Unique Determination of the Parameters of Surface Recombination Centers in Semiconductors

Y. MARGONINSKI AND Y. WALZER Department of Physics, The Hebrew University, Jerusalem, Israel (Received 30 September 1966)

Several *n*-type germanium crystals were subjected to combined measurements of surface recombination and pulsed-field effect. Recombination measurements were performed from room temperature to -10° C. the pulsed-field effect from -20 to -100 °C. The values for the energy E of the surface states obtained by the two methods were in agreement within 1kT or better. The two corresponding values of the capture cross section σ_n for the electrons were in most cases of the same order of magnitude. These combined measurements also enabled us to determine the energy E from surface recombination, when the capture cross sections for holes σ_p and electrons σ_n were equal. Complex experimental data, resulting from the presence of more than one state, could be analyzed uniquely, and thus all the parameters of the states could be evaluated.

1. INTRODUCTION

HE four significant parameters of a surface recombination center are its energy E, density N, and capture cross section σ_p for holes and σ_n for electrons. The most prevalent method to obtain these parameters is to measure simultaneously the surface recombination velocity s and the surface conductance $\Delta \sigma$, both as a function of the surface potential u_s . This technique is well established and has been extensively described in the literatures.^{1,2} It has two important drawbacks, both related to the functional dependence of s on u_s . First, the bell-shaped $s(u_s)$ curve does not determine one unique value for E, but two values: E_1 and E_2 . These correspond to the two values of u_s for which $s = \frac{1}{2}s_M$, where s_M denotes the maximum value of s. E_1 is closer to the conduction band E_c and given by the right-hand branch of $s(u_s)$, E_2 is closer to the valence band E_v and given by the left-hand branch. Only one of the two values corresponds to an actual surface state, the other has no physical significance. Secondly, if more than one recombination center is active in the region investigated, the resultant $s(u_s)$ curve cannot be analyzed uniquely. In other words, there is more than one way to decompose an *experimental* $s(u_s)$ curve into two (or more) separate *theoretical* curves. An example for two completely different analyses of certain experimental data can be found in a recent publication.³ This ambiguity in interpretation may even occur with only one active center, provided its $s(u_s)$ curve is very wide. If E_1 and E_2 are separated by 10kT or more, $s(u_s)$ can always be decomposed into two or even three narrow curves. The sum of these narrow curves is not exactly equal to the original wide one (deviations occur at $s=s_M$ and $s<\frac{1}{5}s_M$) but the difference hardly exceeds the experimental accuracy.

To overcome the first drawback and ascertain the correct energy value E_1 or E_2 , one of the following three methods may be used: (1) Simultaneously with

s, the density ΔN of charges trapped in surface states is measured, as a function of u_s . Analyzing the results of $\Delta N(u_s)$, one may be able to decide which of the two energy values gives a better fit with the experimental curve. This method is very unsatisfactory, because $\Delta N(u_s)$ is notoriously insensitive to changes in E and in most cases one obtains equally good results with either E_1 or E_2 . (2) Two $s(u_s)$ curves are measured, at two different temperatures. Assuming that σ_n and σ_p are temperature-independent, the value of E less affected by changes in temperature should be the correct one. Unfortunately, however, in many practical cases E_1 and E_2 are equally affected by temperature variations. (3) The temperature dependence of s_M is measured. As explained in the literature, $\ln(s_M T)$ versus 1/T yields a straight line, the slope of which is equal to either (E_c-E_1) or (E_2-E_v) . In many cases this method gives good results, but it completely breaks down if $s(u_s)$ is symmetric around the $u_s=0$ axis, i.e., if $|E_1| \approx |E_2|$, the energies being measured with respect to the intrinsic level E_i . To help analyze the results related to more than one active center, the correlation between $s(u_s)$ and $\Delta N(u_s)$ may again be used, but with limited results; too many appropriate pairs of energy and density values (E, N) will fit the $\Delta N(u_s)$ curve to be of much assistance. Summing up, there is only one satisfactory method to overcome the first difficulty, even this often failing, and none at all to overcome the second. Reviewing this situation, it occured to us that Rupprecht's pulsed-field effect⁴ may well provide the answer to both problems. First, here the energy Eis measured with respect to the majority carrier band, enabling states equidistant from the intrinsic energy level E_i to be easily resolved. Secondly, if the experimental results are plotted on a logarithmic scale, each surface state corresponds to a straight line of constant slope and the number of straight lines should therefore be equal to the number of states present. The pulsedfield effect has one disadvantage; it only measures one of the cross sections, the one associated with the ma-

¹ A. Many, E. Harnik, and Y. Margoninski, in *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, Pennsylvania, 1957), p. 85. ² A. Many and D. Gerlich, Phys. Rev. **107**, 404 (1957). ³ M. Margurin and M. Gerlich, Phys. Rev. **107**, 404 (1957).

³ Y. Margoninski and A. Gavron, Surface Sci. 5, 387 (1966)

⁴G. Rupprecht, Phys. Rev. 111, 75 (1958); Ann. N. Y. Acad. Sci. 101, 960 (1963).





jority carrier band. But by combining surface recombination with pulsed-field-effect measurements, one may expect to achieve a unique determination of all surface-state parameters. To test this method, the following measurements were performed on different samples of germanium: (1) combined field-effect measurements of surface recombination velocity s and surface conductance $\Delta \sigma$, at room temperature, (2) measurements of s_M as function of temperature, (3) measurements of Rupprecht's pulsed-field effect. The results of these measurements are reported in this paper.

2. EXPERIMENTAL METHODS

The measurements were performed on four different *n*-type germanium samples which had about the same resistivity (15 Ω cm) but were cut from two different ingots, each parallel to the (111) face. They had the form of a rectangular parallelepiped with approximate dimension of $1.2 \times 0.3 \times 0.05$ cm.

The samples were etched in CP-4A and measured in a vacuum of 0.1 μ of Hg. The recombination measurements were carried out with an ac field² and measured with a Many-type lifetime bridge.⁵ For the pulsed-field effect the same experimental setup was used, with one modification: The ac field-plate supply was exchanged with a dc pulse generator whose output could be varied from -50 to -400 V and whose pulse length was adjustable between 1-50 msec. A fraction of this pulse activated the lifetime bridge and triggered the Tetronix 551 dual-beam oscilloscope. A typical run was as follows: First, combined measurements of s and $\Delta \sigma$ were performed at about 25°C. The temperature was lowered slowly and s_M measured down to about -10° C. This lower limit for recombination measurements was imposed by two reasons: (a) injection decreases sharply with temperature; (b) the simple recombination theory requires that the number Δp of injected carriers be small compared to the density p_0 of *minority* carriers.⁶ For our samples this condition was violated at temperatures below -20° C. From -10 to -100° C the pulsed-field effect was employed. Measurements were taken at a fixed pulse voltage and the time constant of the thermal emission measured with the lifetime bridge. The time constants τ ranged from approximately 200 μ sec to 50 msec. After reaching -100° C the sample was heated and readings taken at a different pulse voltage until the sample had warmed up to -20° C. A complete run took about 4 h. Each sample was subjected to at least two complete runs, and the reproducibility was found to be good.

3. EXPERIMENTAL RESULTS

The inset in Fig. 1(a) is the energy-level diagram: E_c =bottom of conduction band, E_F =Fermi level, E_v =top of valence band. The intrinsic energy value E_i is indicated by the dashed line, u_s is measured with respect to E_i and positive for $E_F > E_i$. In Fig. 1(a) the results of surface recombination measurements on sample EP1/3/3 are shown, taken at 30°C. Two recombi-

⁵ A. Many, Proc. Phys. Soc. (London) B67, 9 (1954).

⁶ A. Many, Y. Goldstein, and N. B. Grover, in *Semiconductor Surfaces* (North-Holland Publishing Company, Amsterdam, 1965), Chap. 5.



156



nation centers are active: a dominant one with E_1 =6.4kT, E_2 =1.4kT and the weaker center with $E_1'=0.9kT$, $E_2'=-5.1kT$. All energies are measured with respect to E_i and quoted for $T = 300^{\circ}$ K. The dashed lines in Fig. 1(a) are the theoretical $s/s_M(u_s)$ curves for the two separate centers; the solid line is the sum of these two curves. The contribution of the weaker center to s_M is negligible, hence the temperature dependence of s_M will only give information about the dominant state. The slope of $s_M T$ versus 1/T equals 6.7 [Fig. 1(b)] corresponding to an energy value of 6.3kT, in very good agreement with $E_1 = 6.4kT$ obtained from Fig. 1(a). The results obtained from the pulsed-field effect are reported in Fig. 1(c). The ordinate is on a logarithmic scale and in units of $[\tau N_c v_T]^{-1}$. τ is the time constant for the thermal emission of electrons from the surface state into the conduction band, N_c the effective density of states in the conduction band, and v_T the thermal velocity of the electrons. As explained by Rupprecht,⁴ the slope of the straight line passing through the experimental points is equal to (E_c-E) and its intercept with the ordinate gives $\gamma \sigma_n$,

where γ is the statistical weight factor of the surface state. As can be seen from Fig. 1(c), the pulsed-field effect also indicates the presence of two surface states, a shallow one with an energy $E_1=7.1kT$ and capture cross section $\sigma_n=1\times10^{-19}$ cm² and a deeper center, whose energy is $E_1'=1.5kT$ and cross section σ_n' $=2.5\times10^{-15}$ cm². The correct energy values in Fig. 1(a) are therefore E_1 and E_1' . Considering that the values for σ_n , as obtained from surface recombination measurements, are 6×10^{-18} and 4×10^{-15} cm², respectively (Table I), the agreement between recombination and pulsed-field measurements can be regarded as satisfactory.

905

The next example illustrates a more complicated analysis. Fig. 2(a) gives the results of recombination measurements on sample EP1/3/1, at 27°C. At first sight one might be tempted to explain the results by the presence of only *one* recombination center with an energy of either $E_1=8.0kT$ or $E_2=-3.5kT$. The temperature dependence of s_M [Fig. 2(b)] is in better agreement with E_2 , but the pulsed-field effect [Fig. 2(c)] points clearly to E_1 . This contradiction was resolved

Sample	Recombination measurements							
	s/s_M			$s_M T$		Pulsed-field effect		
	E_1	E_2	σ_n	E_1	E_2	E_1	E_2	σ_n
EP1/3/3	6.4	(1.4)	6×10 ⁻¹⁸	6.3		7.1	***	1×10-19
	0.9	(-5.1)	4×10^{-15}			1.5		3×10^{-13}
EP1/3/1	8	(2)	2×10 ⁻¹⁹	7.2		7.3		2×10^{-19}
	1.2	(-2.8)		1.2				
Se/6/2	(7.3)	-1.7	1×10^{-14}		-2		-2	2×10^{-10}
Se/6/4	5.8	(2.8)	5×10^{-18}	6		5		1×10^{-10}
	(1.4)	-2.8	2×10^{-15}				-3	1×10^{-14}

TABLE I. Comparison between surface parameters obtained from recombination and pulsed-field-effect measurements.⁴

^a Energies are measured with respect to E_i and quoted in units of kT; $T = 300^{\circ}$ K. Energy values corresponding to virtual centers are stated in brackets. σ_n is in units of cm².



FIG. 3. Measurements on sample EP1/3/1 performed on the following day. The presence of two centers is now clearly evident; the activity of the left center has declined.

when the recombination measurements were repeated on the next day. As clearly illustrated in Fig. 3(a), two recombination centers are active in the region investigated. In Fig. 2(a) these centers contribute equally to s_M , whereas in Fig. 3(a) the activity of the left center has declined. To interpret Fig. 2(a) correctly, the experimental results should be attributed to two centers: a left one, for which $E_1' = 1.2kT$ and $E_2' = -2.8kT$ and a right center, for which $E_1 = 8kT$ and $E_2 = 2kT$. When measuring s_M on the first day, small voltages were applied and only the left center measured. The results of Fig. 2(b) correspond therefore to E_1' , whereas the pulsed-field effect indicated E_1 . On the second day the left center had weakend and the temperature dependence of s_M should give the same results as the pulsedfield effect. This is indeed the case, as illustrated in Fig. 3(b). Pulsed-field-effect measurements performed on the second day gave poorer results, but they clearly indicated the presence of another center at 1.7kT, i.e., a value corresponding to E_1' . The result $\sigma_n = 2 \times 10^{-19}$ cm^2 [Fig. 2(c)] was identical with that obtained from recombination measurements.

Almost all the data on recombination centers published by various investigators since 1957 was based on

the assumption that only the right-hand branch of $s(u_s)$ determines the energy of the surface state. The first exceptions to this rule were published by Frankl⁷ and by Balk and Peterson.⁸ Frankl⁷ found that by assuming $E=E_2$, a much better fit was obtained between the experimental values of $\Delta N(u_s)$ and the corresponding theoretical curve; Balk and Peterson⁸ reported that their experimental results of $\Delta N(u_s)$ could be fitted equally well to either E_1 or E_2 . Unfortunately, neither investigator measured the temperature dependence of s_M ; this was done, however, by Margonnski and Gavron,³ who recently reported new evidence for $E = E_2$. Another such case is illustrated in Figs. 4(a), 4(b), and 4(c). Measurements of s taken at 30° C on sample Se/6/2 yielded $E_1 = 7.3kT$ and $E_2 = -1.7kT$ [Fig. 4(a)]. The solid line in this figure is the theoretical $s/s_M(u_s)$ curve. From $s_M T$ a slope of 11.1 was obtained [Fig. 4(b)], clearly pointing to E_2 . The results of the pulsedfield effect [Fig. 4(c)] were in good agreement with those obtained from surface recombination: $E_2 = -2kT$ and $\sigma_n = 2 \times 10^{-15}$ cm², compared to $E_2 = -1.7kT$ and $\sigma_n = 1 \times 10^{-14}$ cm². In Fig. 3(c) the presence of another state is indicated at a distance of about 4kT from the valence band. Recombination measurements were ineffective in detecting this center, probably because the ac field voltages were insufficient to explore the region near the valence band. Another argument against E_1 is obtained by comparing its thermal emission constant τ to that of E_2 at 217°K. At this temperature E_1 was about 2kT below the Fermi level and therefore filled, whereas at higher temperatures the rapid changes of the surface potential moved E_1 towards and above E_F . The value of τ for a surface state with $E_1 = +7kT$, $\sigma_n = 1 \times 10^{-14}$ cm² at T = 217°K is 0.04 µsec, compared to $\tau = 0.01$ sec for a state of the same σ_n , but $E_2 = -2kT$. After applying a negative pulse, E_1 should reach equilibrium much faster than E_2 (because of its shorter time constant τ) and prevent any detection of E_2 . But this is clearly not the case because E_2 is still dominant at 217°K; therefore a surface state corresponding to the right branch of $s/s_M(u_s)$ does not exist.

In all preceding examples the crystals were etched with CP-4A. Figure 5 reports the results for a different surface treatment. Sample Se/6/4 was first etched in CP-4A, then baked in air at 120°C for 1 h, etched for 1 min in 48% HF, and finally immersed for 1 min in hot (90°C) KOH. The purpose of this treatment was to render the sample sensitive to the influence of copper ions.⁹ The results of the recombination measurements indicated the activity of more than one center [Fig. 5(a)]. The pulsed-field effect [Fig. 5(c)] revealed the presence of two surface states, one at $E_1=5kT$ and the other at $E_2'=-3kT$. The $s_MT(1/T)$ plot [Fig. 5(b)] pointed to an energy of either +6kT or -6kT, the

⁷ D. R. Frankl, Phys. Rev. **128**, 2609 (1962).

⁸ P. Balk and E. L. Peterson, J. Electrochem. Soc. 110, 1246 (1963).
⁹ D. R. Frankl, J. Electrochem. Soc. 109, 238 (1962).





10

positive value being in agreement with E_1 . The experimental results of the recombination measurements were therefore fitted to two $s/s_M(u_s)$ curves, a left one with energies $E_1' = 1.4kT$, $E_2' = -2.8kT$ and a right one, for which $E_1 = 5.8kT$, $E_2 = 2.8kT$ [dashed lines in Fig. 5(a)]. The cross sections obtained from this analysis were $\sigma_n = 5 \times 10^{-18} \text{ cm}^2$ for E_1 and $2 \times 10^{-15} \text{ cm}^2$ for E_2' , in good agreement with the results obtained from the pulsed-field effect, Fig. 5(c). To complete the analysis, Fig. 5(d) gives the results of the measurements of the charges ΔN trapped in the surface states. The theoretical curve [solid line in Fig. 5(d)] passes through the two centers $(E_1=5.8kT \text{ and } E_2'=-2.8kT)$ whose densities were 18×10¹⁰ and 20×10¹⁰ cm⁻², respectively.

When employing the pulsed-field effect, the pulse amplitude should be chosen carefully. If too strong fields are used, field-enhanced emission from the surface states may occur and mask the thermal release effect.¹⁰ The highest voltage used by us was -400 V and, as can be seen from Fig. 6, the energy was independent of voltage from -80 to -400 V. The measurements were taken on sample Se/6/2 and for a temperature range from -5 to -60° C. The center measured was the one appearing in Fig. 4(c), close to the valence band.

Table I summarizes the experimental results.

4. DISCUSSION

For the first time measurements of both surface recombination velocity s and the time constant τ of carrier emission from the states into the majority carrier band have been performed on one and the same sample. The energy values obtained from these two different techniques were in very good agreement and

this indicates that the energy is practically temperature-independent from +30 to -100 °C. The agreement between the cross sections σ_n derived from the two methods was far better than expected, and this is a great surprise. Measurements of s, considered the more accurate of the two methods, are not expected to yield a value of σ_n or σ_p more dependable than its order of magnitude. Therefore we would not have been alarmed to find a discrepancy of even two orders of magnitude between the respective values. However, in all cases the agreement of the two values of σ_n was significantly better than that (see Table I). Many et al.¹¹ reported a difference of 10³ for the values of σ_n obtained by the two methods, but measured on *different* samples. They suggest different surface treatment as a possible explanation, but in view of our present results an error in the analysis of $s/s_M(u_s)$ may also be a probable reason. An example is illustrated in Fig. 7. The $s/s_M(u_s)$ curve is almost symmetric around the $u_s=0$ axis and the two energies associated with the main recombination center are $E_1 = 4.3kT$ and $E_2 = -4.7kT$ [Fig. 7(a)]. As mentioned in the Introduction a plot of $\ln(s_M T)$ versus 1/T is of no aid in this case and never accurate enough to resolve a difference of 10%in its slope [Fig. 7(b)]. The pulsed-field effect yielded a value of E = 4.4kT [Fig. 7(c)], deciding the issue in favor of E_1 . Or did it? From recombination measurements $\sigma_n = 2 \times 10^{-14}$ cm², whereas from Fig. 7(c) one finds $\sigma_n = 1 \times 10^{-17}$ cm². A difference of 10^3 cannot be ignored. A completely different analysis provides the satisfactory answer. Turning to the weak recombination center visible in Fig. 7(a), the two energies associated with it are $E_1'=9.2kT$ and $E_2'=4.2kT$. The second value almost coincides with E_1 , but the two states have

¹⁰ A. Many and Y. Goldstein, Surface Sci. 2, 114 (1964).

¹¹ Reference 6, Chap. 9.



FIG. 5. Measurements on sample Se/6/4 after complex chemical treatment. (d) shows the density of trapped charges ΔN as a function of surface potential u_s . Circles are experimental points, the solid line is the theoretical dependence of $\Delta N(u_s)$.

widely different cross sections; $\sigma_n' = 1 \times 10^{-18}$ cm². By associating the value of E=4.4kT, obtained from the pulsed-field effect, with $E_2' = 4.2kT$ and not with E_1 =4.3kT, the difference between the two values of σ_n is reduced by two orders of magnitude. For the main recombination center the correct energy value would consequently be $E_2 = -4.7kT$. It does not appear in the pulsed-field effect [Fig. 7(c)] because it is too far below the Fermi level to compete with E_2' ; their respective emission constants have the same order of magnitude. The presence of a state around -5kT is also indicated by the trapped charge measurements [Fig. 7(d)]. The solid line in Fig. 7(d) is the theoretical distribution of $\Delta N(u_s)$, due to states at $E_2 = -4.5kT(N=25 \times 10^{10})$ cm⁻²), $E_2' = 3.8kT$, (N=5×10¹⁰ cm⁻²), and $E_3 = 9kT$, $(N = 50 \times 10^{10} \text{ cm}^{-2}).$

The association of recombination centers with the left branch of $s(u_s)$ (Fig. 4) should not be regarded as unusual. After all, the position of a center on $s(u_s)$ is only determined by the relation between the value of E and the ratio σ_p/σ_n , i.e., by the relation between E and u_0 . Here u_0 is the intercept of the axis of symmetry of $s(u_s)$ with the abscissa, and $\sigma_p/\sigma_n = \exp(2u_0)$. If $\sigma_p > \sigma_n$ and the ratio σ_p/σ_n is such that $u_0 > E$, the center will be "left handed," if $u_0 < E$, it will be "right handed." After being subjected to chemical or heat treatments, etc., a recombination center might even "jump" from



FIG. 6. Dependence of the energy E (in units of kT for $T=300^{\circ}$ K) on voltage applied to field plate, measured on sample Se/6/2.

one branch of $s(u_s)$ to the other, but this will rarely happen, because³ the energy required to do so would usually be far too great (>8kT). It is also possible that a center moves from, say, the left branch of one curve to the right branch of a different curve. This will be the case if the crystal is subjected to a treatment greatly increasing σ_p , without affecting σ_n or E. We have found such a change after immersion of a germanium sample in a solution of Cu(NO₃)₂, which caused σ_p to increase by two orders of magnitude.³

For a surface state at a distance of 15kT from E_c it may seem surprising that at a temperature of only -35° C, a pulse of -400 V is sufficient to bring the state close to the Fermi level [Fig. 4(c)]. But one should bear in mind that in the extrinsic range the minority carrier density decreases exponentially with temperature. We also found that at lower temperatures the surface of sample Se/6/2 became strongly *p*-type, moving E_2 towards the Fermi level. The change of u_s with temperature was not monotonic, and below -40° C the energy bands started to straighten out again. At -56° C the surface was so strongly *n*-type that even E_1 was about 2kT below E_F . This change of u_s varied much from sample to sample, indicating the complex behavior of the slow surface states at low temperatures.

5. CONCLUSION

By combining measurements of surface recombination and pulsed-field effect, a significant improvement in the evaluation of the experimental data was achieved. The energy of a recombination center can thus be determined unambiguously for all values of σ_p and σ_n , whereas previously this was only possible if $\sigma_p \neq \sigma_n$. Complex recombination data, resulting from the presence of more than one center, can be analyzed



FIG. 7. The energy E=4.4 kTobtained from the pulsed-field effect (c) can be attributed to either E_1 or E_2' (a), but the corresponding values of σ_n differ by 10⁸. The $s/s_M(u_s)$ curve is almost symmetric around $u_s=0$; therefore the slope of s_MT versus 1/T in (a) fits both E_1 and E_2 .

uniquely and the parameters of all the surface states evaluated.

It sometimes happens that a certain surface state appears only in one of the measurements, either because the field effect does not swing the surface potential sufficiently [Fig. 4(a)], or because carrier emission from one state prevents other states from approaching the Fermi level [Fig. 7(c)]. Therefore the two different techniques complement each other very well. Recombination measurements are best performed in the higher temperature range, i.e., from the onset of the intrinsic region to about -20° C. For the lower temperature range the pulsed-field effect is the more effective. From the experimental point of view both methods are very much alike. They require different voltage supplies for the field plate, but otherwise the same instruments can be used and the mounting of the sample is identical.

ACKNOWLEDGMENTS

The authors are extremely grateful to Dr. Y. Goldstein for his continuous advice and assistance. They are also indebted to Professor Many for most stimulating discussions and many helpful comments.