

The range of application of the method developed in the present investigation is determined by the possibility of carrying out the integration over \mathbf{p} , and the subsequent inverse transform. Approximations have to be made to permit this double integration, and these approximations curtail to a certain extent the great potentialities of the method. Applications to a wider range of problems would be possible if θ_M , the function of the Hamiltonian operator of (2.2), appeared in a simpler and more manageable form than as an inverse

transform. As the method stands, however, it is still applicable to a variety of interesting problems in quantum statistics.

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Effect of a Constant Electrical Field on Germanium Fast Surface States*

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The experimental evidence regarding the effect of electric fields on the fast states of germanium is, at present, contradictory: Litovchenko and Lyashenko explained their experimental results by assuming the fields only affect the density of states but not their energy, this would support the current view on charge transfer through the semiconductor oxide layer. Rzhano *et al.*, on the other hand, reported field-induced changes in energy as well as density. To resolve this question, careful measurements of surface recombination velocity and surface conductivity were performed before and after application of dc fields of about 2×10^6 volts/cm. Though the effect of the field on the surface state density was much smaller than that found by Litovchenko and Lyashenko, the experimental results indicated clearly that the energy and ratio of capture cross sections were indeed unaffected by the field. It was also found that in wet ambients an ac field shifted the unperturbed surface potential by more than $+5kT$.

1. INTRODUCTION

LITOVCHENKO and Lyashenko¹ reported that prolonged application (of over 10 minutes) of strong electric fields $\{ \geq [(0.5-1) \times 10^6 \text{ volts/cm}] \}$ affected the density of the fast germanium surface states. They investigated the field effect (change in surface conductivity $\Delta\sigma$ with applied pulsed field) on a *p*-type germanium specimen, dimensions of $1.5 \times 0.5 \times 0.03 \text{ cm}^3$, cut perpendicular to the 110 axis and of 20–30 ohm-cm resistivity. Their measurements were performed in a vacuum of 10^{-6} mm Hg and in a dry air atmosphere, the effect being present in both ambients. They found a considerable change in the $\Delta\sigma$ vs u_s curve (u_s being the surface potential; i.e., using the notation of Kingston and Neustadter² and of Many and Gerlich³: $u_s = q\phi_s/kT$) after application of a dc field and explained their experimental results by assuming that the surface state energy ($E_t - E_i$) remains constant, whereas the

density N_t of the states does change. This assumption could not be verified experimentally by measuring only the change in surface conductivity, because for each $\Delta\sigma(u_s)$ plot ($E_t - E_i$) as well as N_t are unknown and one parameter can only be determined with a reasonable accuracy if the other is known. However, by performing combined measurements of surface recombination velocity s and changes in surface conductivity $\Delta\sigma$, the energy ($E_t - E_i$) of the recombination centers, the ratio c_p/c_n of the capture cross sections of holes c_p and electrons c_n , and the density of states can be measured and hence all surface state parameters be determined. Combined measurements were therefore performed on a germanium crystal, before and after application of a strong electric field, and the results are published in this paper.

2. EXPERIMENTAL METHOD

The germanium specimen investigated was *n* type, of 17 ohm-cm resistivity, of dimensions $1.45 \times 0.39 \times 0.038 \text{ cm}$, and cut parallel to the (111) plane. It had two soldered end contacts, one Ohmic and the other slightly injecting, and was etched in CP-4A for one minute at 35°C . After etching and rinsing, brass field plates were clamped to the crystal with mica sheets (of 0.004 cm thickness) sandwiched between them. The assembly was placed in a glass tube, subjected for two days to a

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¹ V. G. Litovchenko and V. I. Lyashenko, *Soviet Phys.-Solid State* **1**, 1470 (1960).

² R. H. Kingston and R. F. Neustadter, *J. Appl. Phys.* **26**, 718 (1955).

³ A. Many and D. Gerlich, *Phys. Rev.* **107**, 404 (1957).

TABLE I. Fast surface state parameters of *n*-type sample before and after being subjected to dc fields.

No.	Treatment	$(E_t - E_i)/kT$	$q\varphi_0/kT$	c_p/c_n	$N_t \times 10^{-10}$	s_M	u_{s0}	$(E_t' - E_i)/kT$	$N_t' \times 10^{-10}$
1	Vacuum	4.6	2.1	66	40	690	+2.9	-1	70
2	After application of +550 volts	4.8	2.3	99	44	720	+2.5	-1	45
3	Vacuum	4.9	2.4	121	48	700	+2.8	-1	48
4	After application of +1500 volts	4.9	2.4	121	56	800	+1.7	-1	43
5	Vacuum	4.9	2.4	121	56	800	+1.7	-1	43
6	After application of -1500 volts	4.7	2.2	81	44	855	+1.7	-1	38

wet oxygen atmosphere, and then evacuated to a vacuum of at least 10^{-4} mm Hg. Measurements were taken; a voltage of +550 volts was placed on the field plates for over 12 hours, then switched off, and the second set of measurements taken. The same procedure was repeated with the higher voltages of +1500 volts and -1500 volts. All measurements were taken at 21°C. The technique of the combined surface recombination velocity and surface conductivity measurements, as well as the interpretation of data, were those developed by Many and his coworkers³: the surface potential u_s was changed by an alternating (50 cps) electric field emanating from the brass field plates, and simultaneous measurements of filament lifetime τ and resistance R were taken. From the experimental data two curves were constructed as functions of the surface potential u_s : (1) the fractional surface recombination velocity s/s_M , where s_M denotes the maximum value of the surface recombination velocity s ; (2) the added trapped charge density ΔQ_{ss} in the surface states relative to its value before application of the field, when $u_s = u_{s0}$. From the first curve, the energy $(E_t - E_i)$ of the recombination center and the capture cross-section ratio c_p/c_n were obtained; the analysis of the ΔQ_{ss} vs u_s curve yielded the density N_t of the recombination center as well as the energy $(E_t' - E_i)$ and density N_t' of one additional recombination-ineffective surface state.

3. EXPERIMENTAL RESULTS

The experimental results are summarized in Table I. $q\varphi_0/kT$ is the displacement of the axis of symmetry of the s/s_M curve from the origin, and

$$c_p/c_n = \exp(2q\varphi_0/kT).$$

$(E_t - E_i)$, u_{s0} , $q\varphi_0$, and $(E_t' - E_i)$ are in units of kT , s_M is in cm/sec, and the units of N_t and N_t' are cm^{-2} .

The estimated accuracy of the parameters appearing in Table I is as follows: the error in $(E_t - E_i)$, $q\varphi_0$, and u_{s0} is $\pm 0.3kT$, that in N_t is (10–15)%, s_M is accurate to $\pm 5\%$, and c_p/c_n to about $\pm 50\%$ only. It is much harder to give a valid estimate for $(E_t' - E_i)$ and N_t' , because these two are derived from "curve fitting." A change of $(E_t' - E_i)$ by $\pm 0.5kT$ and a suitable adjustment in N_t' might well result in a different theoretical curve which also fits the experimental points satisfactorily within the range of measurements. The assumption of an error of $\pm 0.5kT$ for $(E_t' - E_i)$ and

$\pm 20\%$ for N_t' seems to be reasonable. From inspection of the experimental data the following results emerge:

1. All changes in $(E_t - E_i)$ and $q\varphi_0$ caused by the electric field are within the limits of the experimental accuracy, whereas some changes in N_t and N_t' exceed the experimental error by a considerable margin.

2. A positive field causes an increase in N_t ; a negative field reduces the density of the recombination centers. These results are in complete agreement with Litovchenko's¹ findings for "small fields."

3. All fields, regardless of polarity, decrease N_t' .

4. The undisturbed surface potential u_{s0} is decreased by a positive field, but unaffected by a negative one. Litovchenko and Lyashenko¹ state that a positive field shifts the surface potential towards the left and a negative field to the right.

5. All parameters listed in Table I are close to those quoted by Litovchenko *et al.*,¹ with one remarkable exception: Their values for N_t and N_t' are smaller by a factor of 10. The great majority of investigators^{4,5} find values of $(10-100) \times 10^{10}$ for N_t and N_t' .

4. DISCUSSION

Generally speaking, our results are in good agreement with those quoted by Litovchenko and Lyashenko.¹ Their assumption that the energy of the recombination centers is not affected by the field is confirmed by the measurements reported here. In Fig. 1(a) the experimental data of lifetime measurements, taken before and after application of a field of $+2.5 \times 10^6$ volts/cm, are given; Fig. 1(b) illustrates the corresponding changes in the added trapped charge density. No change in the s/s_M curve can be observed, Fig. 1(a), but the ΔQ_{ss} vs u_s curves are displaced by about $(1/q)\Delta Q_{ss} = 5 \times 10^{10}$; therefore the energy and ratio of cross sections of the centers are far less affected than the densities. It is remarkable, however, that the change in the densities reported here is so much smaller than that reported by Litovchenko and Lyashenko. Unfortunately their paper¹ contains no figures of the ΔQ_{ss} vs u_s curves for measurements taken after the electric field was switched off (their so called "aftereffect" measurements), but the measurements taken during the application of 0.1×10^6 volt/cm show a relative displacement of $1/q\Delta Q_{ss} = 0.6 \times 10^{10}$ with regard to the field-free data. The meas-

⁴ A. Many, J. Phys. Chem. Solids 8, 87 (1959).

⁵ Y. Margoninski, J. Chem. Phys. 32, 1791 (1960).

urements reported here and illustrated in Fig. 1(b) indicate a displacement of $(1/q)\Delta Q_{ss} = 5 \times 10^{10}$ after application of 2.5×10^6 volts/cm; hence the over-all effect of the field is much more pronounced. There seem to be two possible explanations for this difference in change of surface state densities: (1) Usually the densities are given by the slope of the ΔQ_{ss} vs u_s curve at $u_s = E_t - E_i$. For many results reported in reference 1 and here the undisturbed surface potential u_{s0} is within $3kT$ of the recombination center. Therefore the normalizing constant⁵ required to make $\Delta Q_{ss} = 0$ for zero external field (i.e., for $u_s = u_{s0}$) is of the same order of magnitude as ΔQ_{ss} at $(E_t - E_i)$ and thus causes the slope of the $\Delta Q_{ss}(u_s)$ curve to increase continuously near the recombination center instead of being constant there.⁵ A slight error in determination of this slope might therefore cause an appreciable difference in the value of N_t . (2) Litovchenko assumes that the change in surface state parameters is caused by a penetration or diffusion of ions through the porous oxide layer, under the influence of the electrostatic field. If this is so, the structure of the oxide layer might well influence the magnitude of the effect. Litovchenko *et al.* investigated *p*-type samples etched in CP-4 and perhydrol and then "aged"

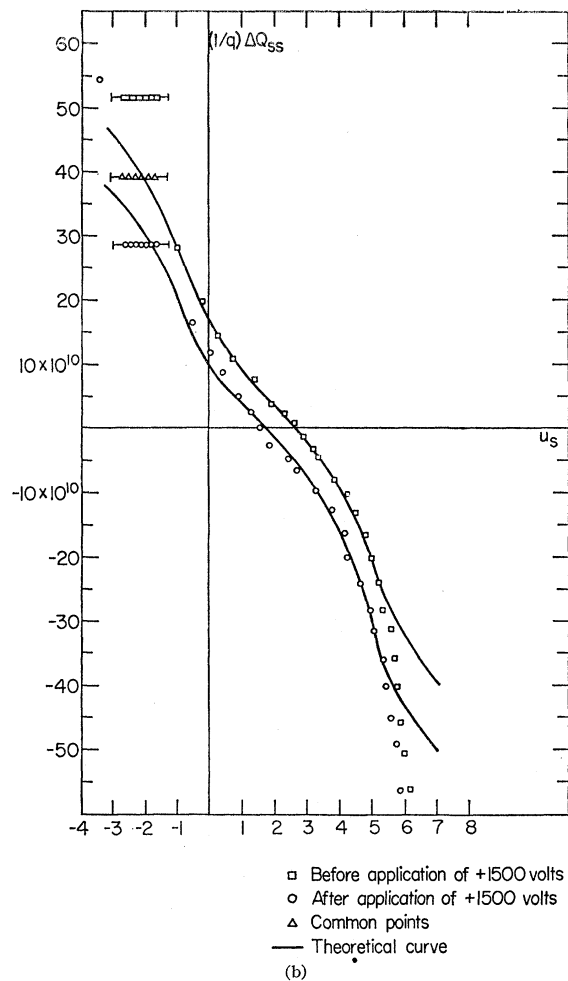
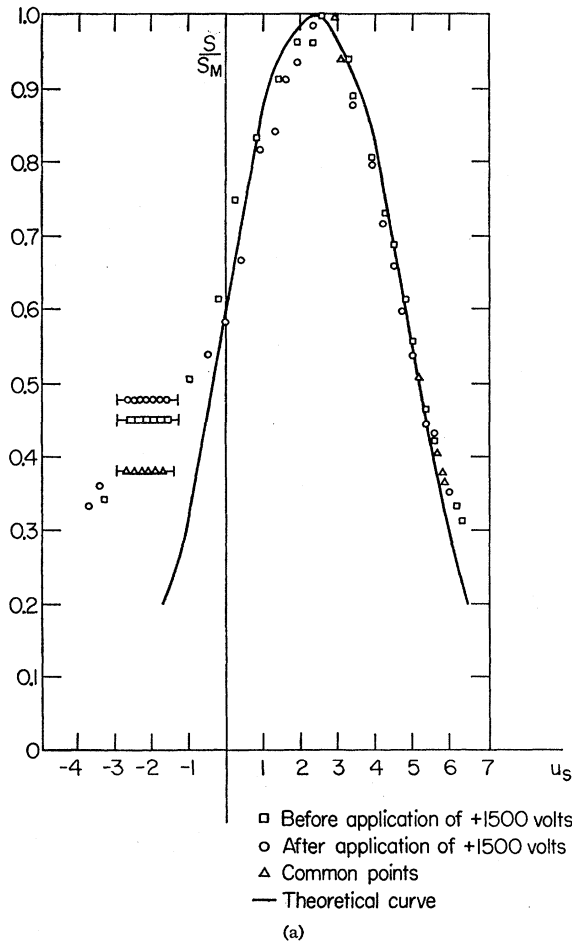


Fig. 1. (a) Measurements of fractional surface recombination velocity, s/s_M , taken before and after application of +1500 volts. The theoretical curve is for $E_t - E_i = 4.9kT$; $u_0 = 2.4kT$. (b) Measurements of added trapped charge density, ΔQ_{ss} , taken before and after application of +1500 volts. The theoretical curves are for $E_t - E_i = 4.9kT$; $E_t' - E_i = -1kT$; $N_t = 48 \times 10^{10} \text{ cm}^{-2}$; $N_t' = 48 \times 10^{10} \text{ cm}^{-2}$ (before application of voltage) and $N_t = 56 \times 10^{10} \text{ cm}^{-2}$ (after application).

by keeping in air for several months, whereas our sample was "quick aged" in a wet oxygen atmosphere. A difference in oxygen structure is therefore conceivable.

It was also reported¹ that when trying to perform measurements in a wet ambient atmosphere even small pulsed fields caused a considerable shift in u_{s0} and therefore these measurements had to be abandoned. This effect was investigated here, using wet nitrogen and wet oxygen as ambients, and careful examination showed that it was not a simple relaxation phenomenon⁶: A sudden switching off of the ac field effect voltage caused the specimen to "undershoot" its R_0 value (R_0 being the specimen's resistance at $u_s = u_{s0}$) regardless of the sign of the field. For negative ac fields (i.e., the injecting pulse riding on the negative crest of the ac field) this "undershooting" might be explained as a simple relaxa-

tion effect,⁶ but not so for positive ac fields: here a sudden switching off should cause an "overshoot." However, it was found possible to perform satisfactory measurements even in wet ambients by using the following artifice. The ac field voltage was kept constant, and first the usual measurements of sample lifetime and resistance were taken for the plus and minus crest value of the ac field. The phase shifter was then adjusted, so that the injecting pulse occurred exactly at the cross-over (from positive to negative values) of the ac field voltage; i.e., at zero field. A resistance measurement taken at this phase-shifter setting is equal to R_0 for this applied voltage. With the injecting pulse occurring at the greatest slope of the ac sine voltage, even a slight error in adjustment could result in a completely wrong R_0 value. The exact setting was found by throwing a switch which caused a phase shift of 180° : By making slight adjustments until a phase shift of 180° did not change the value of the measured filament resistance, the exact value for R_0 could be found. The maximum value of the specimen's resistance was measured by a similar procedure and was found to be voltage independent. An ac field of about 2×10^6 volts/cm shifted u_{s0} by more than $+5kT$. Details of these measurements taken in wet ambients will be reported in another paper.

The effect of ac fields on germanium surfaces was studied by Rzhhanov *et al.*,⁷ who found that a field of approximately 1×10^5 volts/cm increases the energy by $0.8kT$. This is in direct contradiction to the assumption made by Litovchenko *et al.* and to the experimental results reported in this paper. It was first thought that the explanation for this discrepancy may be found in Rzhhanov's technique of measurement, but in a private communication to the author Rzhhanov states, "The change in energy of the levels by $0.8kT$ is only somewhat

more than the error in $E_i = \mp 0.3kT$. It is difficult to insist upon an essential difference in results between our and your experiments in such a situation." Moreover, they reported that the changes in the ratio of cross sections and the cross sections themselves were well within their experimental error, whereas the change in density was from 4.2×10^{10} to 10.1×10^{10} cm⁻². Statz *et al.*⁸ investigated the influence of an electric field on silicon junctions and found the density of states to increase logarithmically with the time of field-application. This logarithmic behavior indicates a migration of ions through the oxide layer; i.e., a positive field would draw negative ions from the silicon oxide interface and towards the surface of the oxide. This would free some bonds at the interface, thereby causing an increase in state density. Statz *et al.* proposed these ions to be Si⁺⁺⁺⁺, but in the light of the experimental evidence presented here, one would have to assume the migration of negative oxygen ions.⁹ This, too, is the explanation by Litovchenko *et al.*, whereas Rzhhanov and his co-workers use a model based on very similar absorption-desorption processes.

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⁸ H. Statz *et al.*, *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, Pennsylvania, 1957), p. 139ff.

⁹ After obtaining additional experimental data, Statz *et al.* [Phys. Rev. **106**, 455 (1957)] concluded that multiple charges could *not* be involved in these processes.

⁶ A. Many *et al.*, Phys. Rev. **101**, 1433 (1956).

⁷ A. V. Rzhhanov *et al.*, Soviet Phys.-Tech. Phys. **3**, 2419 (1958).