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Features of electrochemical processes at the boundary *p*-GaAs–HF water solution

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Abstract. Investigated in this work have been polarization curves typical for the interface *p*-GaAs–HF water solution with the concentration of fluoric acid between 1 and 10 mass.%. The shape of these curves has been compared with that following from analytical expressions obtained with account of the general equation for electrochemical kinetics. This equation was considered for partial cases of electrode potential re-distribution between the Helmholtz layers and space charge region (SCR) in semiconductor. It has been found that the shape of polarization curves corresponds to the state when exchange reactions at the above boundary for the used HF concentrations take place mainly via the valence band with participation of holes, while the electrode potential re-distributes between semiconductor SCR and the Helmholtz layer. Determined also have been the ranges of current density where transfer of current carriers takes place through the boundary p-GaAs–HF water solution (electrochemical stage), exchange currents for cathode and anode biases, coefficient of charge carrier transfer under the cathode bias.

Keywords: gallium arsenide, electrochemical process, fluoric acid, polarization curve, distribution of the electrode potential.

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1. Introduction

The mechanism of electrochemical processes at the interface semiconductor–electrolyte attracts greater and greater interest in relation of perspectives for using semiconductor electrodes in many topical areas of up-to-date technique. And among them: development of the ways for electrochemical photolysis of water and solutions of organic substances with emission of hydrogen, development of cells for solar power engineering [1, 2], creation of sensors for organic substances as well as recently-developed light-controlled potentiometric sensors based on semiconductor electrodes [3]. For a long time, processes based on electrochemical treatment of surfaces are used in technology aimed at production of semiconductor devices, for example, to form passivating coatings by using the method of anodic oxidation [4]. Semiconductor electrodes are also used to determine a number of parameters inherent to the electrode material, namely: density and nature of surface defects, profile of impurity distribution, rate of surface recombination and so on [5, 6]. A separate promising direction is to electrochemically modify the surface, which enables to create ordered 3D nano-dimensional structures on it.

2. Experimental

As an initial material, we used *p*-GaAs plates cut from the ingot grown using the Czochralski method along the direction (100), with the specific resistance 10 Ohm·cm and the surface polished using the chemical-and-mechanical method [7]. On the rear side of the plate, the ohmic contact was formed using burn-in of the In layer at the temperature 400 °C. The plate was mounted on the external surface of electrochemical cell made of organic glass. The contact with electrolyte was provided through the hole of the area 1.2 cm. We used the three-electrode cell with a counter-electrode made of chemically inactive glass-carbon. As a reference electrode, we used the chloride-silver electrode ЭВЛ-1М1 connected with electrolyte via a narrow salt bridge. To minimize ohmic losses, we took special measures (resistance of the electrode and connecting leads was reduced to the value less than 0.1 Ohm). The used electrolyte consisted of HF water solution with the acid concentrations from the range 1 to 10 mass.%. To improve wetting the GaAs plate surface, we added a small amount of ethanol into this solution. Before providing the contact between the plate and electrolyte, its surface was treated with concentrated HF for several seconds, than it was thoroughly washed out with distilled water. The electrolyte was stirred with an electromagnetic mixer.

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3. Results and discussion

In dependence on solution properties and electrode material, there can be realized two limiting cases that are described analytically by using the general equation for the kinetics of polarization at the electrochemical stage. Both cases are considered below. If the concentration of ions in the electrolyte does not exceed the value 0.01 mole/l, then the overpotential both in the Gouy layer and in the diffusion one inside the electrolyte can be neglected [8, 9]. The HF concentrations used in this work satisfy this requirement.

Since for semiconductors of *p*-type conductivity the current passes mainly through the valence band, then we shall consider the respective equations.

1. The electrode potential is concentrated in the Helmholtz layer, and relation between the overpotential in this layer and currents corresponding to anode (i_{pa}) and cathode (i_{pc}) biases are described by the Tafel equation [8, 9]:

$$\eta_a = \left[(RT/\alpha nF)\ln\left(i_{pa}/i_p^0\right)\right] = A_a + B_a \lg i_{pa}, \qquad (1)$$

where

$$A_a = -2.3\cdot[RT/\alpha nF]\ \lg i_p^0 = -[0.0592/\alpha n]\cdot \lg i_p^0,$$

$$B_a = 2.3\cdot[RT/\alpha nF] = 0.0592/\alpha n,$$

$$\eta_c = \left[(RT/\beta nF)\ln\left(i_{pc}/i_p^0\right)\right] = A_c + B_c \lg i_{pc}, \qquad (2)$$

where

$$A_c = -(0.0592/\beta n)\cdot \lg i_p^0,$$

$$B_c = 0.0592/\beta n.$$

Here, α and β denote the charge carrier transfer coefficients for anode and cathode shifts, respectively; *R* – gas constant, *F* – Faraday constant, *n* – number of electrons taking part in a single act discharge – ionization, , i_p^0 – exchange current. Thus, the process of charge carrier transfer through the interface semiconductor-electrolyte is characterized by a linear dependence $\eta - \lg i$. The same linear dependence takes place in electrochemistry of metals, since in the case of metals the potential drop occurs only in the Helmholtz layer.

2. In another limiting case, the potential is concentrated inside SCR of semiconductor. Then

$$i = i_p^0\left[1-\exp(-\eta_1\, nF/RT)\right], \qquad (3)$$

where η_1 is the overpotential in semiconductor SCR. In this case, when the cathode bias is sufficiently high, the cathode current does not change with increasing η_1 and is equal to the exchange current i_p^0, *i.e.*, such an interface possesses rectifying properties.

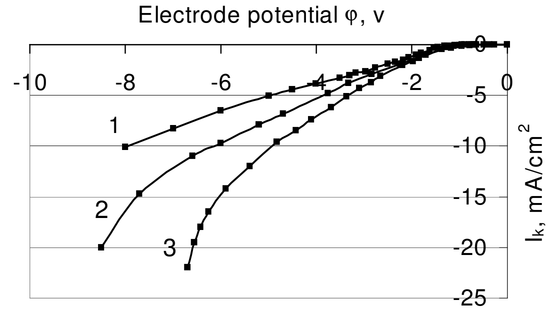

Fig. 1. Polarization curves for the interface *p*-GaAs–HF water solution (cathode range) at the HF concentrations: *1* – 1, *2* – 5, *3* – 10%.

The absence of rectifying effect signs in polarization curves for the case of cathode bias (Fig. 1) is likely indicative of the fact that some part of voltage drops inside the Helmholtz layer, *i.e.*, the electrode voltage is distributed between the Helmholtz layer and SCR of semiconductor. Although, as a rule, in semiconductors (Si, Ge) the dominant part of electrode potential is concentrated in SCR both for equilibrium and non-equilibrium states [8–10]. Partially, the drop of electrode potential inside the Helmholtz layer can be caused by the high density of surface states as well as by a definite degree of semiconductor degeneration. It was confirmed by the calculations for Ge performed in [10]. It is known that transition of non-degenerated GaAs (at least, of *n*-GaAs) occurs when the concentration of majority carriers is approximately two orders lower than that in Si or Ge. Therefore, this factor also can influence on potential distribution at the interface *p*-GaAs–HF water solution.

In our case, the potential was considered as a sum of overpotentials in the Helmholtz layer and SCR of semiconductor. Equations for the total current and total potential can be written as follows:

$$I = i_p^0\left[\exp(-\beta\eta)nF/RT - \exp(\alpha\eta - \eta_1)nF/RT\right], \qquad (4)$$

$$\eta_a = (\alpha\eta + \eta_1) = (RT/nF)\cdot\ln\left(i_a/i_p^0\right) = A_a + B_a \lg i_a, \qquad (5)$$

where

$$A_a = -(0.0592/n)\cdot \lg i_p^0,$$

$$B_a = 0.0592/n;$$

$$\eta_c = \beta\eta = (RT/nF)\cdot\ln\left(i_c/i_p^0\right) = A_c + B_c \lg i_c, \qquad (6)$$

where

$$A_a = -(0.0592/n)\cdot \lg i_p^0,$$

$$B_a = 0.0592/n.$$

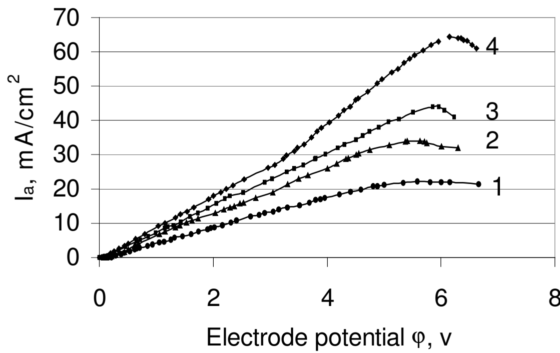

Fig. 2. Polarization curves for the interface *p*-GaAs–HF water solution (anode range) at the HF concentrations: *1* – 1, *2* – 2, *3* – 3, *4* – 5%.

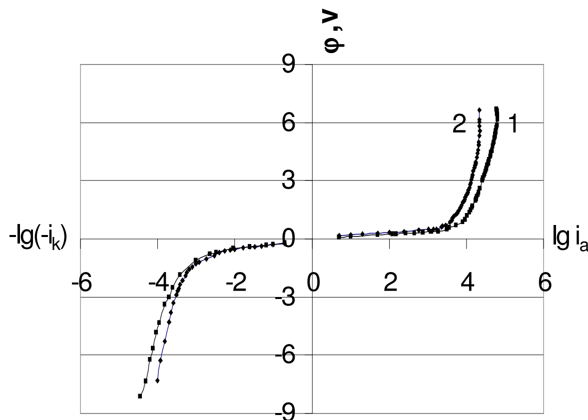

Fig. 3. Experimental polarization curves for the interface *p*-GaAs–HF water solution plotted in semi-logarithmic coordinates. HF concentration in the solution: *1* – 5, *2* – 1 mass.%.

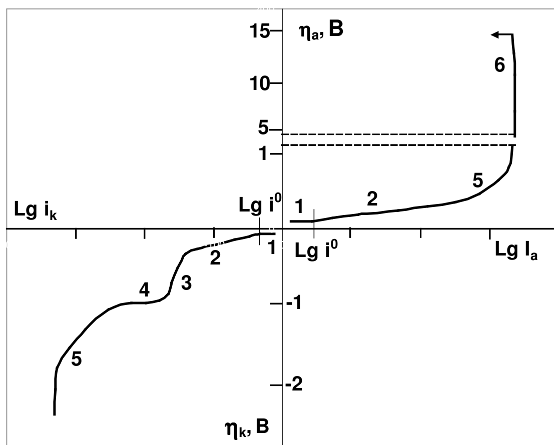

Fig. 4. Theoretical dependence of the overpotential and logarithm of current for cathode and anode polarization for semiconductor possessing *p*-type conductivity in electrolyte [9].

It seems interesting to compare experimental polarization curves (Figs 1 and 2) plotted in the form $\varphi = f(\lg i)$ (Fig. 3) with the general look of calculated polarization curves (Fig. 4) that reflect not only exchange processes but a number of the other polarization phenomena [8, 11]. In the curves of Fig. 4, one could separate the following parts corresponding to: 1) the state close to the equilibrium one; 2) transition of charges through the phase boundary; 3) state of the increasing overpotential, related with the limiting current of minority carriers inside the electrode; 4) generation of electrons on the semiconductor surface due to hydrogen atoms adsorption on the cathode; 5) sharp increase of the overpotential, which can be related with limiting diffusion current of solution particles as well as considerable ohmic drop of the voltage in the electrode; 6) decrease of the current (indicated with an arrow) related with creation of a weakly conducting film on the surface of this electrode.

As it follows from Fig. 3, the anode curves are described by the Tafel equation (see the part 2 in Fig. 4) in the area of current densities up to $2.4\cdot10^{-4}$ A/cm^2 with the slope of straight line $B = 0.11$ V and up to $3\cdot10^{-4}$ A/cm^2 with $B = 0.1$ V for the electrolyte concentrations 5 and 1%, respectively (Fig. 5). In accord with theoretical notions, B can take the value $RT/F = 0.06$ V, when the whole potential drops in SCR and $RT/\alpha F = 0.12$ V (for $\alpha = 0.5$). Here, it is implied that the potential is concentrated within the Helmholtz layer. The graphically obtained B-values have intermediate magnitude, which confirmes our assumption that the potential is redistributed between SCR of semiconductor and the Helmholtz layer in the studied system *p*-GaAs–HF water solution. The exchange current determined from the relation $i_p^0 = 10^{A/B}$ increased with the growth of the electrolyte concentration from 10^{-6} up to $7\cdot10^{-6}$ A/cm^2 is related with the limiting diffusion current of solution particles, since it depends on the concentration of reducing and oxidizing particles near the surface. With the further increase in φ-value, one can observe the decrease of current, which is accompanied by creation of a weakly conducting porous dark film on the GaAs surface (with account of the above signs, it is the film of Ga_2O) as well as by instability of current due to appearance of oxygen on the anode surface. The increase of HF concentration in the electrolyte results in shifting the polarization curves to the side of high current densities with the identical shape of curves (Fig. 2), *i.e.*, leads to intensification of polarization phenomena at this interface.

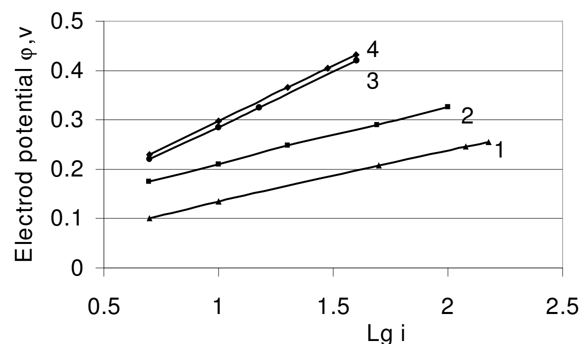

Fig. 5. Tafel curves for anode (curves *1* and *2*) and cathode (curves *3* and *4*) biases. The curves *1*, *3* – one-percent HF solution, curves *2*, *4* – five-percent HF solution.

The cathode bias of semiconductor electrodes is accompanied by hydrogen emission. The polarization curves in the studied system for i values less than $5\cdot10^{-5}$ A/cm^2 satisfy the Tafel relation (part 2), with the slope $B = 0.22$ V and the exchange current $2\cdot10^{-6}$ A/cm^2, independently of the electrolyte concentration.

In acid solutions, the reaction of H_2 emission involves participation of free electrons and hydroxonium ions H_3O^+. Juxtaposition of the B-values with those of calculations performed for various ways for the ion discharge at the cathode [9] enabled us to assume that there takes place the following reaction: $MH_a + MH_a \rightarrow 2M + H_2$, *i.e.*, the slow process dependent on the rate of transferring the minority charge carrier (electron) to the electrode surface, with the following reaction: $MH_a + MH_a \rightarrow 2M + H_2$, which is the fast process. Here, M is the electrode material, H_a – adsorbed hydrogen atom. Thus, in creation of one hydrogen atom one electron takes part ($n = 1$).

Eq. (6) enables to determine the transfer coefficient $\beta = 0.3$ as well as that for the anode bias $\alpha = 0.7$. This relationship between β and α values is responsible for asymmetry of anodic and cathodic branches in the polarization curves.

When the electrode potential is further increased, one can observe the part of slowing the growth of the current density (part 3), which is related with insufficiently pronounced limiting current of electrons in p-GaAs. The similar situation, when the limiting current depends linearly on the electrode potential, was observed in studying the cathode hydrogen emission in the case of p-Ge. It was explained by changing the state of cathode surface caused by adsorption of hydrogen atoms on it. It was ascertained that these atoms are the centers of surface recombination and can manifest acceptor properties. The change of relationship between the rate of surface recombination and the velocity of electron generation with increasing the amount of adsorbed hydrogen atoms, when the electrode potential reaches some definite value (in the considered case, it is close to 8 V), results in accelerating the current growth (part 4) [8]. The same processes of recombination-generation cause instability of the electrode voltage and current, which is observed in the part 3.

4. Conclusions

1. Exchange reactions at the boundary p-GaAs–HF water solution for the used in this work HF concentrations take place mainly due to participation of holes from the semiconductor valence band. Absence of current saturation at the cathode bias as well as the slope value in the Tafel straight lines are probably indicative of that the voltage drop in the Helmholtz layer cannot be neglected, since the electrode voltage is distributed between SCR of semiconductor and the Helmholtz layer.
2. The concentration dependence for the current density range, where the Tafel relation is valid, slope of the Tafel straight line and exchange current values allow assumption that increasing the HF concentration at the anodic bias results in intensification of carriers exchange through the phase boundary GaAs–HF water solution. The shift of polarization curves to the side of high current densities with increasing the HF concentration in electrolyte, while their look is identical, can indicate the absence of concentration dependence of the studied polarization processes.
3. At the cathode bias, the Tafel range, slope of the Tafel straight line and exchange current do not depend on the electrolyte concentration. It is indicative of the fact that polarization processes in the cathode range are defined by the properties of semiconductor. It has been ascertained that, in the process of emission of one hydrogen atom at the electrode, only one electron takes part ($n = 1$). Also determined has been the value of transfer coefficient for the cathode bias: $\beta = 0.3$.

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