INVESTIGATIONS ON VOLTAGE DISTRIBUTION INFLUENCED BY FIELD EFFECT OF GERMANIUM-ELECTROLYTE INTERFACES

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The voltage distribution of Ge-electrolyte interfaces was studied among the circumstances of d. c. and a. c. field effect measurements. The voltage produced along the sample with reference to one of the ohmic contacts of the sample was measured with a needle probe, using a compensation method. It has been pointed out that in the range of cathodic polarization current densities the changes in voltage determined by the sum of drift current and of local field current flowing through the sample considerably differ from the changes expected and show strong inhomogenous voltage distribution.

Introduction

Several papers concerning investigations of field effect of Ge surfaces in aqueous solutions have been published [1—6]. The principle of this kind of measurements is that the semiconductor surface is covered by an electric double layer under electrolyte in equilibrium condition of the system [7], which permits to modulate the surface potential by electrolytic polarization within broad limits. It can be shown trom the results that, in the case of aqueous electrolytes with sufficiently high ($\cong 0,1$ N) concentrations, the drop of the Galvani potential of the Ge surface practically occurs across the space-charge region if the density of surface states is not too high [8—10]. Under these circumstances the surface potential is influenced by the electrolytic polarization of the semiconductor surface with reference to a metal electrode through the formation of an ion layer and it is the surface potential which determines the surface conductivity, the surface recombination velocity of the semiconductor and the capacity of semiconductor-electrolyte interface. In this respect the effect of electrolytic polarization of the semiconductor surface is similar to that of the „dry" field effect.

Despite of numerous advantages of the field effect, the possibilities mentioned above are only theoretical as they do not take into account the complications arising from currents flowing through the sample under the influence of external electric fields. The equilibrium distribution of carriers in the space-charge region is influenced by the field current flowing through the sample, the quality of the surface formed earlier is changed by the electrode reactions starting immediately after switching on the field current; these effects, together with the voltage distribution on the sur-

face caused by the simultaneous effect of field and drift current (the latter used for measuring the surface conductivity) are all factors disturbing the evaluation of field effect measurements.

The present paper deals with the voltage distribution along the Ge sample measured with continuous polarization at different current densities.

Experimental arrangement

The experimental set up used is shown in Fig. 1. It is practically the same as that applied by ROMANOV and KONOROV [4] for field effect measurements under electrolyte, except the needle probe (P) and its compensation circuit (K). A resistor (R) of much higher resistance than the Ge slab is connected in parallel to the ohmic contacts of the sample. This resistor secures the symmetric distribution of polarization current along the sample.
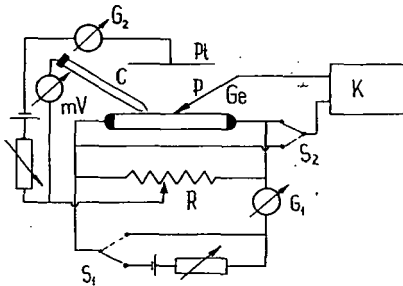
The Ge slab together with the cell containing the electrolyte as well as the manipulator for displacing the (electrolytically sharpened) needle probe were built together with a Zeiss microscope. This arrangement permitted to reproduce the position of the probe on the surface of the sample within a circle of 0,2 mm diameter. Probe pressures higher than 1 kp/mm² were applied. The ohmic contacts and the needle probe — except its edge — were masked by insulating material in order to eliminate the disturbing effects in the electrolyte.

The measurements were made on n-type Ge samples of 22 Ω cm resistivity, 20 mm $\times$ $\times$ 6 mm $\times$ 0,5 mm in size and oriented in (111) direction. The samples were supplied with two ohmic contacts and were inserted in neutral aqueous solution of 0,1 N K₂SO₄ during the measurements. The samples were etched in CP4A for 2 minutes before the experiment.

Fig. 1. Experimental set up. G_1 and G_2 galvanometers, *mV* voltmeter, *Ge* sample, *Pt* platinum electrode, *C* calomel electrode, *P* needle probe, *K* compensation circuit, *R* resistor for symmetrizing of the field current, S_1 and S_2 switches

The investigations were made at cathodic and anodic current densities of 100, 50, 25, 10 and 0 µA/cm² and with drift currents of 0 and 20 µA, moving the probe by steps of 0,5 mm along the middle line of the sample. Before beginning the experiments the samples were polarized with 1000 µA/cm² anodic current density for 5 to 10 minutes. The measurements were started only after the electrode potential had attained its constant equilibrium value at a given current density. Then the voltage drop along the sample was measured as a function of the distance from one of the contacts using a compensation method.

Experimental results

Fig. 2 and 3 show the experimental values of voltage, plotted against the distance from one of the contacts along the sample, obtained at Ge surfaces for different polarization current densities. The solid lines represent the average values of 5 sub-
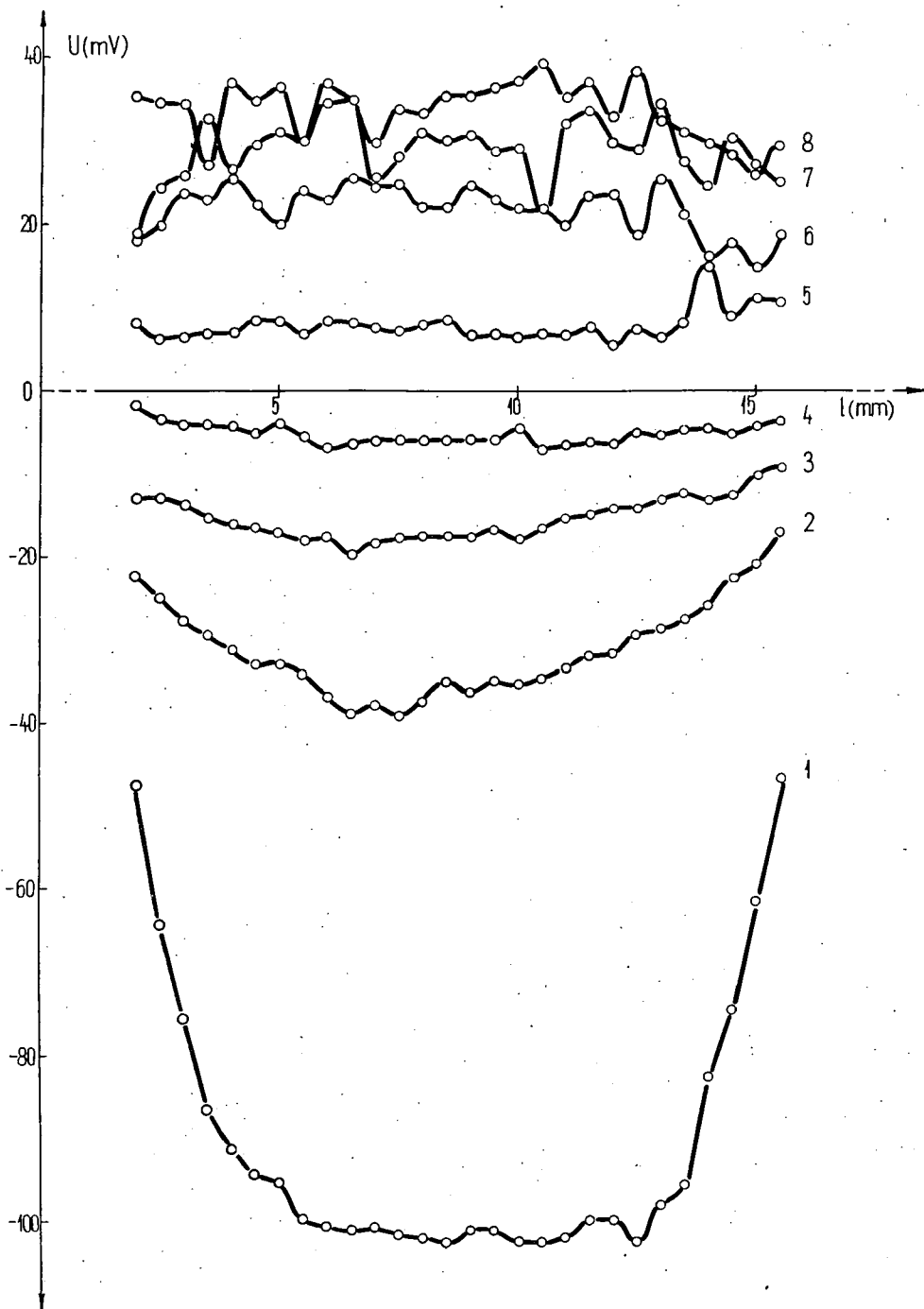
Fig. 2. Experimental values of voltage plotted against the distance from one
of the contacts along the middle line of the surface, obtained at Ge sample № 1
for different current densities with 0 drift current. Curves 1 to 8 measured at field current
densities of 100, 50, 25, 10, 0, −10, −25 and −50 μA/cm² respectively
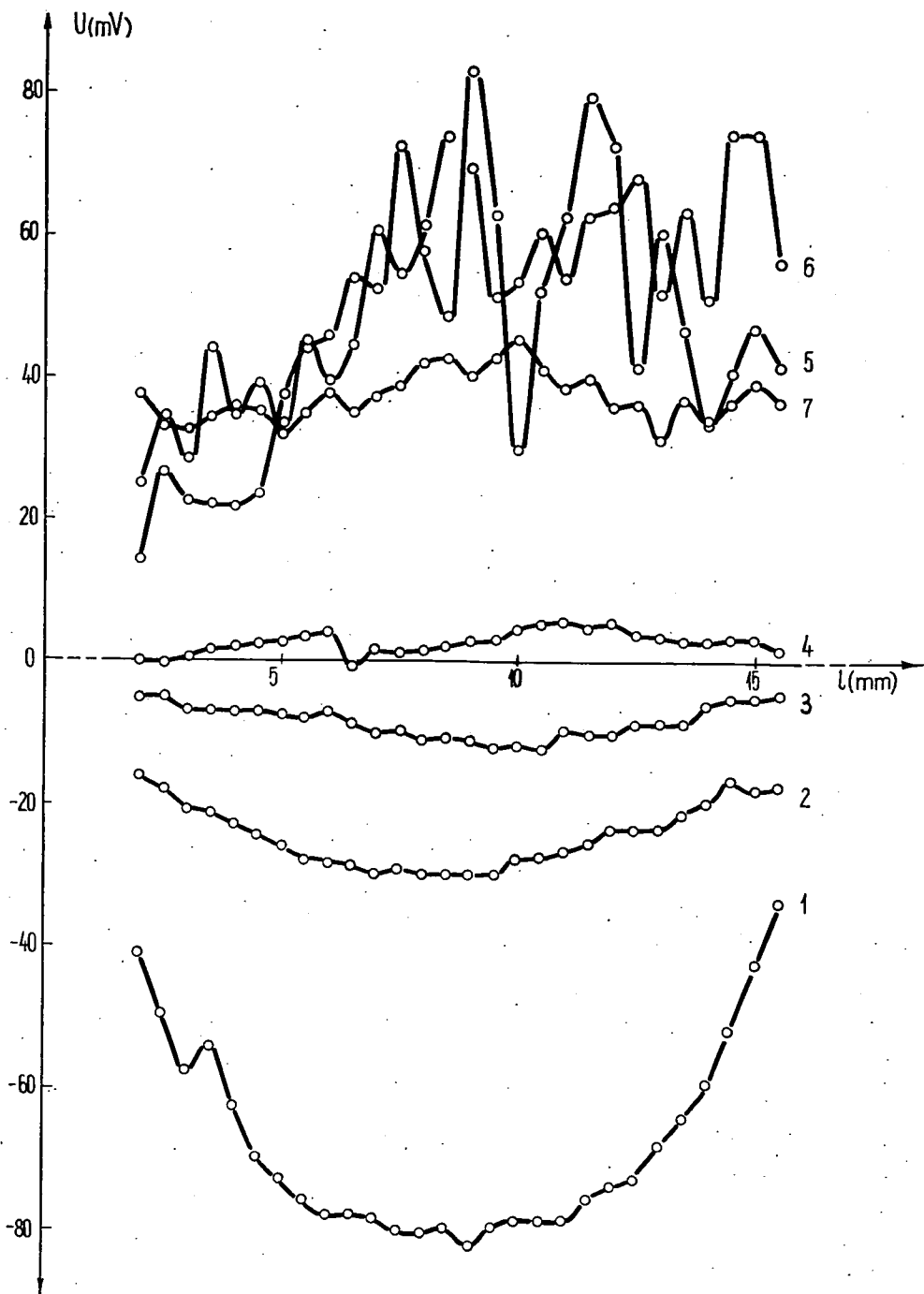
Fig. 3. Experimental values of voltage plotted against the distance from one of the contacts along the middle line of the surface, obtained at Ge sample № 2 for different current densities with 0 drift current. Curves 1 to 7 measured at field current densities of 100, 50, 25, 10, −10, −25, and − 50 μA/cm² respectively
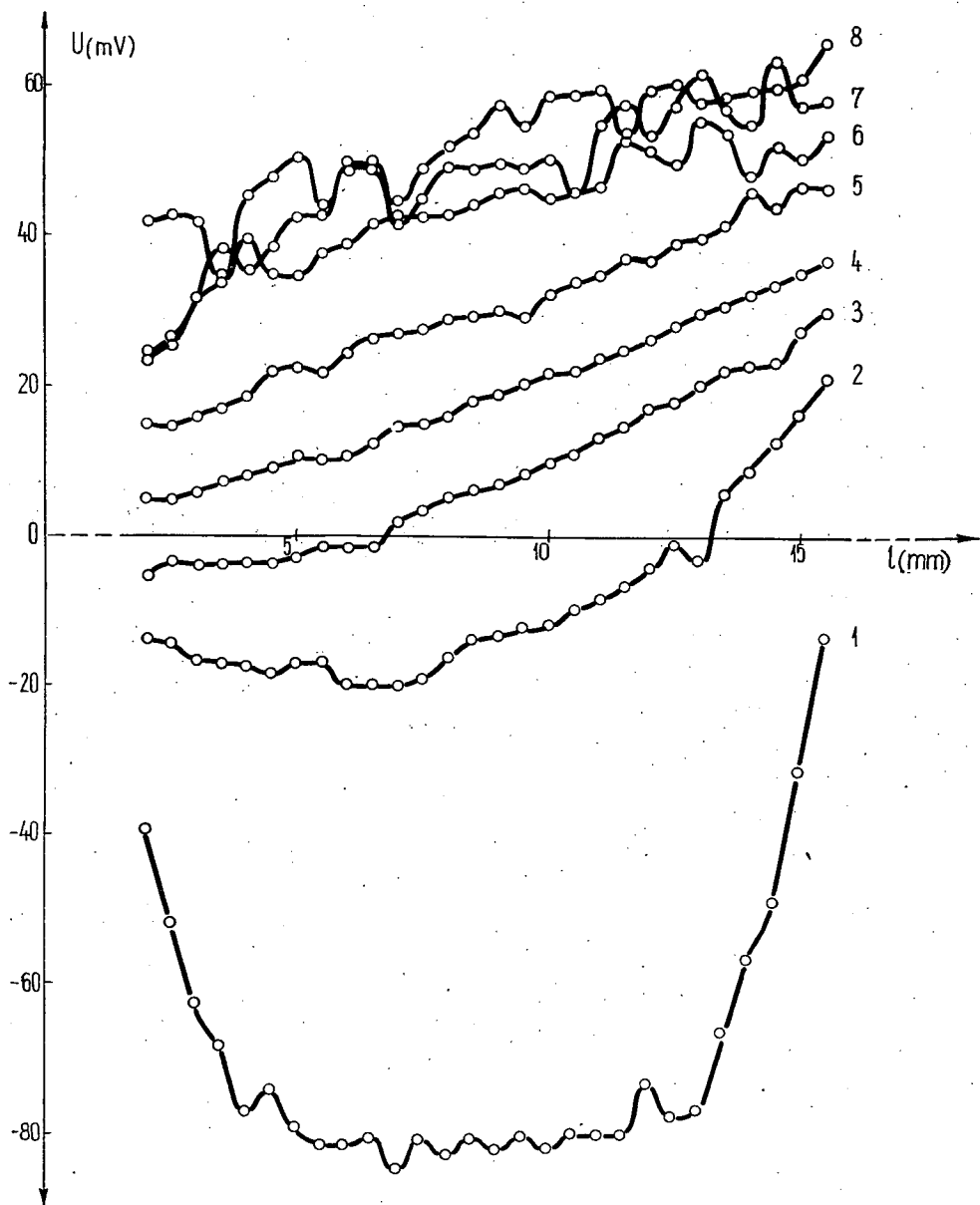
Fig. 4. Experimental values of voltage plotted against the distance from one of the contacts along the middle line of the surface, obtained at Ge sample № 1 for different current densities with $20\mu A$ drift current. Curves 1 to 8 measured at field current densities of 100, 50, 25, 10, 0, −10, −25, −50 $\mu A/cm^2$ respectively

sequent measurements. It can be seen in Fig. 2 and 3 — but most distinctly in Fig. 3 — that the voltage distribution produced along the sample in the case of different cathodic field current densities is strongly inhomogenous and shows certain oscillations. At anodic field current densities there are no oscillations and the voltage distribution is the same as expected from calculation. Similar observations can be made when applying a drift current of 20 μA simultaneously with different field current densities. These results, plotted in Fig. 4, show that, besides the inhomogenous voltage distribution, the voltage produced along the sample is always determined by the sum of the local current densities (drift and field current). In consequence, under the circumstances of both a. c. and d. c. field effect, the voltage distribution and field current density along the sample strongly depend on the distance from the contact and the total field current used.
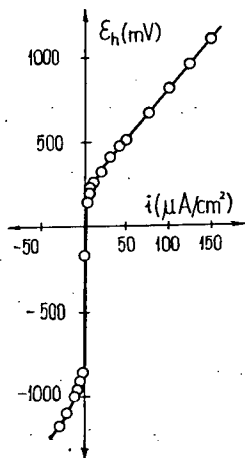
Fig. 5. Dependence of electrode potential on field current density with reference to hydrogen electrode
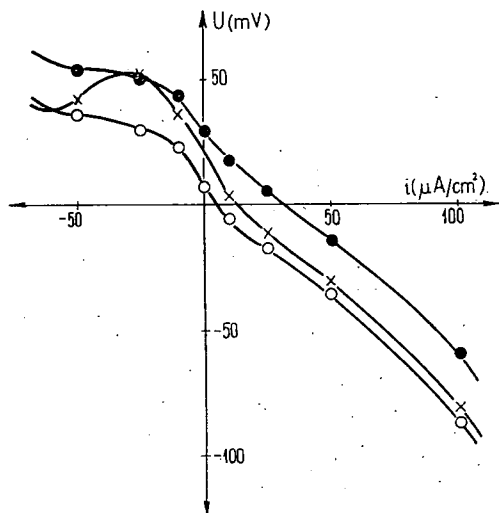
Fig. 6. Experimental values of the surface voltage, obtained with the needle probe at the middle point of the sample, plotted against the field current density. × Ge sample № 2 without drift current, o Ge sample № 1 without drift current, ● Ge sample № 1 with 20 μA drift current

Putting the probe on the same site of the sample 5 times subsequently with the same probe pressure (1 kp/mm²), the following experiences were made:

(i) In the case of dry Ge samples the deviations of the results of 5 measurements did not exceed 0,3 mV.

(ii) Using 0 or small anodic field current densities the deviations were within a range of 3 mV.

(iii) With cathodic current densities, greater deviations within an interval of 10 mV were found. In most cases the voltage obtained at the first contact was the highest. A similar effect could not be found with anodic field currents.

Fig. 5 shows the result of measurements obtained for equilibrium electrode

potentials with reference to hydrogen electrode using a calomel electrode (C in Fig. 1) at different anodic and cathodic current densities.

In Fig. 6 the experimental values of the surface voltage, obtained with the needle probe at the middle point of the sample are plotted against the field current density.

A comparison of Fig. 5 and Fig. 6 shows that the minimum of the surface conductivity is to be found in the initial part of cathodic field current density curve, in good agreement with the results published in [4].

Conclusions

During the field effect measurements in Ge-electrolyte systems the sum of the field currents of different directions and intensities and of the drift current results in a continuously changing current density distribution along the sample and a corresponding voltage change. As a result of the electrochemical reactions occuring on the Ge-electrolyte interface, connected with the formation of germanium monoxide at anodic polarization, besides dependence on time and current density [11, 12], the reaction products also show a dependence on the site along the sample. The inhomogenous voltage distribution produced during the cathodic field polarization is found in the region of conductivity minimum. As a result of the inhomogeneities in the field current density and reaction products along the surface of the sample the evaluation of field effect measurements under electrolyte is complicated.

From the detailed evaluation of our measurements and from the results mentioned in (i), (ii), (iii) it can be concluded that chemical products formed during the cathodic polarization on the Ge surface are of low conductivity and of rather great mechanical stability.

The results obtained with 5 subsequent measurements at anodic polarization show greater deviations than those observed on dry samples, which is probably connected with greater inhomogeneity in the surface layer produced by polarization. However, the inhomogeneities of the surface are not sufficient to explain the greatest deviations found with cathodic polarization of the sample. As to the inhomogeneities in voltage at cathodic polarization, the present results are not sufficient to decide whether they are due to electrochemical or physical effects.

There are two possibilities to explain the great local voltage inhomogeneity obtained at cathodic polarization. It can be supposed that on some sites of the surface, currents flowing in opposite direction than that of the total field current are present; this seems, however, very improbable. If we assume that the layer covering the surface is of high resistivity and very inhomogenous in thickness, the field current flowing through this layer may cause a voltage drop which could be responsible for the inhomogeneous surface voltage distribution. The latter assumption is much more plausible.

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ИССЛЕДОВАНИЕ РАСПРЕДЕЛЕНИЯ ПОТЕНЦИАЛА
НА ПОВЕРХНОСТИ ГРАНИЦЫ Ge-ЭЛЕКТРОЛИТА
ПОД ВЛИЯНИЕМ ЭФФЕКТА ПОЛЯ

Л. Михайлович и А. Шюли

Рассматривается распределение потенциала на поверхности границы Ge-электролита в случае измерения на постоянном и переменном токах. Возникающее напряжение измерялось с помощью зонда, методом компенсации, относительно омического контакта исследуемого объекта. Показано, что распределение потенциала определяется суммой тока, протекающего через исследуемый объект, и локальной плотностью объемного тока. В области плотности тока катодной поляризации распределение потенциала значительно отходит от предположенного, и показывает неоднородный характер.