

TABLE I. Position of the quasi-Fermi level at the surface and the total charge in the surface states for various bias voltages.
(Steady-state case.)

V_a	Run 1		Run 2		Run 3		Run 4	
	ϕ_s (volts)	No. electronic charges/cm ² $\times 10^{-10}$	ϕ_s (volts)	No. electronic charges/cm ² $\times 10^{-10}$	ϕ_s (volts)	No. electronic charges/cm ² $\times 10^{-10}$	ϕ_s (volts)	No. electronic charges/cm ² $\times 10^{-10}$
0.2	0.110	4.97	0.134	6.50	0.158	9.42	0.169	11.4
0.5	0.117	6.26	0.135	7.37	0.160	10.2	0.171	12.3
1	0.119	7.75	0.137	8.70	0.162	11.5	0.173	13.6
3	0.121	11.7	0.138	12.4	0.164	14.8	0.178	16.9
5	0.122	14.7	0.138	15.2	0.165	17.2	0.180	19.4
7	0.122	17.1	0.138	17.5	0.167	19.5	0.182	21.8
10	0.120	20.2	0.138	20.4	0.167	22.3	0.183	24.3
12	0.120	21.9	0.137	22.3	0.167	24.1	0.183	25.9
14	0.118	23.6	0.137	23.9	0.167	25.5	0.183	27.3
15	0.117	24.4	0.137	24.7	0.167	26.3	0.183	28.0
16			0.137	25.5	0.167	27.0	0.183	28.7
18			0.137	26.9	0.168	28.4	0.185	30.2
20			0.137	28.4	0.168	29.8	0.184	31.4
25			0.136	31.6	0.168	32.7	0.184	34.3
45					0.167	42.9	0.183	44.0
70					0.167	52.9		

information about the total density of surface states (i.e., the sum of the densities of the two states).

The computation of ϕ_s and Q has been carried out by using the mobility for holes in inversion layers as calculated by Schrieffer.⁹ This analysis does not make use of the approximations described by Brown¹ or Kingston.¹⁰ The results for the four runs are given in Table I.

It is seen that ϕ_s is essentially constant for each run. It is uncertain whether any significance can be attributed to the deviation of ϕ_s from a constant. The total charge in the surface traps continues to increase with increasing bias voltage. If the slight increase of ϕ_s for voltages approximately below 10 volts is real, then this represents a serious difficulty. From Fig. 1, it may be seen that an increase in ϕ_s means a decrease in the occupancy of the surface states. On the other hand, the requirement of total neutrality gives an increasing charge in the surface states. This difficulty can be avoided by assuming some specular reflection of holes at the surface in Schrieffer's calculation.⁹ Another possible source of error is Schrieffer's simplifying but incorrect assumption of spherical energy surfaces. In addition, the base resistivity used in the calculation may have been incorrect by as much as 20 percent.

In every case, it may be said that the Fermi level is essentially constant and the change in charge very considerable, so that the total density of surface states will be high. It is not possible to give a numerical result for the density of states, because the Fermi level shifts by an amount that is smaller than the probable error of this determination. However, from the measurements described in the accompanying letter,⁸ it may be concluded that this high total density of states is due only to surface states outside the germanium oxide. The charge in the states at the germanium-germanium oxide surface does not change by such a large amount for so little change in the Fermi level.

Kingston¹⁰ has reported that the data for channels on p -type germanium can also be understood by assuming a constant value of ϕ_s . It is interesting to note that our curves, which deviate greatly from the $1/V_a$ relationship measured by Kingston, still give approximately a constant ϕ_s value, indicating that Kingston's approximations are not applicable in our case.

* This work has been supported in part by the U. S. Signal Corps.

¹ W. L. Brown, Phys. Rev. **91**, 518 (1953).

² R. H. Kingston, Phys. Rev. **93**, 346 (1954).

³ S. R. Morrison, J. Phys. Chem. **57**, 860 (1953).

⁴ H. Christensen, Proc. Inst. Radio Engrs. **42**, 1317 (1954).

⁵ A. L. McWhorter and R. H. Kingston, Proc. Inst. Radio Engrs. **42**, 1376 (1954).

⁶ N. Cabrera and N. F. Mott, Repts. Progr. Phys. **12**, 163 (1949).

⁷ W. H. Brattain and J. Bardeen, Bell System Tech. J. **32**, 1 (1953).

⁸ Stutz, Davis, and deMars, following Letter [Phys. Rev. **98**, 540 (1955)].

⁹ J. R. Schrieffer, Phys. Rev. **97**, 641 (1955). The authors thank Mr. Schrieffer for a preprint of this article.

¹⁰ R. H. Kingston (to be published). The authors are grateful for the privilege of seeing a preprint of Dr. Kingston's paper.

Structure of Surface States at the Germanium-Germanium Oxide Interface*

H. STATZ, L. DAVIS, JR., AND G. A. DEMARS

Raytheon Manufacturing Company, Waltham, Massachusetts

(Received January 10, 1955)

IN the accompanying Letter,¹ the conductance of p -type inversion layers on 8 ohm-cm n -type germanium under steady-state conditions has been discussed. In this Letter, investigations of the nonsteady-state conductance and its interpretation in terms of surface states at the germanium-germanium oxide interface are reported.

The time dependence of the conductance g is shown schematically (Fig. 1) when the bias voltage was switched from a value V_1 to a value V_2 . The time-dependent portion of the conductance has the form $\exp(-t/\tau)$, except when the voltage steps $|V_1 - V_2|$ were large compared to V_1 .

The same $p-n-p$ grown junction germanium samples (8 ohm cm n -type) with the same surface treatment as in reference 1 are used. The longer the surface is exposed to wet O_2 and O_3 , the higher the inversion layer conductance and the longer the time con-

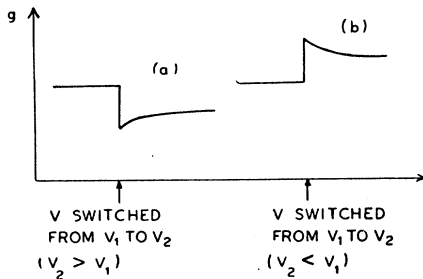


FIG. 1. Time dependence of conductance when bias voltage is switched.

stant τ . The time constant varied from a few seconds to a few minutes and also increased with bias voltage for a given inversion layer.

As may be seen in Fig. 1, the conductance after switching to a higher bias voltage was lower than its steady-state value. The inversion layer contained fewer holes and therefore the total charge in the surface was smaller than under steady-state conditions. If the voltage was switched to a lower value, the opposite was true. These observations can be understood from the fact that the charge in the surface states under steady-state conditions continuously increased with increasing bias voltage. For example, when the bias voltage was switched to higher values, there must have been a transfer of electrons from the germanium to surface states at the germanium-germanium oxide interface and germanium oxide surface (Fig. 1, reference 1). From the measurements, it was concluded that the transfer of electrons was at least partially a slow process. The long time constant can be connected only with charge transfer to states lying at the germanium oxide surface. The inner states at the germanium-germanium oxide interface which were probably responsible for the surface recombination² adjusted to a new quasi-Fermi level in a time which was presumably of the order of the lifetime of the minority carriers in the sample. With the equipment used, changes of such a short duration could not be resolved. It must therefore be assumed that just after the voltage V_2 was applied, the conductance reading corresponded to a situation in which the charge in the outer surface states was still unchanged, but the charge in the inner surface states was already in equilibrium with the bulk of the germanium. The good fit of

the data so obtained, as seen later in Fig. 3, can be considered as strong evidence for the validity of this assumption.

The widely different time constants for the two types of surface states permit one to determine the density of the inner states separately. The measurements were made as follows: The bias voltage V_a was set to some particular value for a long enough time so that the conductance of the inversion layer had reached its steady state value, then switched to some higher value. The conductance, just after switching, was observed, extrapolating back to zero time, if necessary. The original bias was then restored and after a long enough time, the bias voltage was again switched to some other value, the conductance, just after switching, being observed again. Many points (g, V_a) were determined in this way until a smooth curve could be drawn through them. Two typical curves for two different surfaces are shown in Fig. 2. For high enough voltages, zero conductance,

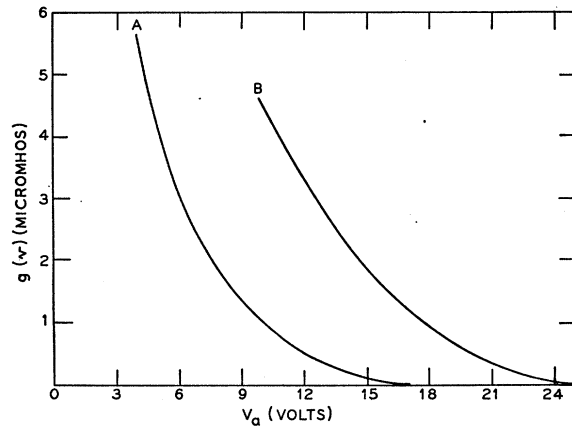


FIG. 2. Nonsteady-state channel conductance versus bias voltage.

i.e., pinch-off, can always be obtained. By switching to lower voltages, the range of the curves could be increased.

The curves of Fig. 2 were analyzed in the same way as steady-state curves in reference 1. The total charge in the surface states and the position of the Fermi level with respect to the middle of the energy gap at the surface (ϕ_s) were computed. However, because of the nature of the experiment, the charge outside the germanium oxide was constant. All the variation in charge along such a curve will be attributed to the inner surface states only.

In Table I, ϕ_s and the total charge are given for the two curves of Fig. 2. According to Brattain and Bardeen, the surface recombination centers lie far away from the middle of the band. Therefore, the charge at pinch-off, i.e., $\phi_s \approx 0$, was taken as the reference point. In Fig. 3, this charge difference is plotted versus ϕ_s for the two cases. The result can be easily interpreted.

The solid curves are theoretical (Fermi distribution) assuming, in both cases, a single level 0.155 eV below

TABLE I. Position of the quasi-Fermi level at the surface and the total charge in the surface states for various bias voltages (nonsteady-state case).

Run A			Run B		
V_a	ϕ_s (volts)	No. electronic charges/cm ² $\times 10^{-11}$	V_a	ϕ_s (volts)	No. electronic charges/cm ² $\times 10^{-11}$
4	0.175	1.76	10	0.190	2.56
5	0.170	1.79	12	0.183	2.60
7	0.162	1.90	14	0.175	2.63
10	0.146	2.07	15	0.173	2.65
12	0.134	2.21	16	0.167	2.69
13	0.127	2.29	18	0.156	2.76
14	0.115	2.36	20	0.143	2.85
15	0.102	2.42	25	0	3.10
16	0.095	2.49			
17	0	2.56			

the valence band. In curves *A* and *B*, the number of these states was $N=1.18 \times 10^{11} \text{ cm}^{-2}$ and $6.90 \times 10^{10} \text{ cm}^{-2}$ respectively. The fit was as good as could be expected. Small ϕ_s values had a relatively larger experimental error because the conductances were very low and therefore not accurate. The number of states at the germanium-germanium oxide interface were so low that they could not have been of the Tamm³ type, in which the number of states correspond exactly to the number of surface atoms (or multiples thereof). The states which were observed must have arisen from impurity atoms or crystalline defects at the surface.

The variation of the time constant can be understood qualitatively by assuming that the transfer of electrons from the semiconductor to the traps was hindered by the large potential wall in the oxide film. The electrons had to move into the conduction band of

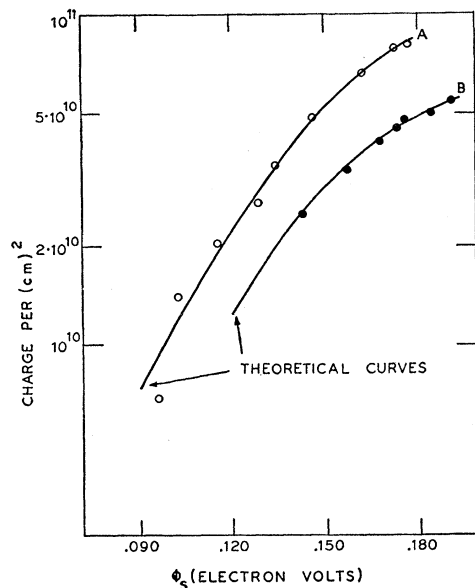


FIG. 3. Charge in surface states at germanium-germanium oxide interface versus position of quasi-Fermi level.

the oxide film. The electric field in the oxide film made the potential wall even higher (see Fig. 1, reference 1). It is obvious that the greater the negative charge outside the oxide and the thicker the film, the higher the barrier. Under steady-state conditions, the charge increased with increasing voltage, and the samples which had been exposed for a longer time to wet O₂ and O₃ had thicker oxide films. This model is in qualitative agreement with the observed time constants.

* This work has been supported in part by the U. S. Signal Corps
¹ deMars, Statz, and Davis, preceding Letter [Phys. Rev. **98**, 539 (1955)].

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

³ I. Tamm, Physik. Z. Sowjetunion **1**, 733 (1932).

Spin-Lattice Relaxation Time of the Si²⁹ Nucleus in Pure Fused Silica

G. R. HOLZMAN, JOHN H. ANDERSON, AND W. KOTH

Mellon Institute, Pittsburgh, Pennsylvania

(Received February 21, 1955)

THE Si²⁹ nuclei in a sample of Corning purified fused silica (ultraviolet quality) were observed to approach equilibrium magnetization exponentially in a field of 9.2 kilogauss at room temperature, with a relaxation time of 10 hours. This time is a mean of two measurements which differ by approximately 1 percent. Measurement of the relaxation time in the earth's field at room temperature yielded a value of 1.3 min. An emission spectral analysis at Mellon Institute on a similar Corning sample gave 120–530 parts per million for the summed paramagnetic impurities.

The measurement procedure used was to record the change in magnitude of the component of the macroscopic magnetic moment in the plane of and coincident with the rotating rf field vector. This change was brought about by immersing the sample in the magnetic field for varying time intervals, and made evident using a Bloch crossed-coil and phase-sensitive detection system (a Varian spectrometer) with an rms radio-frequency magnetic field intensity of 1.3 gauss. The shape of the nuclear magnetic resonance curve was indicative of Bloch's limiting case of rapid passage through resonance and did not change when the modulation amplitude was varied from approximately 0.05 to 0.5 rms gauss. Points on the exponential curve used in determining this unusually long relaxation time were obtained by measuring the peak-to-peak value of the recorded signal.

When the magnetic field is maintained at the resonance value and the rf field intensity is of the order of one gauss, the signal becomes undetectable after approximately one minute. Signal intensity is lost considerably faster at lower rf fields.