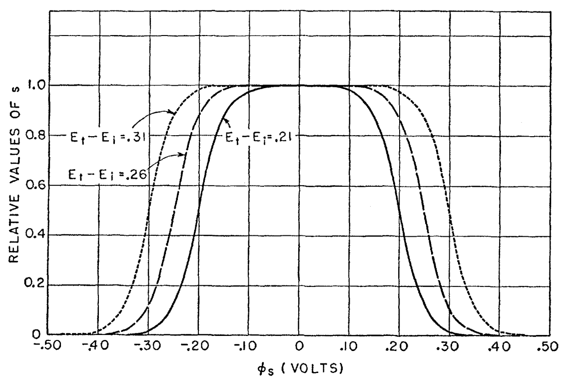

FIG. 4. Variation of the surface recombination velocity, s, as a function of ϕ_s for different departures of the trap energy from the "center" of the band gap.

rapidly with field for $\phi_s=0$, an intrinsic surface. In fact, using Kingston's curves,[9] from the value of the field used, the total range of ϕ_s in Fig. 3(e) may be as large as 0.4 ev.

Some quantitative estimates of the values of s in Fig. 3 can be made using an analysis similar to Webster's.[6] He shows that the reverse saturation current I_s in an alloy diode can be calculated with reasonable accuracy on the assumption that the diode collects all holes generated within a diffusion length L_p of the junction. For the diodes he treats and for those used here, L_p is considerably greater than the wafer thickness W. For the usual range of s values, the lifetime in the wafer is given by $W/(s_1+s_2)$, where s_1 and s_2 are the values of s on the exposed and alloy sides of the wafer, respectively. (This lifetime is always much less than the bulk lifetime so that the latter has been ignored.) The holes generated per unit area of surface are $p_0 s$, where p_0 is the equilibrium hole density in the bulk. Thus we have

$$L_p=\left(\frac{D_pW}{s_1+s_2}\right)^{\frac{1}{2}} \tag{1}$$

and

$$I_s=\pi q p_0[(s_1+s_2)(a+L_p)^2-s_2a^2], \tag{2}$$

where D_p is the diffusion coefficient for holes, q is the electronic charge, and a is the radius of alloy junction.

Differentiation of (2) gives

$$\frac{ds_1}{dI_s}\frac{I_s}{s_1}=\frac{(s_1+s_2)(a+L_p)}{s_1a}-\frac{s_2a}{s_1(a+L_p)}, \tag{3}$$

which for small values of L_p shows that I_s and s_1 are proportional, the result to be expected if the junction collects only those carriers generated on the surface directly opposite the alloy dot.

In our case, $a=0.05$ cm, $W=0.012$ cm, $p_0=1.8\times10^{12}$, and $I_s\sim4\mu A$. Taking $s_1\sim s_2=s$, we get $s\sim500$ and $L_p\sim0.022$ cm.

From Eq. (3), we get

$$ds_1/s_1=2.2dI_s/I_s, \tag{4}$$

so that a 10 percent change in I_s corresponds roughly to a 20 percent change in s_1. The total change of I_s in Fig. 3 may be as great as 30 percent. Rough measurements of the dc value of I_s during the cycle of ambients showed variations of about 30 percent also. Thus the variations in s_1 shown in Fig. 3 must be nearly as great as s_1 itself.

The effect of light on the measurements is consistent with the inferred variations in s_1. One merely needs to remember that the diode current will decrease as s_1 decreases only so long as the hole density p is less than p_0. Shining light on the sample will cause p to become greater than p_0, even directly opposite to the indium-alloy junction for sufficiently bright light. In this case, of course, the larger s_1 the greater will be the fraction of the injected carriers lost by recombination at the surface, and hence, the *smaller* will be the diode current.

Finally, an explanation is needed for Fig. 3(a) and the noise associated therewith. Note that this apparent increase in s_1 comes about for a strongly p-type surface. The reverse biassed diode will extract all the holes between the junction and the exposed p-type surface. If the lateral conductivity of the p-type inversion layer is high enough, all portions of the exposed surface will assume nearly the same electric potential; thus if the hole density near the alloy junction is zero, the hole density everywhere under the p-type inversion layer will tend to zero. That is, the inversion layer becomes back biassed and collects holes from the entire sample, carrying them by surface-majority-carrier conduction to the region of the alloy dot and discharging them there. Therefore, as the surface becomes more p-type, the effective area for collection of holes increases. Thus, even though s_1 may go down, I_s can rise, especially if the surface inversion layer reaches as far as the ohmic contact to the wafer.

Since the holes thus collected move laterally by ohmic conduction, any fluctuation in the conductivity of the inversion layer will result in fluctuations in the amount of bias of the inversion layer directly over the alloy dot. These bias fluctuations result in current fluctuations across the surface barrier under the inversion layer and hence finally result in fluctuations in I_s. According to McWhorter[10] and others, excess noise in semiconductors may be understood as fluctuations in conductivity of the surface layer due to statistical fluctuation of surface-trap occupancy. The observation of high noise in the experiments described here seems to fit this picture quite well.

The interpretation that Fig. 3(a) does not correspond to a minimum in s_1 is borne out by the fact,

[9] R. H. Kingston, J. Appl. Phys. **26**, 718 (1955).

[10] A. L. McWhorter, Phys. Rev. **98**, 1191(A) (1955).

mentioned earlier, that, with light shining on the sample, no maximum in diode current is observed under the conditions of Fig. 3(a).

CONCLUSION

It appears that the qualitative relationship between surface recombination velocity and surface potential for n-type germanium is as predicted by trap theory. Some features of the experiments appear at first to contradict this conclusion; on careful examination they turn out to be consistent, and in addition they lend credence to current theories of surface controlled noise.

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Photoelectromagnetic Effect in Insulating CdS

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The short-circuit photoelectromagnetic current in insulating crystals of cadmium sulfide has been measured in a batch of electroluminescent crystals. The product $(\text{mobility})^3\times(\text{lifetime})$ is found to be 1 $cm^6/volt^3\ sec^2$. The sensitivity of the equipment is sufficient to detect the photoelectromagnetic effect for crystals whose product is as low as 10^{-5} $cm^6/volt^3\ sec^2$.

THE minority carrier properties of insulators are difficult to measure because of the high resistance coupled with the small value of the carrier lifetime and the complications of induced space charge effects due to trapping. Measurements of the transient response due to alpha-particle, optical, or electron beam bombardment of single crystals give the product $\mu\tau$, mobility times lifetime, for either sign of carrier depending on the electrode polarity.[1] It is possible to get μ and τ separately if the response time of the measuring equipment is faster than the lifetime, but as the latter is usually millimicroseconds or less, this condition is seldom reached. Hall measurements on insulators, though they are also difficult because of the high resistance of the crystal and electroding problems, will yield the mobility of the majority carrier,[2] but unfortunately few insulators exist as both n and p type.

The photoelectromagnetic effect gives the product $\mu^3\tau$. It has been successfully used in the study of minority carriers in semiconductors.[3] For some insulators, where the mobility is reasonably high and the lifetime not excessively short, the effect should also be observable.

We wish to report positive evidence for significant minority carrier drift in insulating crystals of CdS from measurements of the short-circuit photoelectromagnetic (PEM) current. Single crystals of pure CdS approximately 2×2×0.05 mm, grown by vapor phase reaction,[4] were provided with ohmic electrodes of gallium[5] on the two ends of the front surface. These crystals had no impurities intentionally added. Their dark resistivities were greater than 10^{10} ohm cm. Light from a Bausch and Lomb 250-mm replica grating monochrometer was focused on the electroded surface in such a way as to give a roughly uniform illumination over the entire face. To prevent the shadows of the electrodes from maintaining a high-resistance region in the path of the PEM current, the light actually struck the contact between electrode and insulator. The effect of the small photovoltage was nullified by reversing the magnetic field at a low frequency.

The light flux onto the crystal was measured with a 929 photocell calibrated against an Eppely thermopile. The short-circuit PEM current, which was at largest about 10^{-9} amp, was measured with a Liston-Becker chopper amplifier of 50-ohm input impedance, which is low compared to the megohm resistance of the illuminated crystal.

Figure 1 shows the gain of the crystal (the external current per incident photon per sec), against wavelength. It is apparent that the PEM gain (solid curve) has the same wavelength dependence[6] as does the normal photoconductive gain measured by inserting a battery in the external circuit. The rapid drop in gain with wavelength above 5000 A is associated with crossing the edge of the fundamental absorption band.

The majority carrier lifetime τ_m comes from the

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[1] K. G. McKay, Phys. Rev. **74**, 1606 (1948).
[2] A. G. Redfield, Phys. Rev. **94**, 526 (1954).
[3] Moss, Pincherle, and Woodward, Proc. Phys. Soc. (London) **B66**, 743 (1953); H. Buillard, Phys. Rev. **94**, 1564 (1954); Kurnick, Strauss, and Zitter, Phys. Rev. **94**, 1791 (1954).
[4] R. Frerichs, Phys. Rev. **72**, 594 (1947).
[5] R. W. Smith, Phys. Rev. **97**, 1525 (1955).
[6] The droop in PEM gain at short wavelength is not felt to be significant. The relative accuracy of the measurements is poorer in this region because of the low emissivity of the tungsten lamp light source.