CCA-682 541.135.4
Conference Paper

Avalanche Breakdown on a Semiconductor *n*-type Gallium Arsenide Electrode*

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Received November 10, 1971

Measurements of the avalanche breakdown potential on *n*-type gallium arsenide electrodes in contact with water or aqueous solutions of $NaNO_3$ and NaCl are reported. Calculations are presented of the dielectric constant and of field strength in the Helmholtz and the space charge layer of the semiconductor. The interfacial electrode capacitance of the GaAs electrode is a complicated function but can successfully be approximated with the equation describing the capacitance of the *p-n* junction in the solid state.

INTRODUCTION

The electrochemical properties of a semiconductor electrode may be considered with assumption that the rate of the electrode reaction is determined by the stage of the electrochemical reaction on the semiconductor surface[1] relative to gallium arsenide.

A second way of considering the electrode process is the assumption that the reaction rate is determined by the stage of carrier transfer through the space charge layer formed as a result of polarization in the semiconductor, and that the stage of the electrochemical reaction is limited by the inflow of carriers on the semiconductor — electrolyte interface[2].

In this case the courses of the resultant reactions would be distinctly and strongly dependent on the electrical properties of the semiconductor-electrolyte interface. Acceleration of the electrochemical electrode reaction should follow as result of decreasing of the dielectric constant of the electrolyte. To larger values of the dielectric constant there would correspond higher values of the electrode potential δU_b, at which a marked start of the electrochemical reaction would follow. On the basis of this assumption it may be stated that the breakdown potential δU_b, should assume the highest values in the pure solvent (largest dielectric constant), and with increasing activity of the electrolyte it should diminish. In two electrolytes with equal activities the breakdown potential should be proportional to their dielectric constants.

EXPERIMENTAL

The experiments were carried out in an electrolytic vessel in a system as described previously[2,3]. Deionized water and *p. a.* reagents were used for the investigations. *n*-Type gallium arsenide oriented along the (111) axis was used with

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* Based on a lecture presented at the *22nd Meeting of the International Society of Electrochemistry,* Dubrovnik, Yugoslavia, September 1971.

mobility $\mu = 2000$ cm^2/V. sec and with a concentration $\sim 1 \times 10^{18}$/cm^3 which corresponds to the resistance $\varrho = 0.003$ ohm. cm and $\sim 2 \times 10^{17}$/cm^3 what equals to the resistivity $\varrho = 0.02$ ohm. cm. The ohmic junction to the surface of gallium arsenide was carried out by vacuum evaporation of layer of indium, the heating of this layer under hydrogen, and subsequently soldering the wire by an indium solder.

The measurements were carried out at a constant temperature of 25° C under argon, which was simultaneously used for intensive mixing of the near-electrode space. The purity of the argon was 99.999%.

In Fig. 1 the method of fixing the electrode in the glass cork is represented schematically. The real surface of the investigated electrode was 0.385 cm^2. Account was taken of the coefficient of roughness of 1.3.

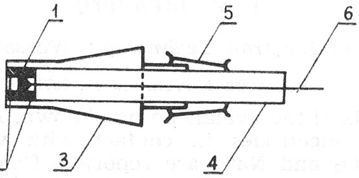

Fig. 1. Stopper for GaAs electrode. *1* — GaAs electrode; *2* — washers; *3* — ground joint; *4* — supporting pipe; *5* — rubbers; *6* — wire.

The measurement of the electrode potential was carried out with respect to a calomel electrode. A platinum electrode with 6 cm^2 of surface was used for polarization. Measurements of the dependence of the electrode potential on the applied current intensity (direct current method) was performed after stabilization of the stationary potential of the electrode in complete darkness.

RESULTS AND DISCUSSION

As a result of the performed investigations the potential — polarization current density curves were obtained, shown in Figs. 2—4. The anodic polarization determines, the barrier direction for the created *p-n* junction, cathodic polarization denotes the conduction direction.

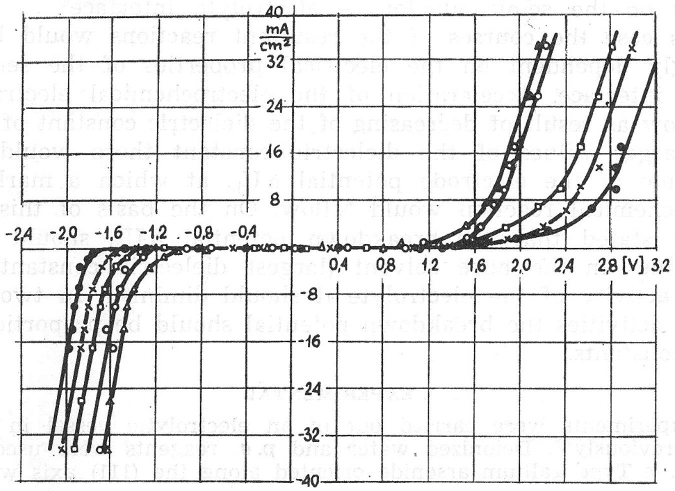

Fig. 2. Polarization curves of *n*-type GaAs $N_D = 1 \times 10^{18}$/cm^3. ● H_2O; ○ 1 *M* $NaNO_3$; × 0.01 *M* $NaNO_3$; □ 0.1 *M* $NaNO_3$; △ 1 *M* NaCl.

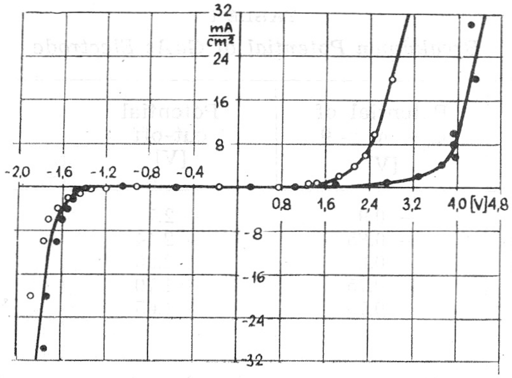

Fig. 3. Dependence of polarization curves on carriers concentration in 0.1 *M* $NaNO_3$. ○ $GaAs_n$ $1 \times 10^{18}/cm^3$; ● $GaAs_n$ $2 \times 10^{17}/cm^3$.

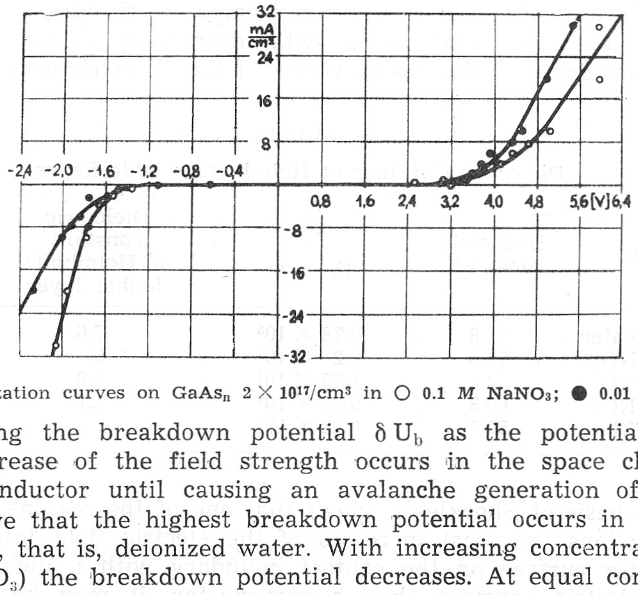

Fig. 4. Polarization curves on $GaAs_n$ $2 \times 10^{17}/cm^3$ in ○ 0.1 *M* $NaNO_3$; ● 0.01 *M* $NaNO_3$.

Determining the breakdown potential δU_b as the potential at which a positive increase of the field strength occurs in the space charge layer in the semiconductor until causing an avalanche generation of carriers[2,3], we can observe that the highest breakdown potential occurs in the case of a pure solvent, that is, deionized water. With increasing concentration of the solution ($NaNO_3$) the breakdown potential decreases. At equal concentrations (1 *M* $NaNO_3$ and 1 *M* NaCl) the breakdown potential is greater in 1 *M* $NaNO_3$ than in 1 *M* NaCl. A similar phenomenon occurs in the case of cathodic polarization in the conduction direction.

In order to establish the proper potential affecting the field strength in the space charge layer a measurement of the potential of planar bands was carried out and the absolute value of the breakdown potential was assumed to be the sum of the potential of planar bands and of the breakdown potential for each solution under investigation. In Table I the values of the breakdown potential δU_b are given.

The assumption that the field intensity causing avalanche breakdown in the space charge layer in gallium arsenide is constant and equal according to Sze[4] $F_b = 4 \times 10^5$ V/cm, the occurrence of a pure process of avalanche breakdown in the case of so strongly doped semiconductor is problematic

TABLE I

Breakdown Potential of GaAs Electrode

Electrolyte	Potential of $\varphi_b - \varphi_s = 0$ [V]	Potential cut-off [V]	Breakdown potential [V]
deionized H_2O	— 0.9	+ 2.7	3.6
0.01 *M* $NaNO_3$	— 0.85	+ 2.44	3.29
0.1 *M* $NaNO_3$	— 0.8	+ 2.25	3.05
1 *M* $NaNO_3$	— 0.75	+ 1.70	2.45
1 *M* NaCl	— 0.70	+ 1.65	2.35

and the occurrence of Zener or tunnel effect becomes probable. The mentioned value of the field intensity in the space charge layer corresponds to the breakdown potential, according to Sze[5] — 4.4 V, it is larger than the values obtained in the case of the investigated electrolytes.

The sequence of electrolytes with decreasing values of breakdown potential coincides with decreasing values of the dielectric constant (Table II)[6].

TABLE II

Dielectric Constant at Helmholtz Double Layer

Solution	Dielectric constant	F_H [V/cm]	Dielectric constant of Helmholtz double layer	$\frac{F_{sp.\,ch.}}{F_m}$
deionized water	71.8	2.78×10^5	7.6	1.2
0.01 *M* $NaNO_3$	71.5	2.2×10^5	6	1.3
0.1 *M* $NaNO_3$	69.7	1.75×10^5	4.8	1.4
1 *M* $NaNO_3$	60.3	0.62×10^5	1.7	1.75
1 *M* NaCl	59.0	0.43×10^5	1.2	1.8

On the basis of Shockley's[7] views that one of the reasons for breakdown in *p-n* junctions are local increases of the electric field intensities on the semiconductor surface on the contact boundary with a dielectric having a smaller dielectric constant than semiconductor, it may be stated that at mean field strength, space charge layer and Helmholtz layer lower than the intensity of breakdown field F_b the field strength in the space charge layer achieves the value sufficient to start the breakdown $F_b = 4 \times 10^5$ V/cm. In Table II the values of the dielectric constant are given calculated in the Helmholtz layer, resulting from the following equations:

$$(F_H + F_{sp.\,ch})/2 = F_m \quad (1)$$

$$\varepsilon_{sol}/\varepsilon_s = F_H/F_s \quad (2)$$

where

F_H — field strength in the Helmholtz layer of thickness $w_{II} = 3 \times 10^{-8}$ cm [V/cm],

$F_{sp.ch.}$ — field strength in the space charge layer in GaAs,

F_m — mean field strength in the space charge layer and in the Helmholtz layer for $w_m = w_H + w_{sp.ch.}$

The order of calculated value of dielectric constant in the Helmholtz layer in the case of pure water is the most similar as that on the basis of data compiled in Table II.

The order of magnitude of the values obtained corresponds to the data on the structure of a double layer elaborated by Bockris[8] and Conway[9]. This conformity speaks rather in favour of recognizing the correctness of the reasoning presented that the process determining the reaction rate on the semiconducting electrode is carrier transport through the space charge layer.

The mean values of the electric field strength in the total space charge and Helmholtz layers were from 1.2 times to 1.8 times smaller than the field strength in the semiconductor depending on the chemical composition of the solution. The cathodic (conduction) direction indicates a similar dependence of the electrode potential on the properties of the solution which is another analogy with the *p-n* devices.

The experimental examination of the potential distribution was made by recording polarization curves on an electrode of gallium arsenide of high purity and high resistivity. (Figs. 3 and 4). The potential breakdown in 0.1 *M* $NaNO_3$ increases of about 1.5 V (Fig. 3) that is 1.5 times as much. For *p-n* junction[4] in a solid state the potential breakdown is 2.4 times as much in the case of the discussed differences of concentrations.

Taking into account the presented argumentation we may conclude that the dielectric constant in double layer as a result of the action of higher electrical field is smaller and equals to 3 but not 4.8 (Table II).

The increase of the polarization potential of anode may also cause the passivation of the surface of semiconductor electrode (Fig. 4). When the surfaces of the electrode were very accurately polished, also the passive films were subject to rather hard breakdown; in range of anode polarization, in the solution of higher concentration (in 0.1 *M* $NaNO_3$), higher potential of breakdown was observed, than in the more diluted solution (0.01 *M* $NaNO_3$). It confirms the previous observation that the area of investigation of clean properties of semiconductor origin is limited to some lower anode potentials in the solutions not enabling the passivation of the surfaces.

The measurements of the electrode capacity in the case of *n-p* junction present should point out the dependence of the capacity from the electrode potential analogous to the dependence of the capacity of the junction in solid state devices. In this case it should be listed experimentally the obtained results with the theoretical curve drawn on the basis of the equation of the unitary capacity of the *p-n* junction[4]:

$$C_{sp.\,ch} = \frac{dQ}{d\Phi} = \sqrt{\frac{q_0 \cdot \varepsilon_0 \cdot \varepsilon_s \cdot N_D}{2\,|\Phi_{bi} \pm \Phi_E|}} \qquad (3)$$

where

q_0 — elementary load $= 1.6 \times 10^{-19}$,
ε_0 — dielectric constant of vacuum $= 8.854 \times 10^{-12}$ F/m,
ε_s — dielectric constant of semiconductor,
N_D — donors concentration (or acceptors) in m^{-3},

Φ_{bi} — diffusion potential (built in) of real, *p-n* junction at the given concentration of donors (acceptors),

Φ_E — electrode potential (positive in the anode area, negative in the cathode area upon the diffusion potential Φ_{bi}).

In Fig. 5 introduced are the results of the measurements of the capacity of electrode of GaAs of the *n*-type $N_D = 1 \times 10^{18}/cm^3$ as regards the curve drawn on the basis of the equation (3). For the $NaNO_3$ solutions of the concentration of 0.01 *M* to 0.1 *M* the theoretical curve is between the experimental curves. With the increase of the concentration the measured capacity increases (1 *M* $NaNO_3$), with the dilution the measured capacity decreases (H_2O). Analogous reaction of the capacity — potential relationship was observed on the electrode of $GaAs_n — N_D = 2 \times 10^{17}/cm^3$ (Fig. 6) and on the electrode of $Si_p — N_A = 4 \times 10^{19}/cm^3$ (Fig. 7).

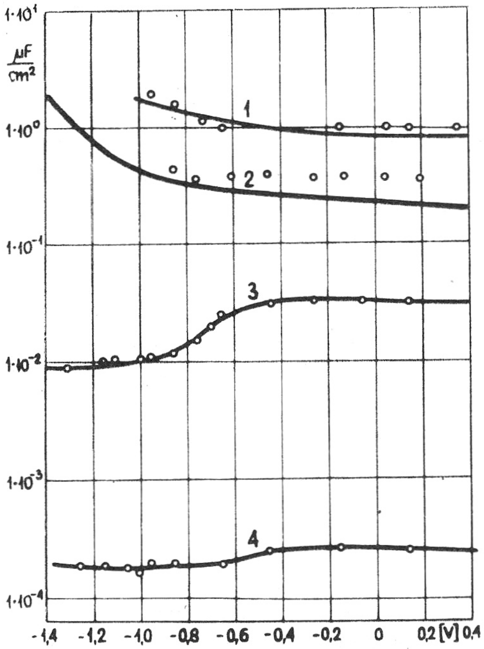

Fig. 5. Capacity *vs.* potential on $GaAs_n$ $1 \times 10^{18}/cm^3$. *1* — in 1 *M* $NaNO_3$; *2* — theoretical curve experimental points for 0.1 *M* $NaNO_3$; *3* — in 0.01 *M* $NaNO_3$; *4* — in H_2O.

Considering the capacity of the electrode as regards an electrolyte C_m as a sum of serial capacities of a double layer and a layer of a space charge, we have

$$C_m = C_{sp.\,ch.} + C_e \tag{4}$$

where

C_m — measured capacity,

$C_{sp.ch.}$ — capacity of the space charge layer of semiconductor,

C_e — capacity of a double layer of an electrolyte.

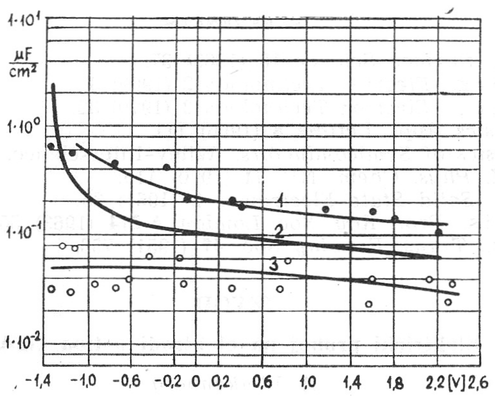

Fig. 6. Capacity *vs.* potential on $GaAs_n$ $2 \times 10^{17}/cm^3$. *1* — in 0.1 *M* $NaNO_3$; *2* — theoretical curve; 3 — in 0.01 *M* $NaNO_3$.

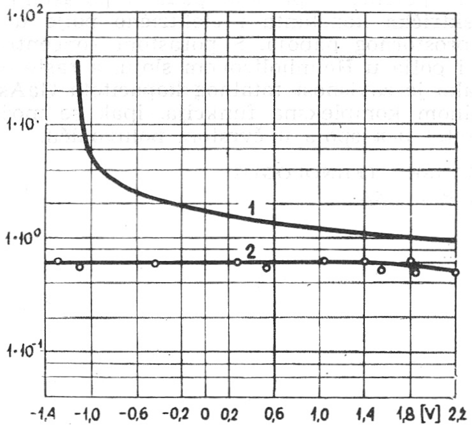

Fig. 7. Capacity *vs.* potential on Si_p $4 \times 10^{19}/cm^3$. *1* — theoretical curve; *2* — in 0.1 *M* $NaNO_3$.

Here we can see that the measured capacity C_m should yield the equation $C_m \leqslant C_{sp.ch.}$ and since the value C_e is negligible as being very large in comparison with $C_{sp.ch.}$ On the basis of measured values we may assume that the capacity of the layer of spatial charge under the influence of the increase of concentration of the electrolyte increases above the value computed with the equation (3). This increase of capacity being the result of local growth of carrier concentration near the semiconductor surface. The enlargement of the electrolyte concentration leads to the increase of density of charges on the interface semiconductor-electrolyte.

To conclude we may state that the present mechanism of electrolytic reaction is a reasonable interpretation of the real course of the process, although the occurrence of the tunnel mechanism cannot be excluded. The dependence of the GaAs electrode capacitance on the potential is rather complicated but in first approach equation of capacity of *p-n* junction gives quite good conformity of theory with experimental results for solution concentrations of 0.01 *M* to 0.1 *M*.

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IZVOD

Električki proboj na elektrodi *n*-tipa GaAs

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Opisana su mjerenja električkog proboja (avalanche breakdown) na elektrodama *n*-tipa GaAs u kontaktu s deioniziranom vodom te vodenim otopinama $NaNO_3$ i NaCl. Pokazano je da potencijal proboja pada s porastom koncentracije $NaNO_3$. Izračunati su i dielektrička konstanta i električno polje u Helmholtzovom dijelu dvosloja te u sloju prostornog naboja. S porastom koncentracije elektrolita opada vrijednost konstante i polja u Helmholtzovom sloju, a raste električno polje u sloju prostornog naboja. Iako je zavisnost totalnog kapaciteta GaAs elektrode u kontaktu s elektrolitnom otopinom kompleksna funkcija, ipak se može dobro aproksimirati jednadžbom za kapacitet *p-n* spoja u čvrstom poluvodiču.

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Primljeno 10. studenoga 1971.