spectra of Teflon and polyethylene which have been exposed to γ rays at -196° and of some biological materials which have been frozen in air, and contain C–O–O· radicals[14-17], and also the potassium peroxide radical K–O–O·,[18] *i.e.* it resembles spectra which are apparently characteristic of peroxy-radicals R–O–O·. This fact supports the hypothesis that the radical present in the peroxide-radical condensate is the hydroperoxy-radical H–O–O· (perhydroxyl).

3. Study of the kinetics of the decomposition of the condensate prepared from dissociated water vapour showed that disappearance of the yellowish colour (between -110° and -100°) is accompanied by slight oxygen evolution (3–4 wt.% of the total quantity of oxygen evolved)[6]. From the concentration of radicals in the condensate and their assumed nature, the quantity of oxygen which should be evolved by their recombination can be calculated. If these radicals are OH, which recombine to form H_2O and O_2, the proportion of "radical" oxygen in the total amount of the gas evolved would be 1–1.5 wt.%. If, however, it is assumed that the radicals are HO_2, recombining to form H_2O_2 and O_2, the proportion of "radical" oxygen is raised to 2.5–3 wt.%. Comparison of these figures with the quantity of oxygen evolved at -110° to -100° favours the second hypothesis. This is confirmed also by thermal data[4,5,7].

Thus analysis of the available experimental data indicates that the radical present in the peroxide-radical condensates is very probably HO_2, not OH as assumed by Kaitmazov and Prokhorov[8,9].

Knowing the nature of the radical, we can calculate its maximum concentration in the peroxide-radical condensates. It proves to be practically identical, 0.4 wt.%, in the two cases. Since the condensates are similar in character, the equality of the maximum weight concentration of the radicals may perhaps be an indication of a limiting density of packing of the radicals in the given matrix.

SUMMARY

1. An investigation has been made of the electron-paramagnetic-resonance spectrum of peroxide-radical condensates prepared both from dissociated water vapour and by the interaction of liquid 100% ozone with atomic hydrogen. Considerable paramagnetic absorption is observed in both cases, the electron-paramagnetic-resonance spectra being identical and having a complex form apparently connected with the anisotropy of the g factor of solid condensates.
2. The concentration of radicals in the peroxide-radical condensate obtained from dissociated water vapour can fluctate considerably, owing to the inhomogeneity of the condensate itself. This complication does not arise with the condensate prepared from liquid ozone and atomic hydrogen, where the radical concentrations are quite stable.
3. Comparison of the present results with those obtained for peroxide-radical and similar systems by electron-paramagnetic-resonance and other methods shows that the condensates apparently contain the HO_2 radical, not the OH radical.
4. The maximum concentration of the HO_2 radical is ~0.4 wt.% with respect to the total weight of the condensate, and differs little with the method of preparation.

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Lomonosov Moscow State University

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THE STATE OF ANODICALLY POLARISED GERMANIUM SURFACE IN ACID SOLUTIONS

E. A. Efimov and I. G. Erusalimchik

The electrical properties, reliability, and stability of semiconductor devices are determined largely by the treatment of the semiconductor surface, such as electrochemical etching. Very few papers have been published on the state of the surface of a germanium electrode in the process of anodic dissolution.

Formation of a film of GeO type on a germanium anode at high current densities was first observed visually by Jirsa[1]. Turner[2] in his study of electrochemical dissolution of germanium concluded that as a result of anodic polarisation with I = 0.3 mA cm^{-2} an oxide film forms on germanium, which can be cathodically reduced with the consumption of 4×10^{-4} C cm^{-2}. Similar results were obtained by Bardeleben[3], who found that the quantity of electricity required to remove oxygen from a germanium surface was independent of the type of the semiconductor conductivity and amounted to $\sim 10^{-3}$ C cm^{-2} when the current density of the preliminary anodic polarisation was 10^{-4} A cm^{-2}.

In this work the state of the surface of a germanium anode was studied over a wide range of current densities (10^{-5}–10^{-1} A cm^{-2}) in 0.1 N H_2SO_4 at 20°. All the experiments were made with polycrystalline degenerate germanium without semiconductor properties. The concentration of impurities was about 0.01%, so the germanium was very pure from the chemical point of view. Degenerate germanium was used in order to exclude the possible complications in the electrode processes arising from the passage of current through a semiconductor electrode. Preliminary experiments have shown that the kinetics of anodic dissolution and the structure of the electrical double layer at the electrolyte boundary were identical for the degenerate and p-type germanium. Thus the $\varphi - \log I$ and $c - \varphi$ curves were practically coincident for the two forms of germanium. This is to be expected since anodic dissolution of p-type germanium is not retarded by a deficiency of holes at the semiconductor–electrolyte boundary.

EXPERIMENTAL

The state of the surface of anodically polarised germanium was investigated by the charging curve-method using an ENO-1 oscillograph.

The germanium electrode was subjected to anodic polarisation of predetermined duration at various current densities, after which the $\varphi - Q$ curves were obtained at a cathodic current density of 10^{-3} A cm^{-2}. Particular precautions were taken to ensure that the electrolyte contained no dissolved oxygen. Before each experiment the germanium electrode was etched in CP-4 and then brought to a steady potential by careful cathodic polarisation.

Fig. 1 shows the cathodic charging curves obtained after preliminary polarisation for 10, 20, and 60 sec at φ = = 0.35 V (I = 5×10^{-4} A cm^{-2}). In all cases an arrest in the rise of potential was observed at ~ -0.13 V which was due to the removal of oxygen from the germanium surface. The quantity of electricity required for this purpose increased with the duration of the preliminary anodic polarisation amounting to $\sim 10^{-3}$, $\sim 3 \times 10^{-3}$, and $\sim 6 \times 10^{-3}$ C cm^{-2} for 10, 20, and 60 sec respectively. The potential of ~0.75 V corresponds to the evolution of hydrogen at the pure germanium surface at $I_c = 10^{-3}$ A cm^{-2}. The shape of the curves in Fig. 1 shows that all the oxygen present on the germanium surface is removed in the cathodic polarisation and that its quantity depends on the duration of the anodic polarisation. The absence of horizontal portions on the curves in Fig. 1 implies that no specific chemical surface compound forms at 0.350 V. According to Law and Meigs[4], 1 cm^2 of the apparent germanium surface (assuming a roughness factor of 1.3–1.5) contains, on average, $1.2 \times \times 10^{15}$ atoms.

In our case 10^{-3}–6×10^{-3} C cm^{-2} is required to remove oxygen, corresponding to 2–13 oxygen atoms per surface atom of germanium. Evidently several monolayers of both adsorbed oxygen and oxide phase form on the surface of the germanium anode at a potential of 0.35 V, since it is difficult to imagine 13 monolayers of oxygen bonded with the surface by adsorption forces alone.

Apart from the curves in Fig. 1, cathodic charging curves were obtained for anodic polarisation at potentials of 0.15 V (I = 10^{-5} A cm^{-2}), 0.30 V (I = 10^{-4} A cm^{-2}), and 0.33 V (I = 2.5×10^{-4} A cm^{-2}). All these curves are similar to those of Fig. 1. They likewise have no horizontal portions and the removal of adsorbed oxygen begins at a potential of ~ - 0.13 V. The quantity of oxygen in these cases also increases with the duration of the preliminary polarisation. Moreover, the quantity of electricity consumed in the removal of oxygen depends also on the potential of the anodic polarisation. Thus with anodic polarisation of 60 sec duration the quantity of electricity amounts to 4×10^{-4}, 2×10^{-3}, and 6×10^{-3} C cm^{-2} at potentials of 0.15, 0.30, and 0.33 V respectively, corresponding to ~1–13 monolayers of oxygen.

The nature of the charging curves obtained after a preliminary anodic polarisation at 0.38 V is different (Fig. 2). In this case there is an arrest resembling a plateau at a potential of - 0.13 V when the duration of polarisation exceeds 60 sec. When the potential of the preliminary anodic polarisation is higher still, the arrest occurs also after a shorter duration of polarisation.

The quantity of electricity required to remove all the adsorbed oxygen (for a duration of polarisation of 60 sec) is in this case also ~6×10^{-3} C cm^{-2}. This value remains

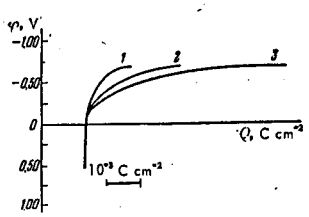

Fig. 1. Charging curves obtained after a preliminary anodic polarisation at φ = 0.35 V for:
1) 10 sec; 2) 20 sec; 3) 60 sec.

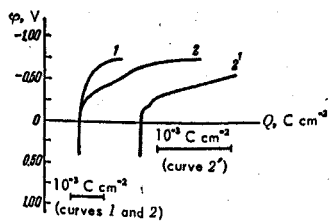

Fig. 2. Charging curves obtained after a preliminary anodic polarisation at φ = 0.38 V for:
1) 10 sec; 2) and 2') 60 sec.

practically unaltered when the potential of the anodic polarisation is increased from 0.38 to 0.51 V.

The appearance of the horizontal arrest on the charging curves at a potential of ~ - 0.13 V suggests that, with anodic potentials higher than 0.38 V, part of the electrochemically adsorbed oxygen becomes more strongly bonded with the surface until a surface chemical compound is formed. The quantity of electricity consumed during this horizontal arrest, at potentials from 0.38 to 0.51 V, increases with the duration of the preliminary anodic polarisation until it reaches $4.5-5 \times 10^{-4}$ C cm^{-2}, and then does not change any further. This shows that a monolayer of a chemical compound forms on the germanium surface involving one atom of oxygen per surface atom of germanium.

Fig. 3 shows the charging curves obtained after preliminary anodic polarisation at φ = 0.57 V ($I = 2.5 \times 10^{-2}$ A cm^{-2}). In this case the horizontal arrest at a potential of - 0.13 V is observed only when the duration of the anodic polarisation is very short (~ 1 sec). The curves for polarisations of 10, 20, and 60 sec display overpotential showing that for some time the potential corresponding to hydrogen evolution becomes lower than - 0.75 V. This is probably due to the formation on the surface of germanium, in the anodic polarisation at 0.57 V, of a more stable oxide which is difficult to reduce in the cathodic polarisation. Apart from reduction, hydrogen is evolved on the surface of this oxide – at more negative potentials than in the case of the pure germanium surface. The quantity of electricity required to remove oxygen rapidly increases in this case (for example for a duration of 60 sec it amounts to ~ 2.3×10^{-2} C cm^{-2}) and does not tend to any limiting value when the duration of the anodic polarisation increases.

The charging curves have also been obtained after anodic polarisation at potentials of 0.61 V ($I = 5 \times 10^{-2}$ A cm^{-2}) and 0.65 V ($I = 10^{-1}$ A cm^{-2}). They are similar to the curves in Fig. 3. The difficulty of reducing the oxide increases considerably and the potential corresponding to hydrogen evolution at the oxidised germanium surface becomes still more negative. After anodic polarisation at φ = 0.65 V, it is not possible to decrease the potential of hydrogen evolution to - 0.75 V corresponding to the clean germanium surface. In this case a yellowish-brown oxide film, reminiscent of GeO in appearance, may be observed visually on the electrode surface.

The conclusions based on the charging curves agree well with the results of the capacitance measurements. The differential capacitances and resistance of the germanium electrode are plotted in Fig. 4.

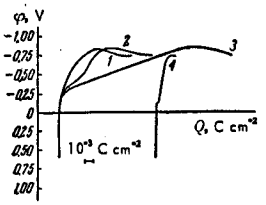

Fig. 3. Charging curves obtained after a preliminary anodic polarisation at φ = 0.57 V for:
1) 10 sec; 2) 20 sec; 3) 60 sec; 4) 1 sec.

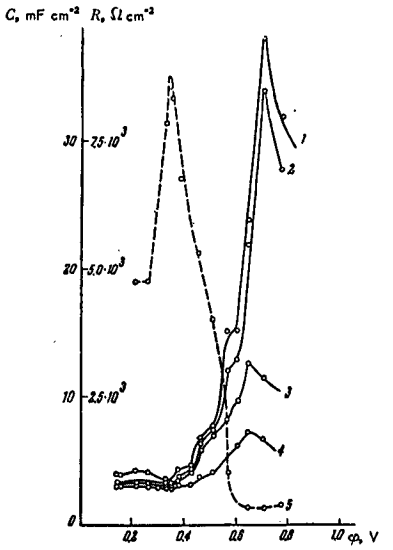

Fig. 4. Capacitance and resistance of a germanium electrode in 0.1 N H_2SO_4 at various frequencies:
1) capacitance at 60 c/s; 2) capacitance at 200 c/s; 3) capacitance at 1000 c/s; 4) capacitance at 5000 c/s; 5) resistance at 60 c/s.

The low capacitance at potentials less positive than 0.35 V confirms the conclusion reached above regarding the presence of electrochemically adsorbed oxygen on the surface. This is very plausible because the zero-charge point of germanium in acid solutions is close to - 0.6 V.

The potential of 0.38 V at which a horizontal arrest is observed, after polarisation, on the curves in Fig. 2 coincides almost exactly with the minimum in the capacity and the maximum in the resistance of the germanium electrode (Fig. 4).

The potential of 0.57 V at which more stable and thick oxide layers begin to form on the electrode surface is close to the range 0.60–0.65 V in Fig. 4 where the electrode resistance acquires a constant minimum value and the capacitance falls rapidly. The capacitance in the range 0.38–0.57 V is a pseudocapacitance determined by the anodic dissolution of germanium which proceeds rapidly.

SUMMARY

1. The state of the surface of anodically polarised germanium in 0.1 N H_2SO_4 has been investigated by the charging curve and capacitance methods.
2. It has been concluded that electrochemical adsorption of oxygen takes place on the germanium surface in the process of anodic polarisation at potentials less positive than 0.38 V. The quantity of adsorbed oxygen increases with an increase in the potential and the duration of the anodic polarisation. At the same time the bonding of oxygen with germanium becomes stronger and an oxide phase is formed.

3. At potentials more positive than 0.38 V a monolayer of a definite surface chemical compound begins to form on germanium involving one oxygen atom per germanium atom. This compound has a high resistance and can be completely reduced cathodically.

4. At potentials of 0.57 V and higher thick layers of oxide similar to GeO form on the surface of the germanium anode. The thickness of this oxide film increases with an increase in the potential and the duration of the polarisation. The oxide cannot be completely reduced in the cathodic polarisation. The potential of hydrogen evolution is greater on this oxide than on the clean germanium surface.

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ANGULAR MEAN VALUES IN THE LATTICE THEORY OF LIQUIDS

Yu. V. Gurikov

The lattice theory of liquids, while possessing neither the rigour nor the generality of the method of integral equations, does give, at the present time at any rate, better quantitative results, especially at high densities of the material.

The free-volume theory in its original form[1] was especially successful in predicting the critical temperature of several inert gases and in providing a qualitative explanation of some well-known empirical rules, such as those of Guldberg and Guye and of Trouton.

It was later established[2] that, even if allowance is made for the force fields due to the second and subsequent layers of neighbouring molecules, the free-volume theory leads to a considerable difference (about twofold) between theoretical and experimental values of critical volumes and coefficients PV/RT. It must be emphasised that the critical pressure is overestimated by a factor of 4. Calculated values of the internal energy, on the other hand, are somewhat lower than the corresponding experimental values. This suggests that the theory gives an incorrect idea of the relation between repulsive and attractive forces among the molecules in a liquid. It may be supposed that the free-volume theory owes its success to the cancelling of errors resulting from simplifying assumptions.

In addition to the hypothesis that a liquid has a quasi-crystalline structure, the following assumptions are made: (1) a molecule in a cell is subject on the average to a spherically symmetrical force field produced by the remaining molecules in the liquid; (2) the potential energy of a molecule in a cell can be obtained by finding the unweighted mean w.r.t. the angular coordinates of this molecule, which is equivalent to the hypothesis of the independent motion of molecules in neighbouring cells, and tends to increase the repulsive contribution to the thermodynamic properties of a liquid; (3) the potential energy of a molecule in a cell is calculated on the assumption that neighbouring molecules are located in their mean positions, *i.e.* at the centres of the corresponding cells, but this takes no account of many configurations in which molecules are very close together in a liquid; (4) interaction between molecules which are not nearest neighbours can be neglected. The original theory of Lennard-Jones and Devonshire is to some extent inconsistent, in that the calculation of the free volume takes account only of the interaction with the first shell of nearest neighbours, while the zero-point energy (when all the molecules are located at the centres of their cells) is calculated exactly. Hirschfelder and his collaborators[2] based their calculations on three shells. The present calculations of the corresponding integrals are based on only two shells.

The present paper proposes a stricter correlation between the motion of molecules in neighbouring cells. Assumption (3) is retained in order to simplify the analysis, although formally, following an idea of Kirkwood's[3], the theory can easily be generalised to include the effect of the vibration of molecules in neighbouring cells.

Angular Averaging

Let us consider two neighbouring cells, numbered 1 and 2, with the distance a between their centres unambiguously defined by the volume of the liquid per molecule. With a face-centred lattice $v = \frac{1}{4}a^3$. The molecule in cell 2 is fixed at the centre of this cell. Let $d\omega_1 = r_1^2 \sin\theta_1 \, d\theta_1 \, d\varphi_1$ be an element of area on the surface of a sphere of radius r_1 within cell No. 1, the centre of which is taken as the origin, while the line passing through the centres of the two cells is chosen as the z axis. If we denote integration over the surface of the whole sphere of fixed radius r_1 by the symbol $\oint$, we can represent the process of angular averaging introduced by Lennard-Jones and Devonshire as

$$\psi(r_1, a) = \oint u(r_{12})\, d\omega_1 \Big/ \oint d\omega_1,$$

where $r_{12} = (a^2 + r_1^2 - 2ar_1 \cos\theta_1)^{\frac{1}{2}}$ is the distance between the molecules in cells 1 and 2.

According to Eqn. (1), all positions of the molecule on the sphere of radius r_1 are equally probable. In a physically more soundly based process of angular averaging, different points on this sphere should be weighted differently, maximum probability being assigned to those points whose distance from the molecule in cell 2 corresponds to the first maximum of the radial distribution function. Recently Dahler *et al.*[4] proposed a new method for angular averaging†:

$$\exp\{-\psi(r_1, a)/uT\} = \oint \exp\{-u(r_{12})/kT\}\, d\omega_1 \Big/ \oint d\omega_1. \qquad (2)$$

† A more general method of angular averaging is suggested in ref. 4, for the case in which the motion of the molecule in cell 2 is taken into account.