Influence of Wet and Dry Ambients on Fast Surface States of Germanium*

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Simultaneous measurements of surface recombination velocity and added trapped charge density in the fast states as a function of surface potential were carried out on an n-type specimen which was subjected to the following gaseous ambient cycles: (a) room air-vacuum, (b) dry air-vacuum, (c) dry oxygen-vacuum, (d) dry nitrogen-vacuum, (e) wet nitrogen-vacuum, and (f) wet oxygen-vacuum. The most important results of these measurements were: (1) Dry nitrogen had no influence whatsoever on any of the surface-state parameters, (2) dry oxygen affected only the density of states and the unperturbed surface potential, and (3) wet nitrogen and wet oxygen had almost the same and most pronounced effect on the fast surface states.

1. INTRODUCTION

IT is somewhat surprising to note that although the influence of a wet ambient on the fast germanium surface states was already reported by Brattain and Bardeen[1] in 1953, no serious effort has been made since that time to find out how much of this influence is due to the carrier gas and how much to the water vapor. In order to find out whether the effect of a wet ambient can be separated, so that one part of it can be ascribed to the carrier gas and the remainder to the presence of the water vapor, one and the same n-type germanium specimen was subjected to the following wet and dry ambient cycles, and in this order: (1) room air-vacuum, (2) dry air-vacuum, (3) dry oxygen-vacuum, (4) dry nitrogen-vacuum, (5) wet nitrogen-vacuum, and (6) wet oxygen-vacuum. Nitrogen and oxygen were selected because they are the main constituents of air; hence an attempt could be made to explain the results of the first cycle by studying the subsequent treatments. In view of the complicated behavior of the germanium surface states it was quite surprising to find that in general the results of these measurements could indeed be explained quite consistently by separating the effects of the three gases involved: nitrogen, oxygen, and water vapor.

2. EXPERIMENTAL METHOD

The germanium crystal with dimensions $1.88 \times 0.39 \times 0.047$ cm had a resistivity of 17 ohm cm (at room temperature) and was cut parallel to the (111) plane. During the entire period of measurements the crystal had to be re-etched and reground three times and its final thickness decreased to 0.038 cm. The specimen had two soldered end contacts, one ohmic and the other slightly injecting. It was etched in CP-4A solution for 1 min at 35°C. After etching and rinsing with distilled water the crystal was placed between the field plates (mica spacers of 0.004-cm thickness and phosphor-bronze plates) and inserted into the experimental tube. Special precautions were taken to avoid any grease films, paints, etc., in the tube. All connections between the experimental glass tube and the vacuum or gas-handling system were made through metal vacuum valves to eliminate vacuum stopcock grease. The ground joint of the experimental tube was ungreased (but covered with a thin layer of graphite powder to prevent sticking) and sealed from the outside with Apiezon wax.

Commercial grade Airco oxygen and Linde dry nitrogen were used. The gas-handling system incorporated P_2O_5 and dry-ice traps for the dry ambient cycles and two water bubblers for the wet cycles. The stated minimum purity of Linde dry nitrogen is 99.7%. To remove any oxygen traces the gas was bubbled through an alkaline solution of pyrogallol before reaching the water bubbles. These precautions were entirely satisfactory, as gas discharge from the ac field-effect voltage in wet nitrogen did not change the resistivity or lifetime of the sample. As ozone is known to have a great effect on germanium surfaces,[2,3] the presence of oxygen would have been noticed immediately during a gas discharge. In the wet ambients, gas discharge from the ac field-effect voltage commenced at about 500 v (for oxygen as well as nitrogen); in a vacuum of 10^{-4} mm Hg, an ac voltage of 1000 v could be applied without any breakdown.

The sequence of the cycles was the following. The tube was evacuated and the crystal remained in vacuum for over two weeks, so that it became stabilized. It was then put through one dry air-vacuum cycle. Starting again from vacuum, dry oxygen was admitted to the tube and remained there for at least two days. The tube was then evacuated and kept at 10^{-4} mm Hg for two days, after which dry nitrogen was admitted. The same procedure was employed for the wet cycles. Wet cycles and room air-vacuum cycles were repeated to check the reproducibility. After the first wet oxygen cycle the tube was evacuated, it was kept at 10^{-4} mm

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

[2] A. V. Rzhanov, Soviet Phys.-Tech. Phys. **2**, 2274 (1957) (translation).

[3] E. Harnick and Y. Margoninski, J. Phys. Chem. Solids **8**, 96 (1959).

TABLE I. Parameters of fast surface states for n-type sample after treatment with different ambients.

No.	Time after first run (days)	Ambient	E_t-E_i (kT)	u_0 (kT)	c_p/c_n	N_t (10^{10} cm^{-2})	u_{s0} (kT)	s_M (cm/sec)	c_p (10^{-7} cm^2 sec^{-1})	$E_t'-E_i$ (kT)	N_t' (10^{10} cm^{-2})
					A. Air-vacuum						
1	0	Room air	5.3	2.3	99	30	+1.5	435	6	-2.0	10
2	2	Vacuum	4.6	1.5	20	20	+2.0	830	4.0	-2.0	29
3	17	Vacuum, after 15 days	5.0	1.6	25	33	+1.0	830	4.0	-2.0	25
4	21	Dry air	5.0	2.0	55	50	-3.7	980	4.5	-1.0	13
5	23	Dry air, after 2 days	5.1	1.8	37	52	-3.2	920	3.7	-1.0	10
6	23	Vacuum	4.9	2.4	122	47	-1.3	1050	6.7	-1.0	7
7	148	Vacuum	5∓0.4	1.5	20	45	+2.9	675	3.0	-2.0	95
8	150	Room air	5.9	0.6	3.3	70	-1.3	420	8.3	-2.0	7
					B. Dry ambients						
9	32	Vacuum	4.6	1.6	25	28	+1.3	1000	4	-2.0	14
10	37	Dry oxygen, after 2 days	4.6	1.9	45	60	-3.7	1400	3.3	-2.0	14
11	37	Vacuum	4.6	1.9	45	41	-3.3	1720	6.0	-2.0	16
12	37	Vacuum	4.7	2.0	55	40	-0.4	1530	6.6	-2.0	13
13	39	Dry nitrogen	4.7	2.0	55	40	-0.4	1530	6.6	-2.0	13
14	44	Dry nitrogen, after 5 days	4.7	1.7	30	33	+1.9	1378	5.0	-2.0	20
15	44	Vacuum	4.5	2.0	55	40	+1.3	1330	4.5	-2.0	17
					C. Wet ambients						
16	122	Vacuum	4.9	2.6	181	60	+1.6	820	6	-2.0	53
17	129	Wet nitrogen, after 7 days	4.6	-0.4	0.45	80∓20	-(1.3-3.0)a	870	0.1	...	...
18	133	Wet nitrogen, after 11 days	5.9	(-0.1) to (+0.9)	0.8-6.0	150∓30	-(1.3-3.0)a	810	0.4-1.0	...	...
19	134	Vacuum	5.4	2.4	122	100	+1.1	1790	9.0	-2.0	80
20	136	Vacuum	5.4	2.4	122	100	+1.1	1790	9.0	-2.0	80
21	138	Wet oxygen, after 2 days	7.0	1.0	2.7	210∓50	-(1.3-3.0)a	285	0.8	...	...
22	141	Vacuum	4.0	2.5	148	36	+3.1	1050	4.0	-2.0	90
					D. Baking						
23	65	Vacuum	5.4	2.4	122	30	+2.3	1660	29	-1.0	28
24	66	Vacuum after baking	4.1	2.4	122	23	+1.3	2740	17.0	-2.0	37

a At zero field.

Hg for three days and then baked in vacuum for 3 hr at 90°C. All measurements were performed at 20–21°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 co-workers.[4] Because, in wet ambients, the unperturbed surface potential u_{s0} shifts on application of an ac field,[5] a somewhat modified technique of measurement was used.[6] For a fixed ac field voltage the phase shifter was adjusted so that the injecting pulse occurred exactly at the crossover (from positive to negative values) of the ac field voltage. A resistance measurement taken at this phase shifter setting is equal to R_0, the specimen resistance corresponding to u_{s0} for this applied fixed ac voltage. The lifetime measurements were made in the usual way, with the injecting pulse occurring at the crest of the ac field voltage.

[4] A. Many and D. Gerlich, Phys. Rev. **107**, 404 (1957).
[5] V. G. Litovchenko and V. I. Lyashenko, Soviet Phys.-Solid State **1**, 1470 (1960) (translation).
[6] Y. Margoninski, Phys. Rev. **121**, 1282 (1961).

3. EXPERIMENTAL RESULTS

Table I summarizes typical results. The notation is that used by Kingston and Neustadter[7] and Many and Gerlich.[4] The $E_t - E_i$ is the energy of the recombination center, u_0 is the intercept of the axis of symmetry of the s/s_M curve with the abscissa (s denoting the surface recombination velocity and s_M its maximum value), u_{s0} is the unperturbed surface potential in units of kT. The hole, electron capture probabilities are c_p, c_n, respectively [$c_p/c_n = \exp(2u_0)$]. The density of the recombination centers per square centimeter is N_t. The energy and density of the recombination ineffective charge traps are $E_t' - E_i$ and N_t'.

The experimental accuracy depended somewhat on the ambient. The most accurate results were obtained with dry ambients and room air. The estimated errors were ∓$0.3kT$ for $(E_t - E_i)$ and u_0; ∓50% for c_p/c_n, ∓(10–15)% for N_t, and ∓5% for s_M. For $(R_M - R_0) \geq 3$ ohm (R_M denotes the crystal's maximum resistance)

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

u_{s0} is accurate to $\mp 0.2kT$, but if $R_M = R_0$ then it can only be stated that u_{s0} lies between $(-1.3)kT$ and $(-3)kT$, e.g., measurements No. 17, and 18, and 21. $(E_t' - E_i)$ and N_t' are derived from "curve fitting" and hence are less accurate; an error of $\mp 0.5kT$ for the energy and $\mp 20\%$ for the density seems to be reasonable. The density N_t is usually obtained by measuring the slope of the $\Delta Q_{ss}(u_s)$ curve (i.e., added charge density versus surface potential) at $u_s = E_t - E_i$, but this could not be done for the wet ambients, because the shift in u_{s0} with applied ac field voltage rendered this $\Delta Q_{ss}(u_s)$ curve meaningless. Therefore, N_t was calculated from the experimental data for all points within the range of $\mp 1kT$ of $(E_t - E_i)$ and the average of these densities was taken to be the final result. The accuracies for these data are given in the table; that for the corresponding energies is about $\mp 0.5kT$. The results will now be discussed for each ambient treatment separately.

A. Air-Vacuum

On changing from room air to vacuum, all cycles cause a decrease in $(E_t - E_i)$, an increase in N_t', and a shift of u_{s0} towards more positive values. For most runs, N_t decreased considerably but two runs showed an increase from 53×10^{10} cm^{-2} to 65×10^{10} cm^{-2}, and from 70×10^{10} cm^{-2} to 80×10^{10} cm^{-2}, respectively. No definite behavior could be found for u_0, the most sensitive of all parameters. These cycles seemed to have little effect on $(E_t' - E_i)$ but it must be emphasized that, unless the experimental data clearly contradicted it, all $\Delta Q_{ss}(u_s)$ curves were analyzed with the assumption that $(E_t' - E_i)$ was not changed by the ambient.

Vacuum-dry air cycles had little effect on the energy but increased the density of states and, as already reported by many investigators,[8] moved u_{s0} towards negative values. The reproducible changes in filament lifetime of a germanium crystal subjected to a series of dry air-vacuum cycles, observed by Madden and Marsh in this laboratory,[9] are therefore mainly due to the change in the undisturbed surface potential. The u_{s0} value for vacuum is always inside or very near the plateau region of the s/s_M curve [i.e., between (-1) and $+3kT$] for all the reported measurements, whereas for all dry air measurements it is situated well to the left of the plateau, i.e., in the region of higher lifetimes.

B. Dry Ambients

The experimental results show that dry nitrogen has no influence on any parameter of the surface states. Subsequent vacuum-dry nitrogen cycles were either identical (Nos. 12, 13) or showed differences well within the experimental accuracy (Nos. 14, 15). This

[8] M. Kikuchi, J. Phys. Soc. Japan 12, 436 (1957).
[9] H. H. Madden and J. E. Marsh, Scientific Rept. No. 9, AFCRC-TN-58-151.
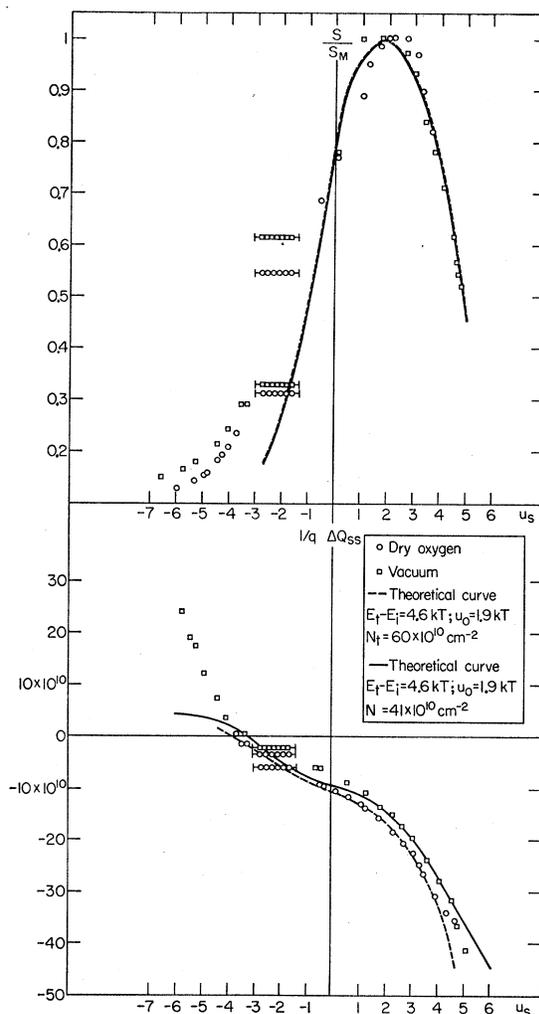

FIG. 1. Measurements of fractional surface recombination velocity $s/s_M(u_s)$ and added trapped charged density $\Delta Q_{ss}(u_s)$ in a dry oxygen atmosphere and in vacuum. The figure refers to measurements 10, 11 of Table I.

result was confirmed by the following experiment. With the crystal in vacuum, the Many bridge was carefully adjusted to the values of R_0 and τ_0 for the sample, these being the resistance and lifetime values corresponding to u_{s0}. Dry nitrogen was then slowly admitted to the tube and the R and τ oscilloscopes were observed to detect any changes in these values. This experiment was repeated twice and it was always found that during the whole process, beginning with the vacuum of 10^{-4} mm Hg and ending with dry nitrogen of atmospheric pressure, the Many bridge was always accurately balanced. Dry nitrogen is therefore a perfect "carrier gas," well suited to investigate the influence of water vapor on the germanium surface states.

Dry oxygen causes an increase in the density of states and moves u_{s0} to the left by $5kT$. Figure 1 gives
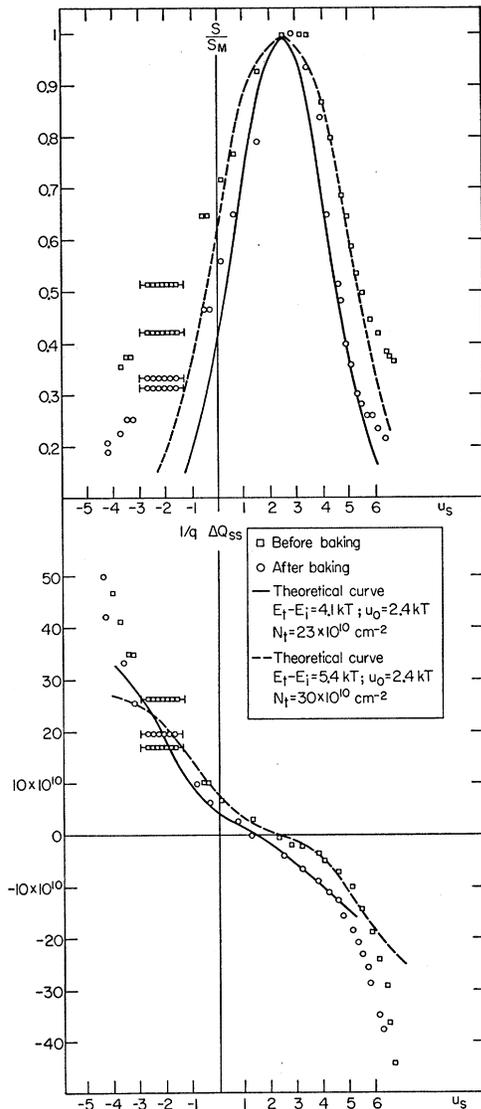
FIG. 2. Measurements of fractional surface recombination velocity $s/s_M(u_s)$ and added trapped charge density $\Delta Q_{ss}(u_s)$ before and after bakeout of sample. The figure refers to measurements 23, 24 of Table I.

the experimental results for two measurements, one taken in a dry oxygen atmosphere and the other in vacuum immediately after the oxygen was evacuated. Whereas the lifetime measurements indicate a common s/s_M curve, the $\Delta Q_{ss}(u_s)$ measurements clearly show the parallel-shift characteristic of surface states having the same (E_t-E_i) and u_0 value, but differing in u_{s0} and N_t.[6] No values for the parameters could be given for measurements performed immediately after admitting dry oxygen to the tube because the surface potential became so negative that even the highest electric field proved to be insufficient to pass over the plateau of the $s/s_M(u_s)$ curve. In conclusion, it seems quite clear that the changes found in the dry air-

vacuum cycles are solely due to the presence of the dry oxygen, a result to be expected.

Baking in vacuum decreased the energy and density of states and shifted u_{s0} towards the left; it had no effect on the capture probabilities. (See Fig. 2.) Near (E_t-E_i) the two experimental curves for ΔQ_{ss} vs u_s clearly show the nonparallel displacement which is characteristic of states different in density as well as energy.

C. Wet Ambients

In studying the influence of wet nitrogen, i.e., of water vapor, it was necessary to distinguish between an immediate effect and a long-term change. The most striking change found after admission of water vapor is a pronounced decrease in c_p/c_n; indeed $c_n>c_p$ and the recombination center changed from an acceptor to a donor type. A swing of u_{s0} towards the left is also noted. After about eight days stay in the wet ambient atmosphere the long-term change predominates, thus indicating a considerable increase in energy and density (No. 18). Unfortunately, the experimental data of run 18 (Fig. 3) did not permit a determination of u_0 with any reasonable accuracy and it can only be stated that u_0 is between (-0.1) and $(+0.9)$. No evaluation of surface parameters could be made from measurements performed immediately after the admission of wet nitrogen, as the field effect did not swing the surface potential over the plateau of the $s/s_M(u_s)$ curve. Because u_{s0} changed with applied field, no $\Delta Q_{ss}(u_s)$ curve could be constructed and hence no information was obtained about the charge traps.

The effect of wet oxygen is exactly the same as the long-term effect of water vapor, i.e., it causes an increase of energy and density of states (Fig. 4), and a large decrease in u_0 and u_{s0}. From the measurements taken immediately after admission of wet oxygen
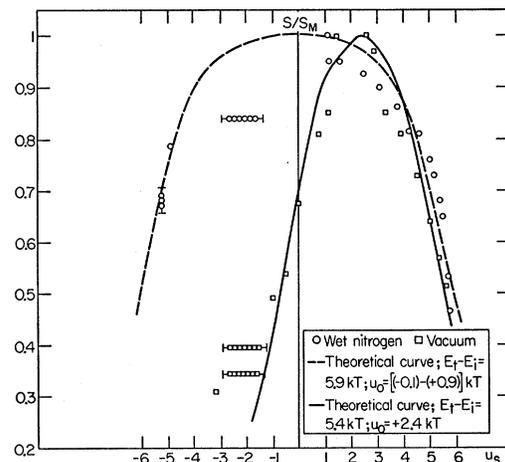

FIG. 3. Measurements of fractional surface recombination velocity $s/s_M(u_s)$ in a wet nitrogen atmosphere and in vacuum, referring to measurements 18, 19 of Table I.
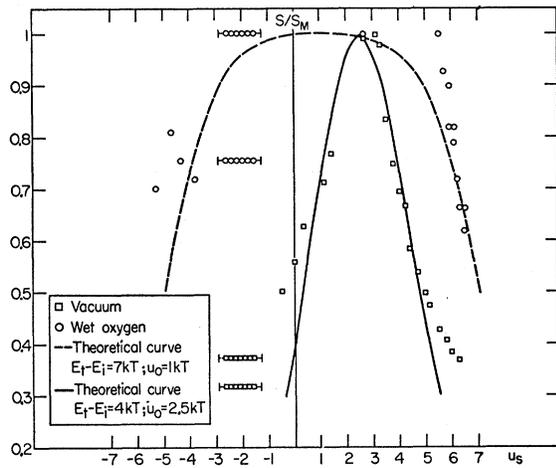
FIG. 4. Measurements of fractional surface recombination velocity $s/s_M(u_s)$ in a wet oxygen atmosphere and in vacuum, referring to measurements 21, 22 of Table I.

(following measurement No. 20) it could only be inferred that (E_t-E_i) was greater than $6.5kT$ and N_t seemed to be over 600×10^{10} cm^{-2}. The removal of wet oxygen caused all surface parameters to change in the direction back towards their normal vacuum values, but many went beyond these values; the energy decreased to $4kT$, the lowest value measured, and u_{s0} shifted to its most positive position of $3.1kT$. It was always found that a wet oxygen atmosphere produced a surface with the lowest recombination velocity.

With no field applied, $R_0=R_M$ and u_{s0} was in the region of minimum surface conductivity, i.e., between (-1.3) and $(-3)kT$. In a wet nitrogen atmosphere and after application of an ac field of 2×10^6 v/cm u_{s0} shifted to $+5kT$. The value of R_M was almost unaffected by the field. This shift in u_{s0} occurred for both carrier gases. Since water has a very high dielectric constant, the most plausible cause of this excess conductivity is ionic conduction in the adsorbed water layer. This has been suspected for a long time,[10] but Eriksen et al.[11] discarded this assumption because, even after passing a current of 80 μa for 18 hr through a water layer adsorbed on a germanium p-n diode, they observed no pressure rise in their closed system. After discussing the original experiment with the authors, two possible reasons were found to account for the constancy of pressure despite ionic conduction: (a) The total amount of water liberated was equivalent to over 10^5 molecular layers, hence the slow adsorption of water molecules could have been a very severe rate limiting factor. No data for the rate of adsorption of H_2O on germanium oxide are available, but for a clean germanium surface an additional uptake after two or three molecular layers is almost undetectable.[12] (b) The

total volume of liberated hydrogen was 0.5 cm^3. Taking a volumetric absorption coefficient of 0.017, about 30 cm^3 of water are sufficient to dissolve this amount of hydrogen. The experiment was performed in an atmosphere oversaturated with water vapor and a water manometer was employed. Hence, 30 cm^3 of water may well have been present in the closed system.

4. DISCUSSION

The most striking result of the measurements reported here is the enormous influence of water vapor on the recombination centers. By comparing the long-term results of the wet nitrogen and wet oxygen, it is apparent that the carrier gas has little effect, since the results of these two cycles are the same. Only the increase in (E_t-E_i) after admission of wet oxygen is much greater than that found after the wet nitrogen treatment. An increase in the energy of states is almost always accompanied by an increase in density, because the slope of the $\Delta Q_{ss}(u_s)$ curve increases with increasing u_s and hence, other things being equal (e.g., for similar values of u_{s0}), the greater the energy, the greater the slope of the curve at $u_s=(E_t-E_i)$. In other words, the closer the state is to the bands, the greater is its density. Calculations on a model of an impurity semiconductor suggested[13] that the lower end of the conduction band is not sharply defined, but "tails off" into the forbidden band.[14] A similar intrusion of density of states from the conduction band into the energy gap for semiconductor surfaces might explain this relation between energy and density.

No detailed explanation for the pronounced effect of water vapor on the surface states can be offered. A positive water molecule on the surface, being preferentially adsorbed, would decrease c_p and turn the center more donorlike. But it would also tend to decrease the center's energy, contrary to the experimental evidence. Rather than expecting the water to affect the states already present at the germanium-oxide interface, one has to assume that by partly dissolving the germanium oxide, new centers are created and these dominate the recombination processes.

The results of the room air-vacuum cycles could be explained as being caused mainly by the removal of water vapor, as this would lead to the observed decreases in energy and density, i.e., cycles 1, 2 being equivalent to 18, 19.[14a] This assumption is strengthened by observing that heating in vacuum, i.e., additional removal of water vapor, resulted in further decrease of energy and density.

The effect of humidity on the surface states has been

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[13] H. Schlosser, Bull. Am. Phys. Soc. 6, 27 (1961) and H. M. James and A. S. Ginzbarg, J. Phys. Chem. 57, 840 (1953).
[14] Some experimental confirmation for the case of a real lattice was reported by Pankove in Phys. Rev. Letters 4, 20 (1960).
[14a] A similar observation was made by H. H. Madden and H. F. Farnsworth, Phys. Rev. 112, 793 (1958).

studied by Wang and Wallis,[15] Rzhanov *et al.*,[16] Dorda,[17] and Flietner.[18] The surfaces of Wang and Wallis' *n*- and *p*-type crystals were oriented in the (110) plane and they cycled their sample through ozone, dry oxygen, and wet nitrogen. Measurements were taken after the crystal had stayed for about 1 hr in the ambient. They reported that the density of states increased tremendously after exposure to ozone, gradually recovered in dry oxygen, and again increased in wet nitrogen, the energy of states and c_p/c_n being unaffected by the ambient. Rzhanov *et al.*[16] subjected their *p*-type specimen to cycles of dry nitrogen, vacuum, slightly ozonized oxygen, and wet nitrogen, but they only mention that wet nitrogen, after a sufficiently long time, restored the initial properties of the specimen. After baking the sample in vacuum (at 100°C for a few hours) they reported a slight decrease in N_t, an increase in $(E_t - E_i)$, and inconclusive changes in c_p/c_n. Dorda[17] measured *n*- and *p*-type germanium at different relative humidities and concluded that dehydration of the surface oxide causes a decrease in the surface-state densities. Flietner[18] performed field-effect measurements in dry oxygen, wet nitrogen, and wet ozone atmospheres. The surfaces of his *n*- and *p*-type crystals were inclined less than 8° to the (111) planes. He found "little or no reactions for dry oxygen, wet nitrogen cycles" and stated that moist oxygen, following a dry oxygen cycle, affected only the unperturbed surface potential u_{s0}. Wang and Wallis' findings and Flietner's results disagree therefore with our data and the reason for this may be either because of objectionable techniques of measurements or different crystal orientation, or both. Wang and Wallis used the "small field effect" but were unaware of the u_{s0} shift in wet ambients, which could introduce serious errors. Flietner performed only surface-conductivity measurements and these are quite insensitive to changes in energy and density of the traps. Wang and Wallis' results could be explained by the different crystal planes. This explanation cannot be supported from the available information because so little is known about the effect of crystal planes. Difference in chemical treatment seems an unlikely explanation; all investigators used either CP-4 or CP-4A and recent work on chemical treatment[19] indicated that such etches yield reproducible surfaces.

All of the dry ambient measurements reported here can be explained by assuming that dry oxygen increases the density and ratio of capture cross section of the states and has very little effect on the energy. This same behavior, although accompanied by an increase in $(E_t - E_i)$, was reported by Harnick *et al.*,[3] and Margoninski.[19] Both found that etching in HNO_3 generally caused these three surface parameters to increase. Slow oxidation of the germanium surface seems, therefore, to cause an enhancement of surface parameters, which surmise is further supported by the fact that baking in dry air or in an oxygen atmosphere causes this same increase.[20,21]

Many and Gerlich's[4] results, however, are in direct contradiction to all dry ambient measurements reported here. Subjecting their *n*-type sample to vacuum, dry oxygen, and dry nitrogen cycles, they invariably found: (a) decreases in energy, density, and c_p/c_n when changing from vacuum to dry oxygen, and the opposite trend when going back from dry oxygen to vacuum; (b) a decrease in energy on changing from dry oxygen to dry nitrogen and an increase when changing from dry nitrogen to vacuum, N_t and c_p/c_n being almost unaffected by this treatment. No explanation for this contradicting experimental evidence can be suggested, other than difference in surface orientation.

ACKNOWLEDGMENTS

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