PHYSICAL REVIEW VOLUME 107, NUMBER 2 JULY 15, 1957

Distribution and Cross Sections of Fast States on Germanium Surfaces in Different Gaseous Ambients

A. MANY AND D. GERLICH*
Department of Physics, The Hebrew University, Jerusalem, Israel

(Received April 1, 1957)

Simultaneous measurements of surface recombination velocity and trapped charge density in the fast states as a function of surface potential are carried out on germanium surfaces at fixed gaseous ambients and temperatures. The surface potential is varied over a range of about 10 kT/q by the application of ac fields normal to the surface. For the surfaces studied, the distribution in energy of the fast states is found to consist of four discrete sets of levels. Only one of these sets is significant in the recombination process, being characterized by relatively high capture cross sections for holes and electrons. Another set has negligible cross sections and appears only in the field-effect data. The two remaining sets of levels lie outside the range of surface potential attained and little can be said about their properties. Detailed investigation of the surface recombination process shows that the energy level of the recombination centers is temperature-dependent, increasing slightly as the temperature is decreased. The field-effect data indicate that such is also the case for the other surface states.

Repeated measurements on the same sample over a long period *in vacuo* and in various gaseous ambients show that the structure of the fast states is markedly affected by these ambients. Initially, with the sample *in vacuo*, rapid changes in interface structure take place: the energy levels, the density, the ratio of the capture cross section for holes to that for electrons, as well as the cross sections themselves, all decrease with time. After a few days *in vacuo*, stabilization is essentially reached; following that, repeated exposures to different ambients result in reproducible changes in structure which persist for many weeks.

INTRODUCTION

IT is now well established[1] that there are two distinct kinds of surface states associated with the free surface of germanium. These are referred to as "fast states" and "slow states." The former are characterized by the fact that charge in them can follow rapidly changes in the space-charge region, the times involved being of the order of microseconds or less.[1] These states are in good electrical contact with the bulk and are probably situated at the interface between the germanium and the germanium oxide layer. The slow states, on the other hand, are characterized by long time constants, of the order of seconds or minutes, and are more closely associated with the structure of the oxide layer and the adsorbed chemical material.[1]

The present paper is concerned with the study of the properties of the fast states on etched germanium surfaces. Such information can be obtained by varying the surface potential and following the resulting changes in surface properties. The variation in surface potential can be effected either by exposing the filament to different gaseous ambients, such as those used in the Brattain-Bardeen cycle,[2] or by the application of strong electric fields normal to the surface (field effect). The validity of the former procedure rests on the assumption that the variation in gaseous ambient leaves the distribution and other properties of the fast states unaffected. Experimental evidence will be presented here that this assumption is not altogether justifiable. The use of the field effect is therefore preferable provided, of course, that a sufficient swing in surface potential can be obtained. This is indeed the case with the techniques used in this laboratory; the variation in surface potential is of the same order of magnitude as that obtainable by gaseous ambients.

Simultaneous measurements of surface recombination and surface conductance as a function of the capacitatively applied field have been carried out on a number of germanium filaments at different fixed ambients and temperatures. From these measurements, the dependence of surface recombination velocity and trapped charge density in the fast states on surface potential can be deduced.[3–9] These physical quantities depend on the distribution and capture cross sections of the fast states. The recombination data can yield information only on those states which have sufficiently large cross sections to be effective in recombination. The field-effect results, on the other hand, give information on the density distribution of all fast states, irrespective of their cross sections. The combined measurements can thus determine, among other things, which of the different fast states are active in recombination. It is

---

[*] This work represents part of a dissertation to be presented by D. Gerlich to the Faculty of Science of the Hebrew University in partial fulfillment of the requirements for the degree of Ph.D.

[1] R. H. Kingston, J. Appl. Phys. **27**, 101 (1956).

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

[3] Many, Harnik, and Margoninski, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957).

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

[5] Brown, Brattain, Garrett, and Montgomery, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957).

[6] Garrett, Brattain, Brown, and Montgomery, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957).

[7] W. H. Brattain and C. G. B. Garrett, Bell System Tech. J. **35**, 1019 (1956).

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

[9] S. Wang and G. Wallis [private communication (to be published)].

found that in most cases the experimental data can be satisfactorily accounted for by four discrete sets of surface levels. One of these sets is a recombination center, being prominent in both the field effect and the recombination data. Another set is definitely not active in the recombination process, although its density is comparable to that of the first. It is difficult to draw definite conclusions regarding the two remaining levels, as they are situated outside the range of surface potential values attained experimentally.

A marked effect of the surrounding ambients on the distribution and characteristics of the fast states is observed. Initially, with the freshly etched sample in a vacuum of 10^{-5} mm Hg, rapid changes in surface structure take place. After a few days, stabilization is essentially reached. It is then found that repeated runs in vacuum and in gaseous ambients result in reproducible changes in structure which persist for many weeks.

STATISTICS OF SURFACE-STATE DISTRIBUTION

For a given distribution in energy of fast states, both the surface recombination velocity s and the trapped charge density Q_{ss} depend on the surface potential φ_s. Considering one set of states having a single energy level, the application of Shockley and Read's theory of bulk recombination[10] to a semiconductor surface leads[3] to the following expression for s:

$$s=\frac{N_t c_p(p_b+n_b)}{2n_i\exp(q\varphi_0/kT)\{\cosh[(E_t-E_i-q\varphi_0)/kT]+\cosh[q(\varphi_s-\varphi_0)/kT]\}},\tag{1}$$

where $\varphi_0\equiv(kT/2q)\ln(c_p/c_n)$, c_p and c_n are the capture probabilities per state per unit time for holes and electrons, respectively, n_i is the intrinsic carrier concentration, p_b and n_b are the bulk hole and electron concentrations, N_t is the number of states per unit area, and $(E_t-E_i)/kT$ is the difference between the states' energy and the intrinsic Fermi level, measured in units of kT. The surface potential φ_s is defined by $q\varphi_s\equiv E_F-E_i+qV_s$, where E_F is the Fermi level and V_s the barrier height.

Equation (1) predicts that s has a maximum value (s_M), and is symmetrical about $\varphi_s=\varphi_0$. A plot of s as a function of φ_s gives the values of c_p/c_n and $|E_t-E_i-q\varphi_0|$. From the latter quantity, two values for the energy level E_t-E_i of the recombination centers can be deduced; one corresponds to the actual position of the centers, the other is spurious. To determine the energy level unambiguously, either the temperature dependence of s_M or two s *versus* φ_s curves for different temperatures must be experimentally known.[3]

The trapped charge density in the fast states, for one set of states having a single energy level E_t, is given by the Fermi distribution function as

$$Q_{ss}=-\frac{N_t}{1+\exp[(E_t-E_i-q\varphi_s)/kT]},\tag{2}$$

or by a sum of terms of this type when several sets of levels are present. The charge density in Eq. (2) is measured in units of the electronic charge q.

EXPERIMENTAL METHOD

The filaments studied were etched in CP4 and placed between two thin mica sheets. The outer faces of the sheets were coated with silver paint to serve as electrodes in the application of the transverse field. This assembly was then inserted into a cryostat in which the ambient gas and temperature were controlled. The quantities actually measured were filament lifetime τ_f and filament resistance R_f, both as a function of the applied voltage between the electrodes and the filament. These were measured by means of the circuit shown schematically in Fig. 1. The double bridge on the right is identical with that described previously.[3] It is activated by a voltage pulse, and τ_f and R_f are measured by means of the series combination RC and the decade resistance R_D, respectively, the two cathode-ray oscilloscopes serving as null indicators. In the technique described previously,[3] however, the surface potential was varied by the application of dc fields, a procedure which rendered the measurements very difficult due to the relaxation effects arising from the charging up of the slow states. This difficulty is removed and the accuracy appreciably increased in the present technique by the use of ac fields of suitable frequency (usually 50 cps). The ac voltage applied to the plates and the triggering signal for the pulse generator are both supplied by two secondary windings of the same transformer. The phase-shifting network shown on the left in Fig. 1 is adjusted so that the pulse applied to the bridge coincides with either the positive or negative crest of the voltage applied to the plates. As the pulse

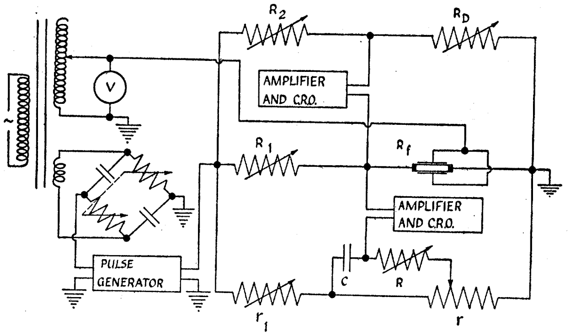

FIG. 1. Double-bridge circuit for the simultaneous measurement of lifetime and surface conductivity.

---

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

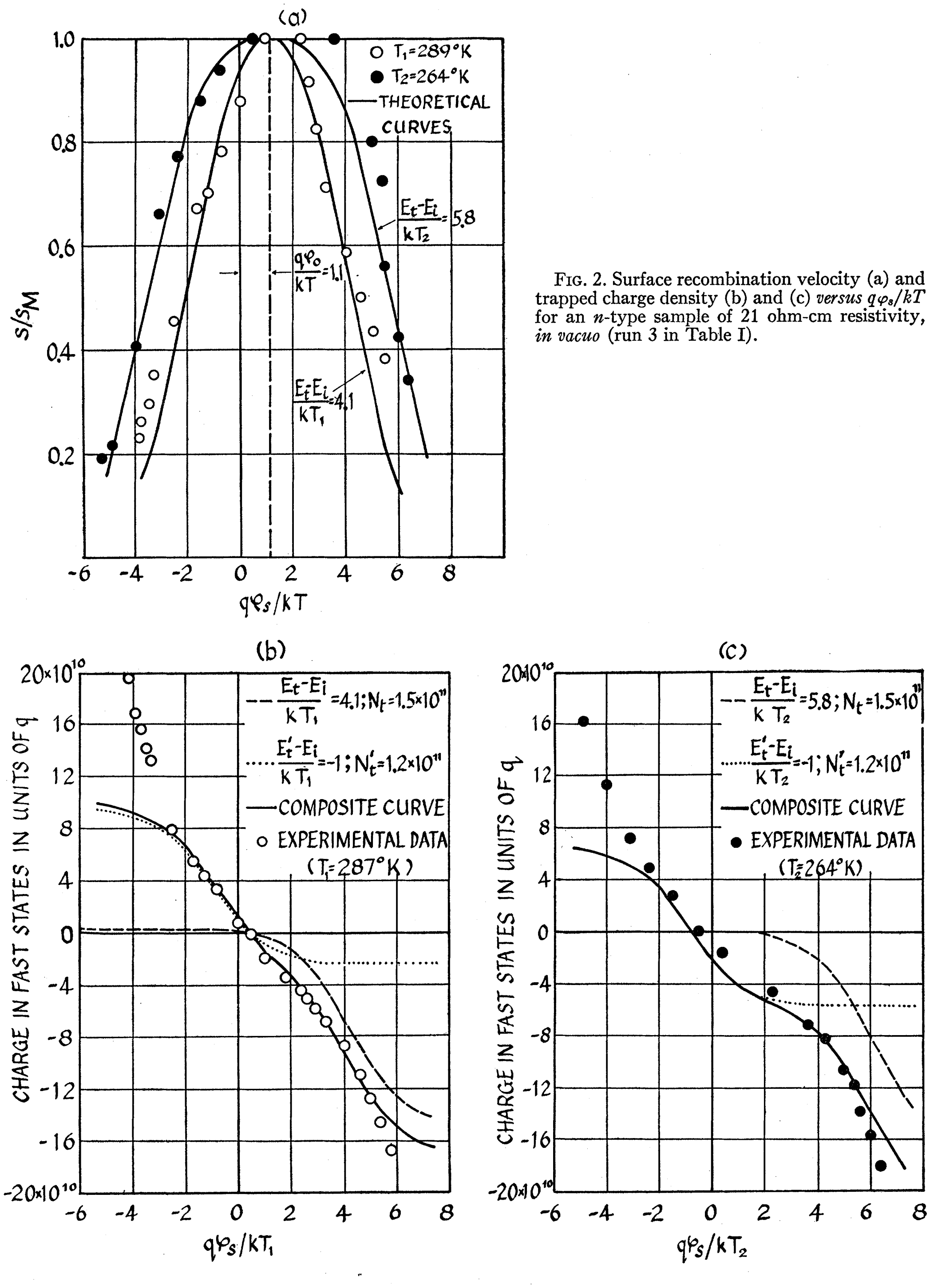

FIG. 2. Surface recombination velocity (a) and trapped charge density (b) and (c) *versus* $q\varphi_s/kT$ for an n-type sample of 21 ohm-cm resistivity, *in vacuo* (run 3 in Table I).

duration is much shorter than the period of the ac voltage, this arrangement ensures a constant field at the surface throughout the application of the pulse. By varying the amplitude of the ac voltage, τ_f and R_f, which are measured in the double bridge activated by the pulse, can be determined as a function of this amplitude.

The measured R_f values are used to evaluate the corresponding changes in surface conductance and from these, the φ_s values are determined,[11–13] using

---

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

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

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

TABLE I. The properties of the two sets of levels, E_t and E_t', of an n-type sample of 21 ohm-cm resistivity and crystallographic orientation (100) as affected by various ambients.

Run	Ambient	Time (days)	$(E_t-E_i)/kT$		s_M (cm sec^{-1})		$N_t\times10^{-11}$ (cm^{-2})	c_p/c_n	$(c_p/v_T)\times10^{14}$ (cm^2)		$(E_t'-E_i)/kT$	$N_t'\times10^{-11}$ (cm^{-2})
			T_1	T_2	T_1	T_2		T_1, T_2	T_1	T_2	T_1, T_2	
1	Vacuum	0(0)	6.0	···	340	···	3.7	30	2	···	1	0.6
2	Vacuum	1(1)	6.0	7.0	500	1100	2.9	25	3	3.5	1.4	0.7
3	Vacuum	2(3)	4.1	5.8	450	1100	1.5	9	0.7	2	−1	1.2
4	Vacuum	1(4)	4.5	···	650	···	1.6	14	1.5	···	−1	0.9
5	O_2	1(5)	3.9	5.1	390	710	1.2	2	0.6	0.9	−1	0.7
6	Vacuum	1(11)	4.7	5.6	450	1000	1.6	4	1.2	1.8	−1	0.9
7	O_2	6(18)	3.5	5.2	420	760	1.2	2	0.4	0.8	−1	0.7
8	Vacuum	1(19)	4.1	5.4	490	1050	1.5	2	0.7	1.3	−1	1.0
9	Vacuum	7(26)	4.4	5.4	550	1100	1.4	2	1.3	1.5	−1	0.7
10	O_2	7(33)	3.5	5.0	380	670	1.2	2	0.6	0.7	−1	0.7
11	N_2	2(45)	2.9	4.6	460	1020	1.2	2	0.4	0.7	−1.3	0.8
12	Vacuum	1(46)	4.0	5.6	530	1200	1.4	3	1.2	1.6	−0.7	1.0
13	H_2	1(48)	3.9	5.1	580	1000	1.4	3	1.0	1.1	−0.5	1.0
14	$N_2(+H_2)$	1(50)	4.0	···	540	···	1.4	5	1.0	···	−0.5	0.9
15	N_2	3(55)	3.3	···	490	···	1.0	5	0.7	···	−1	1.2
16	O_3	¼(61)	4.2	···	260	···	1.3	7	0.7	···	0	0.7
17	Vacuum	5(66)	3.7	5.6	540	1500	1.6	4	0.6	1.6	−0.7	1.2

the Schrieffer mobility correction. The surface recombination velocity s at each φ_s value is computed[14] from τ_f. Finally, from the ac amplitude, in conjunction with the predetermined capacitance between the plates and the filament (usually in the range 50–100 micromicrofarads), the total induced surface charge density is determined. By subtracting the theoretically known space-charge density[11,12] corresponding to the different φ_s values, the trapped charge density as a function of φ_s is obtained. This latter procedure is essentially identical with that devised by Brown,[4] but here the measurement is taken point by point.

RESULTS

The measurements were carried out on n-type samples. The bulk lifetime was large enough to ensure that with the thicknesses used (about 0.02 cm) and the s values encountered bulk recombination was negligible compared to surface recombination. Repeated runs of s and Q_{ss} *versus* $q\varphi_s/kT$ at two temperatures were taken *in vacuo* and in different gaseous ambients over a period of several weeks. Fairly high accuracy is required to detect changes in surface structure in the various ambients. This is obtainable with the techniques used provided the samples have suitable properties. For one thing, the filament should be carefully etched so as to insure a uniform surface potential. The method of lifetime measurement used here[15] is easily able to determine nonuniformities in the microscopic sense. (There is no available means of detecting irregularities on an atomic scale.) Another factor is that n-type is much more suitable for this investigation than p-type material. This latter is due to the following considerations. The accuracy in the vicinity of the surface-conductance minimum is inherently low.[3] Whereas in n-type samples this region ($\varphi_s<0$) occurs outside the range of φ_s which yields pertinent information on the significant states, in p-type samples it coincides with the interesting range ($\varphi_s>0$). The high accuracy also permits a more detailed investigation of the surface-recombination mechanism than was possible in a previous paper.[3] In order to enable precise and unambiguous analysis of the recombination data, only those surfaces were studied in which essentially one single set of recombination centers was present.

In Fig. 2 typical results for an n-type sample of 21 ohm-cm resistivity and crystallographic plane (100) are shown. The measurements were taken three days after etching, the filament having been kept during this time in a vacuum of 10^{-5} mm Hg (run 3 in Table I). The circles and dots in Fig. 2(a) represent measured values of s/s_M *versus* $q\varphi_s/kT$ for the two temperatures $T_1=287$°K and $T_2=264$°K. The quantity s_M in each case is the maximum value of s for the corresponding temperature, while T equals T_1 and T_2, respectively. The theoretical solid curves are plots of Eq. (1) with $\varphi_0=1.1(c_p/c_n=9)$, $|(E_t-E_i-q\varphi_0)/kT_1|=3.0$, and $|(E_t-E_i-q\varphi_0)/kT_2|=4.7$. This means that $(E_t-E_i)/kT_1=1.1\pm3.0$ and $(E_t-E_i)/kT_2=1.1\pm4.7$. If one assumes that E_t-E_i is temperature-independent, the actual levels are those[3] for which their ratio is equal to $T_1/T_2(=1.09)$. Obviously, of the two possibilities, 4.1 and 5.8 fulfil this condition much more closely. However, the fact that this ratio is somewhat larger than T_1/T_2 indicates that E_t-E_i is temperature-dependent to some extent, increasing with decreasing temperature. This same characteristic is also exhibited in the measured temperature dependence of s_M. This conclusion is confirmed in all other samples studied and is definitely beyond the limit of error. On the other hand, $q\varphi_0/kT$ and hence c_p/c_n is seen to be temperature-independent. As will be shown in Table I, c_p and c_n themselves are also temperature-independent within the limits of error.

In Figs. 2(b) and 2(c) the complementary data of the trapped charge density Q_{ss} in the fast states *versus* φ_s are shown, Q_{ss} having been set equal to zero for the φ_s value corresponding to the undisturbed surface (zero field). The calculations show that Q_{ss} constitutes about 90% of the total field-induced charge. The ultimate aim

---

[14] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

[15] A. Many, Proc. Phys. Soc. (London) **B67**, 9 (1954).

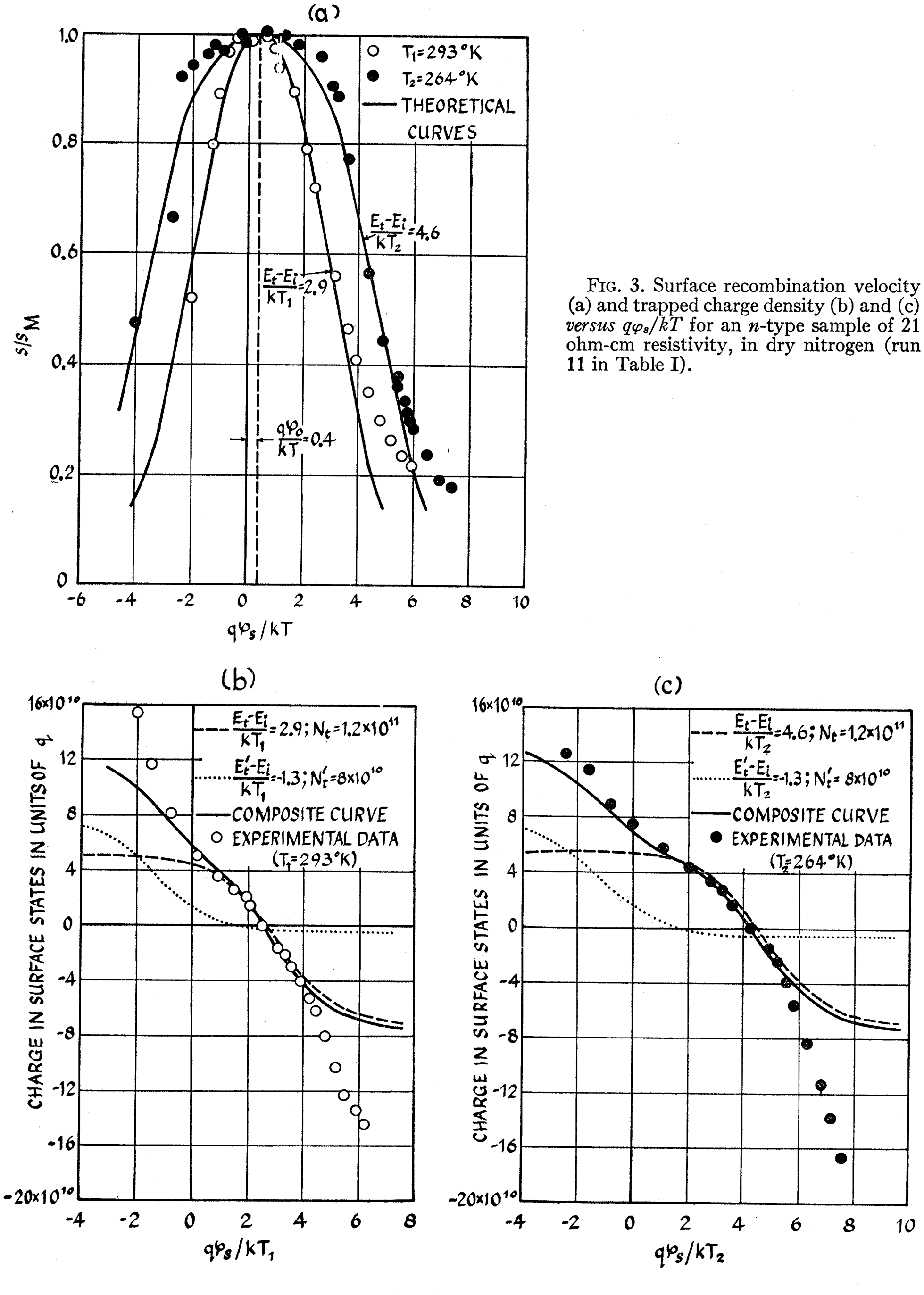

FIG. 3. Surface recombination velocity (a) and trapped charge density (b) and (c) *versus* $q\varphi_s/kT$ for an n-type sample of 21 ohm-cm resistivity, in dry nitrogen (run 11 in Table I).

of the analysis is to fit the experimental data by a sum of terms of the type given by Eq. (2). The states deduced from the recombination data form the basis of this analysis, as their energy levels are accurately known from data which is independent of the field-effect results. The fact that the swing in φ_s is sufficiently large to enable the Fermi level at the surface to pass through these states makes it possible to determine N_t quite reliably. It follows from Eq. (2) that the slope of the Q_{ss} *versus* $q\varphi_s/kT$ curve at $q\varphi_s=E_t-E_i$ is equal to $N_t/4$. If one considers Fig. 2(b), for example, this slope leads to a value of 1.5×10^{11} cm^{-2} for N_t. The dashed curve represents Eq. (2) for this value of N_t and for $E_t-E_i/kT_1=4.1$. It is seen that the experimental points and the dashed curve differ by a constant quantity over an appreciable range of $q\varphi_s/kT$. This is taken to mean that in this range another set of states is saturated with electrons. Using this saturation value and the experimental points in the range of $q\varphi_s/kT$ from -2 to 2, the energy and the density of this other set of levels is determined as $(E_t'-E_i)/kT_1=-1$ and $N_t'=1.2\times10^{11}$ cm^{-2}, respectively. The corresponding Q_{ss} function is shown as the dotted curve in Fig. 2(b). As can be seen from the s/s_M data, this set of levels does not contribute to the surface recombination. The solid line is the sum of the dashed and dotted curves, and is seen to fit the experimental data over a wide range. The same values of N_t and N_t', with $(E_t-E_i)/kT_2=5.8$ and $(E_t'-E_i)/kT_2=-1$, are used to construct the curves in Fig. 2(c). The two sets of levels just discussed cannot account for the experimental points at negative and extreme positive values of φ_s. This question will be taken up subsequently.

Figure 3 represents similar measurements on the same filament, but in a gaseous ambient of dry nitrogen following a series of different ambients during a period of six weeks (run 11 in Table I). The analysis is carried out in a completely analogous manner to that in the previous case. In accordance with the known effect of nitrogen on the slow states,[1] the value of φ_s for the undisturbed surface shifts to the right. For this reason the levels corresponding to $(E_t'-E_i)/kT=-1.3$ are already saturated at zero and positive fields, and hence in this range the experimental data are completely accounted for by the recombination set of levels alone. Here again, however, the two sets of levels E_t and E_t' cannot account for all the experimental data. Another pair of sets above and below E_i seems to be present as well. One set is situated near the conduction band, and a fit with the experimental data at large positive φ_s yields for $N_t\exp[-(E_t-E_i)/kT]$ the values 2×10^8 and 6×10^7 at T_1 and T_2, respectively. Essentially the same values are obtained from all the other measurements on this sample. The fact that an exponential expression is used in this fit indicates that the energy level of this set is far removed from E_i, i.e., by at least 6–7 kT. It is likely that this level may be responsible for the small departure of the experimental s/s_M values from the theoretical curves [Fig. 3(a)] for φ_s large and positive.† Regarding the other set, situated below E_i, little can be said. The experimental accuracy is low, the pertinent φ_s region being near the minimum of the surface conductance. A rough estimate indicates that the position of this level is at least 5 kT below E_i. A general characteristic of sufaces in gaseous ambients which is almost absent *in vacuo* is the slight charging up of the slow states by the applied ac field, due to the asymmetrical process of charging and discharging. This is manifested by small shifts of the quiescent value of φ_s (corresponding to zero applied field) during the measurements of the field effect. To avoid this, the latter are carried out rapidly.

Figures 2 and 3 are typical examples of a large number of runs on the same sample from immediately after etching to 10 weeks later. Some of these runs are summarized in Table I, where the density and characteristics of the two sets of levels E_t and E_t' are given for different ambients. In the third column of Table I, the times of exposure to the various ambients are given, beside which is indicated, in parentheses, the over-all time elapsed since the etching. In all cases the cryostat was continually evacuated for not less than 24 hours prior to a change in ambient. Most runs consisted of measurements at $T_1\approx288$°K and at $T_2=264$°K. Only dried ambients were used, so as to permit measurements at the lower temperature. c_p/c_n is obtained from φ_0 while c_p/v_T, where v_T is the thermal velocity of the holes, is evaluated from s_M, N_t, and E_t-E_i, by using Eq. (1). The values of $E_t'-E_i$ and N_t' are derived from the field-effect data as described in connection with Fig. 2.

The estimated accuracy of the quantities appearing in Table I is as follows. For the recombination levels the margin of error in $(E_t-E_i)/kT$ is ±0.3, while that in N_t is about 15%. An appreciably larger error is involved in $(E_t'-E_i)/kT$ and in N_t' as they are inferred but indirectly and from the field-effect data only. Regarding c_p/c_n and c_p/v_T, their accuracy is inherently poor as they are given by exponential terms in φ_0 and $(E_t-E_i)/kT$. The values quoted may differ by a factor of the order of 2.

The most pronounced feature in Table I is the relatively rapid change in surface structure during the first few days in vacuum after etching. The energy levels, density of states, and c_p/c_n decrease appreciably from run 1 to run 3. Following the latter, the structure has more or less reached stabilization. There is, subsequently (runs 4–10), a persistent and reproducible change between vacuum and oxygen, the oxygen tending to lower the energy levels, the density of states and the capture cross sections. Although this difference is bordering on the limit of error, its systematic occurrence makes this conclusion fairly reliable. Beginning at run 11, other ambients are introduced. Here again, changes in surface structure are seen to take place. E_t-E_i, for example, is still further decreased by the nitrogen, while the effects of hydrogen and ozone are more similar to that of vacuum. In contrast to oxygen and nitrogen, the effects of hydrogen and to some extent ozone persist for several days after their removal and continuous evacuation, as can be seen from run 14.

Another example of the change in surface structure between vacuum and oxygen is shown by the recombination data in Fig. 4(a). The sample used is n type, of 18 ohm-cm resistivity and no particular crystallographic orientation. One set of measurements was carried out in vacuum, shortly after etching, while the other was performed after 24 hours of exposure to

---

† *Note added in proof.*—Another possible explanation for this departure is that the Schrieffer mobility correction which was used in extracting the values of surface potential from the surface conductance data is not sufficiently accurate. For example, it has been pointed out by Ham and Mattis (American Physical Society Meeting, Toronto, June 22–24, 1955) that in calculating the mobility in thin channels it is necessary to take into account the anisotropy of the constant energy surfaces.

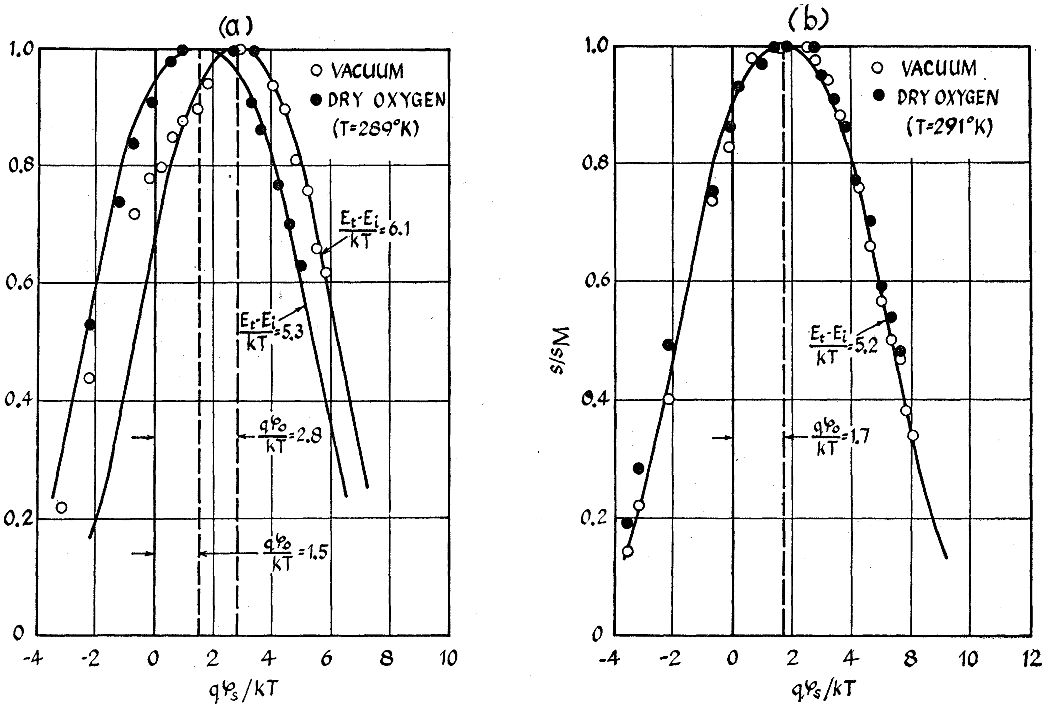

FIG. 4. Surface recombination velocity *versus* $q\varphi_s/kT$ for an n-type sample of 18 ohm-cm resistivity, *in vacuo* and in dry oxygen: (a) shortly after etching; (b) two weeks after etching.

oxygen. Figure 4(b) represents similar measurements but two weeks later. It is seen that the structure, at least as far as the recombination levels are concerned, has reached stabilization, differences between vacuum and oxygen being no longer detectable.

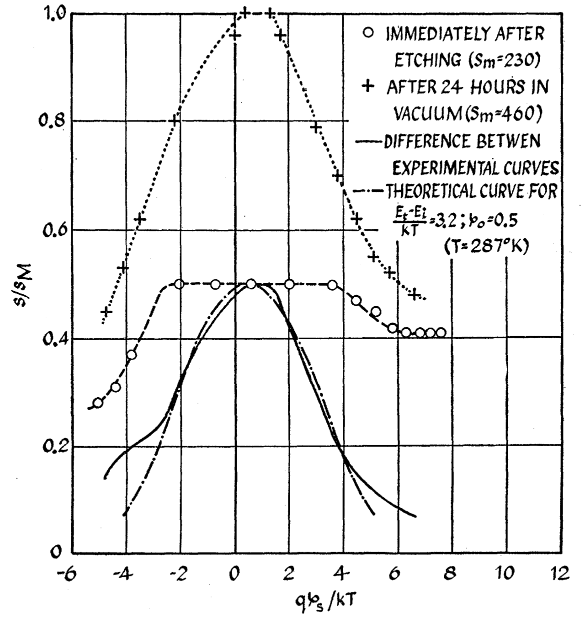

FIG. 5. "Growth" of recombination centers during the 24 hours following etching, for an n-type sample of 18 ohm-cm resistivity, *in vacuo.*

The "growth" of new recombination centers as a result of the exposure of a freshly etched surface for 24 hours to the low pressure of 10^{-6} mm Hg is illustrated in Fig. 5. The sample is the same as that in Fig. 4, but following another etching. The experimental results both immediately after etching and 24 hours later exhibit a complex structure in the sense that more than one set of levels is significant in the recombination process. Subtraction of the two experimental curves, however, gives an s/s_M curve which is typical of a single set of recombination levels, thus indicating that in the growth process only one set is evolved.

DISCUSSION

An important advantage in the experimental procedure described is the possibility of determining accurately the energy level of one set of surface states (the recombination centers). In this manner the analysis of the complementary field-effect data is rendered unambiguous to a large extent. The field effect by itself is hardly sufficient to determine uniquely the distribution in energy of the states; different distribution functions, ranging from a discrete scheme to a continuous one can equally account for the experimental data. The conclusion reached in this work, that for the surfaces examined the distribution of the fast states is essentially discrete, is believed to be fairly reliable. Perhaps the most obvious proof of the discrete nature of this distribution, apart from the good fit in the field-effect data, is given by the closeness of the fit between the recombination results and the theoretical expression [Eq. (1)] corresponding to one discrete set of levels. For a given surface, this fit is separately maintained for each temperature, but different values for the energy level of the centers should be used in each fit. It appears that a change in surface chemistry occurs with variation of the temperature. This is conceivable in view of the effect of the gaseous ambients on the surface structure, an effect which could be influenced by temperature. Such a variation, however, leaves the capture cross sections unaltered (Table I), at least within the experimental accuracy. The rise of energy with decreasing temperature is also exhibited by the other sets of levels deduced from the field effect. This can be seen, for example, from Fig. 2(c) (corresponding to the lower temperature), where a better fit could be obtained with a higher value of E_t'. The reason for choosing the same value of E_t' for both temperatures was merely to reduce the number of adjustable parameters to a minimum. It is possible that such changes in surface structure with temperature prevented Brown *et al.*[5] from carrying out a unified analysis of the field-effect data at different temperatures.

Of the four energy levels deduced, fairly complete information can be obtained only about the two lying closest to E_i, namely E_t and E_t'. The fact that E_t' does not contribute to the recombination process indicates that its capture cross section for at least one type of carriers is negligible compared to that of E_t. This shows that the assumption of Garret and Brattain[8] that the capture cross section is independent of the energy of the level is not always justifiable.

The results presented in this paper show conclusively that the ambients affect the structure of the fast states, in agreement with results reported previously[3] and with those reported by Wang and Wallis.[9] It should be noted that only the effects of prolonged exposure of the surface to the different ambients, of the order of several hours or more, could be investigated here. This is due to the fact that the measurements require about two hours for each run and it was necessary to ensure that the surface had reached equilibrium with the surrounding ambient before starting the run. Brattain and Garrett[7] and Montgomery and Brown,[16] on the other hand, find no such effect of the different ambients on the interface structure. It is possible that with the relatively short exposure times used in the Brattain-Bardeen ambient cycle, no appreciable change in interface structure can take place.

The behavior of the surface during the first few days after etching is different for the two samples described in Fig. 5 and Table I, respectively. In the former case additional states seem to have "grown" during the 24 hours following etching. In the latter case, on the other hand, it appears as if the growth of the new states (energy level of about 4 kT) is simultaneously accompanied by the vanishing of the original states (energy level 6 kT).

Several authors[3,9,16,17] report different values for the parameters characterizing the pertinent fast states. The spread in these values is within the range of the changes encountered here in a single sample over a period of several weeks and in the various ambients; almost all reported values can be found in Table I. In other words, the present results show that in general a surface cannot be uniquely characterized by a single set of parameters, as its structure depends on its past history after etching. Sample orientation and chemical treatment are probably important factors affecting the interface structure, but preliminary results indicate that differences due to such factors are smaller than those induced by exposures to the various ambients.

Although several general statements about the interface structure could be made from the results reported, the main issues remain unanswered. For one thing, no explanation can be given for the change in energy of the fast states with temperature. The effect of gaseous ambients on the fast states, especially several weeks after etching—during which time a stable oxide layer has presumably been established—is most surprising, in view of the separation of these states from the outer surface of the oxide. Finally, much has to be done in order to establish the origin of the various fast states; to what extent they are determined by sample orientation, bulk imperfection, chemical treatment, and gaseous ambients. The factors responsible for the characteristics of each individual set of levels, such as its density and cross sections, need also be clarified.

ACKNOWLEDGMENTS

The authors wish to express their indebtedness to Dr. E. Harnik of this laboratory for most stimulating discussions and many helpful comments. Thanks are also due to Mr. N. Grover who helped in the preparation of the manuscript.

---

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

[17] Statz, deMars, Davis, and Adams, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957).