Pressure Dependence of the Barrier Height in Tunnel $n$-$GaAs/Au$ Junctions

E.M. Dizhur$^1$, A.Ya. Shul’man$^2$, I.N. Kotel’nikov$^2$, A.N. Voronovsky$^1$

$^1$Institute for High Pressure Physics of the RAS, Troitsk 142090, Moscow Reg., Russia
$^2$Institute of Radioengineering and Electronics of the RAS, Moscow 103907, Russia

Abstract

The theory of tunnel current-voltage ($I$-$V$) characteristics of metal-semiconductor junctions based on the self-consistent solution of Poisson equation allows to get the Schottky-barrier height and the charged impurity concentration directly from the tunneling data. This approach was applied to the analysis of the low temperature experiments on tunneling under pressure up to 3 GPa in a piston-cylinder gauge. Here we present the barrier height versus pressure for heavily doped $n$-$GaAs$ ($N_e \sim 5 - 7 \times 10^{18} \text{cm}^{-3}$) tunnel junctions and compare the obtained pressure dependence of the Schottky barrier with known behavior of the band gap under pressure taking into account the influence of the $L$- and $X$-valleys and DX centers.

The knowledge of doping level and the potential barrier height at the interface as well as their dependence on pressure is important for studies of the semiconductor structures where the surface band bending region is essential. Our previous works $[1,2]$ showed that it is possible to carry out qualitative low-temperature tunneling spectroscopy experiments at pressure up to 3 Gpa using stand-alone high-pressure cell. The aim of this work is to extend this technique to quantitative study of band bending region in heavily-doped semiconductors under high pressure.

The pinning of the Fermi level that determines the magnitude of Schottky barrier may be attributed to metal-induced gap states $[3]$. In the particular case of the Au contact to $n$-$GaAs$ (100) plane the barrier formation was studied by photoemission spectroscopy on $N_e = 5 \cdot 10^{18} \text{cm}^{-3}$ doped material $[4]$. The barrier height $\Phi_s = 1$ eV was obtained at Au coverage beginning from 1 monolayer. This value coincides with the results obtained in $[5]$ by means of tunneling spectroscopy for the same or less doped case, however, the junctions with higher doping level indicated decreasing the barrier height. Nevertheless, too little is known about the barrier in the case of heavily doped GaAs, especially under pressure exceeding approximately 1.5 GPa, when the electron states related to above lying $L$- and/or $X$-minima might overlap with the states in $\Gamma$-minimum of the conduction band occupied by the electrons.

Obtaining the suitable data experimentally is rather a difficult task in the case of heavily-doped semiconductors, because the free carrier tunneling across the barrier prevents from implementation of the usual techniques like capacitance-voltage ($C$-$V$) or barrier photo-e.m.f. measurements $[5]$. The use of tunneling current itself instead seems to be a promising solution.

The tunneling measurements under pressure started as early as in 1963 $[6]$, and since then were sporadically used for investigations of $p$-$n$ tunnel diodes, Schottky junctions, quantum wells and so on. The only known example of such an approach to the tunnel Schottky junction...
has been demonstrated in the work [7] where $Pb/n-GaAs$ ($N_e \approx 5 \cdot 10^{18} \text{cm}^{-3}$) structures under pressures up to 1.7 GPa were studied. However, the barrier height as a function of pressure was not determined.

One should note that the interpretation of the results obtained from the tunneling measurements crucially depends on the validity of the model describing the dependence of the tunneling current on the bias voltage.

In this paper we present the results of experimental study of tunneling in Schottky junction $Au/n-GaAs(Te)$ at a doping level exceeding $N_e \approx 5 \cdot 10^{18} \text{cm}^{-3}$ under pressure up to 3 GPa.

The pressure up to 3 GPa was generated at room temperature in a stand-alone high-pressure cell of a piston-cylinder type [3] filled with 40% transformer oil and 60% pentane mixture as a pressure transmitting medium. After slow cooling down to low temperatures the cell of a piston-cylinder type [8] filled with 40% transformer oil and 60% pentane mixture as a

$\Delta T_c = -0.495P + 0.039P^2$ (the pressure $P$ in GPa) within 0.02 GPa accuracy.

The tunnel junctions with intimate $Au-GaAs$ interface were made by a method described in [10] and the stability of the samples under pressure was ensured by hf sputtering of a $SiO_2$ film approximately 200 nm thick on the $GaAs$ surface coinciding with the (100) plane. This film was deposited around a gold electrode 0.25 and 1 mm in diameter. Next, two copper contacts to the gold electrode were deposited by evaporation (see the inset in Fig. 2). Using this contact formation technology, the $I-V$ characteristics were reproducible and returned to the initial curves after releasing the pressure. Parameters of the junctions under investigation are presented in Table 1 along with two junctions studied in [7] and included for comparison.

In Fig. 1 the results of measurements are presented in terms of junction conductance $\sigma(V) = dI/dV$ at 4.2 K versus bias voltage $V$ for different pressures $P$. At $P \lesssim 2$ GPa the known drop of the tunnel conductance with pressure takes place usually ascribed mainly to an increase of the barrier height. However, at $P \geq 2$ GPa drastic changes appear in the shape and magnitude of $\sigma(V)$ curves. This effect is clearly manifested by the curve at $P = 2.5$ GPa for the sample 1 on the left panel and the curve 2.2b for the sample 2.

It is worth mentioning the observation of some instabilities and other unobvious behavior of $\sigma(V)$ at $P \approx 2$ GPa. For example, some kind of switching can occur. The curve 2.2b on the middle panel of Fig. 1 was obtained in a couple of days later than 2.2a and differs from the latter not only by value but also by the overall shape. The pressure cell was warmed up to ambient temperature but not unloaded between the runs. This is neither the pressure leakage since we control the pressure by measuring superconductivity of $Sn$ wire placed in situ, nor the sample damage since after releasing pressure the characteristics of the samples returned to the original ones. Previously the similar behavior was noted for the tunnel $p-n GaAs$ junctions at 1.8 GPa [11], but there the switching took seconds. In the case of the sample 1 at 2.15 GPa a small hysteresis in $\sigma(V)$ curves appeared as the direction of the bias sweeping was changed and, besides, $\sigma(V)$ decreased by about 10% during heating from 4.2 K to 77 K instead of usual increase.

The determination of the bulk electron density $N_e$ and the surface barrier height $\Phi_s$ from $I-V$ characteristics of Schottky-barrier tunnel junctions was suggested and experimentally tested on $n-GaAs/Au$ contacts in [10] [5]. This approach was based on the expression for tunnel current including quasi-classical formula for the barrier transparency and the exact first integral of the Poisson equation for Coulomb potential in the semiconductor. The present investigation required further modification of the theoretical description to account for possible decrease of the free electron density in $\Gamma$-valley of the conduction band under hydrostatic pressure at high doping level of $n-GaAs$ substrates.

This effect is known to exist in the case of $Si$-doped $GaAs$ at $0 \leq P \leq 1.5$ GPa and is
referred to as an appearance of DX-centers \cite{12,13}. The properties of $GaAs(\text{Te})$ are much worse understood in this respect. In \cite{14,15} the measurements of Shubnikov- de Haas effect in the bulk samples with $N_e = 7 \cdot 10^{18} \text{cm}^{-3}$ revealed no change up to $P = 1.5$ GPa. Therefore, the absence of emersion of DX($\text{Te}$) states resonant with $\Gamma$-conduction band which could capture free electrons, was claimed. On the other hand, high-pressure photoluminescence study \cite{16} revealed the appearance of a hole recombination center in the 1.5-2 GPa range. Our previous low-temperature high-pressure experiments with tunnel $n$-$GaAs(\text{Te})/Au$ junctions combined with X-ray microprobe analysis have also shown such effects (usually ascribed to the presence of active DX centers) as twice lower electron density in the bulk than that of the charged impurity density in the depletion layer of Schottky barrier and weak traces of persistent photoconductivity in tunnel $I$-$V$ characteristics \cite{1,2}. It is known for very long time that the free electron density in $\text{Te}$-doped $GaAs$ becomes less than the impurity atom density beginning from $N_e \gtrsim 5 \cdot 10^{18} \text{cm}^{-3}$ and never exceeds $10^{19} \text{cm}^{-3}$ being up to two times less than total $\text{Te}$ concentration \cite{17}. Nevertheless, no firm information is available up to now about the energy position of DX($\text{Te}$) level in $GaAs$, its dependence on pressure, free carrier density, etc. \cite{15,18}.

Besides above-mentioned problems, at high pressure limit of the present investigations a possibility existed to encounter the free electron transition from $\Gamma$-valley to subsidiary $L$- and/or $X$-valleys of the conduction band.

To take into account the possible difference between bulk free electron density in $\Gamma$-valley and charged impurity density in the depletion layer within the scope of the theoretical consideration, on one hand, and to avoid unjustified detailed elaboration of DX($\text{Te}$)-center model, on the other hand, the following assumptions were accepted:

1. Only $\Gamma$-valley free electrons take part in tunneling process forming the tunnel current since these electrons have the smallest effective mass and the lowest barrier height.

2. In the high electric field of the Schottky barrier all electrons possibly captured by any kind of traps should be released due to the tunneling ionization. As a result, the density of the positive charge in the depletion layer may be inhomogenous and may differ from the bulk free electron density. According to the investigations of deep impurity-center tunneling ionization by DC and terahertz range electric field \cite{19} the characteristic value of the field should be of order of $10^5 \text{V/cm}$. Due to the exponential field dependence of the ionization rate deep levels are supposed to be totally emptied in the region with electric field of comparative or higher magnitude. The electric fields in Schottky barrier can even exceed such values. Thus, the simplifying suggestion has been accepted that in the depletion layer the border between the region with partially ionized centers and totally ionized ones is very sharp and may be described as a step-like discontinuity in the charged impurity distribution.

The data treatment procedure is based on the expression for the density of tunnel current that may be written as:

$$I (V, T) = \frac{e m_c}{\pi \hbar^2} \int_0^\infty dE \left[ f (E, T) - f (E + eV, T) \right] \int_0^\varepsilon dE_\| D (E, E_\|, V) .$$  \hspace{1cm} (1)

Here $f(E, T)$ is the Fermi distribution function with temperature $T$, $E$ is the electron energy, $E_\| = (\hbar k_\|^2/2m_c)$, $k_\|$ is the electron wave vector along the junction plane, $m_c$ is the electron effective mass at the bottom of $\Gamma$-valley of the conduction band, $V$ is the bias voltage. The quasi-classical expression for the barrier transparency $D$ in Franz two-band approximation can be presented in the form

$$D (\varepsilon, E_\|, V) = \exp \left(-\frac{2\sqrt{2m_c \mu_F} L_s}{\hbar} \int_{\varepsilon}^{\phi_F} \frac{d\psi}{d\psi/dx} \sqrt{(\psi - \varepsilon)[1 - (\psi - \varepsilon)/\varepsilon_T] + \varepsilon_\|} \right) .$$  \hspace{1cm} (2)
where all variables denoted by small symbols in the integrand are in dimensionless form, i.e. the total energy \( \varepsilon \) and the barrier potential \( \psi \) are normalized by the characteristic energy \( \mu_F^0 = \hbar^2 k_F^2/2m_e \), and spatial coordinate \( x \) is normalized by the characteristic length \( L_s = \sqrt{\mu_F^0}/8\pi\varepsilon^2N_e \). The other quantities denote: \( k_F = (3\pi^2N_e)^{1/3} \), \( \mu \) is the Fermi energy of electron plasma in the semiconductor, \( \varphi_0 = \varphi_s + \mu - eV/\mu_F^0 \) is the band-bending height at the semiconductor-metal interface, \( \epsilon_\Gamma \) is the band gap for \( \Gamma \)-valley, and \( \kappa \) is the low-frequency dielectric constant of the semiconductor.

It is necessary to note the importance of exact integration over \( \varepsilon_\parallel \) in Eq. (1) because the Schottky barrier becomes very thin at such high electron densities. It was also necessary to include the exchange potential in highly degenerate electron gas into the consideration for correct description of the shape of the barrier potential and, therefore, the tunnel \( I-V \) characteristics over the bias region of the order of Fermi energy \( \mu \approx 150 - 200 \text{ meV} \) in our samples. The details of exact calculation of Eq. (2) for the transparency with account for the self-consistent solution of the Kohn-Sham and Poisson equations may be found in \[20\]. Here the further generalization was made to account for the two-band energy spectrum of electrons.

Due to the complicated situation with the origin of the distinction between the free electron and impurity atom concentrations discussed above, the following simplified approach was accepted. In the bulk of the semiconductor the neutrality condition requires that the electron density \( N_e \) should be equal to the positive charge density \( N_+ \). This constant value is denoted by \( N_0 \) to distinguish it from the variable densities \( N_e(x) \) and \( N_+(x) \) depending on the spatial coordinate \( x \) (see Fig. 2). Inside the depletion layer the high barrier electric field may give rise to additional ionization of impurity atoms by the tunneling process and hence to the increase of the positive charge density.

Thus, beside the \( N_0 \) and the surface potential \( \Phi_s \) the maximum density of ionized impurity atoms in the depletion layer and the electric field \( E_{cr} \) below which the density of charged ions is equal to that of free electrons have been chosen as fitting parameters. In other words, the Fermi energy \( \mu \) of electrons in \( \Gamma \)-valley and the density ratio \( N_+/N_0 \) of ionized impurity atoms in the high-field region of the barrier were also considered as free parameters to be determined by fitting procedure. This is the main difference of the present approach from that developed in \[5\].

The experimental data were fitted to the model using known pressure dependence of the energy gap \( E_\Gamma = 1.514 + 10.8 \cdot 10^{-2}P \) (\( P \) is in GPa, \( E_\Gamma \) is in eV) \[21\], the dielectric constant \( d\kappa/dP = -0.0881/\text{GPa} \) \[22\] and assuming the pressure dependent electron effective mass at the bottom of \( \Gamma \)-valley in the form \( m_e(P) = m_e(0)(1 + \Delta E_\Gamma(P)/E_\Gamma) \). A good coincidence of the measured and calculated \( I(V) \) curves was attained using a minimum least square four-parameter fitting. Even the differential resistance turned out well fitted, except for the immediate vicinity of zero bias for the highest pressures, where a finer structure is revealed (see, for example, the right panel in Fig. 1).

It is seen from the Table 1 that at \( P = 0 \) the \( N_+/N_e \) ratio differs from unity for all the samples with \( N_e > 5 \cdot 10^{18} \text{cm}^{-3} \). The corresponding magnitudes of the characteristic electric field for tunnel impurity ionization turned out really well above \( 10^5 \text{ V/cm} \) as it was suggested. Thus, our results point out that in heavily-doped GaAs(\( Te \)) the density of the positive impurity charge inside the barrier region is remarkably larger than the free electron density in the bulk. Fig. 2 shows an example of the electron and charged impurity distributions in Schottky barrier for zero and some negative biases as they have been self-consistently calculated for values of the respective parameters corresponding to the sample 1 at \( P = 0 \). This implies that not all the impurity atoms in the bulk of heavily-doped GaAs take part in supplying free electrons even at \( P = 0 \). The similar results have been obtained at \( P > 0 \) for all the junctions, including sample 2.
The variation of the Schottky-barrier height $\Delta\Phi_s(P)$ calculated by the above described way is presented in Fig. 3. and Fig. 4. shows the pressure dependence of the measured and calculated zero-bias resistance of the junctions. Both the calculated $\Delta\Phi_s(P)$ and the measured $\log(R_0(P))$ grow slower with $P$ than it is predicted by the equality $\Delta\Phi_s(P) = \Delta E_T(P)$ observed in [7] using $C$-$V$ measurements on lightly doped junctions. Moreover, there is a sharp drop of the both quantities at the pressure $P > 2.1$GPa. This drop together with the distortion of $\sigma(V)$ curves seen in Fig. 1 can indicate some changes in the Schottky-barrier shape due to a redistribution of impurity charge in the depletion layer and/or a change in Fermi level pinning mechanism at the semiconductor-metal interface. The temporal instability of the junction characteristics observed in this range of the pressure (in particular, see the above discussion of curves 2.2a – 2.2b in Fig. 1) may be responsible for different pressure dependence $\Delta\Phi_s(P)$ in the case of the sample 3.

The pressure dependence of the Fermi energy of electrons in $\Gamma$-valley for all the samples under study is shown in Fig. 5 as it was calculated from the found $N_e$ values. It turned out much more regular in comparison with $\Delta\Phi_s(P)$ dependencies in Fig. 3 and allows to see the strong enhancement of the electron concentration in the case of sample 1 at $P = 2.15$ GPa. The similar enhancement takes place in $\Delta\Phi_s(P)$ for this junction. It is of interest to note that just in this pressure range the crossing of energy position of $L$- and $X$-minima should occur as can be seen from band diagram in Fig. 5.

Preliminary conclusions may be described as follows:

1. The position of the Fermi level at metal-semiconductor interface is shifted closer to the middle of the band gap at $N_{T_e} > 5 \times 10^{18}$ cm$^{-3}$ resulting in some decrease of Schottky-barrier height and its pressure dependence.

2. After the crossing of energy position of $L$- and $X$-minima takes place the pressure dependence of the barrier height and the tunnel junction resistance changes its slope from positive to negative.

3. Right in the region where the band minima crossing occurs the most explicit temporal instability of tunnel $I$-$V$ characteristics takes place.

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### Table 1. Samples Data

| Identity | S1 | S2 | S3 | S4 | GS4[6] | GS5[6] |
|----------|----|----|----|----|--------|--------|
| Legend   | ▲  | ●  | ▼  | ■  |        |        |
| Plane    | (1 0 0) | (1 0 0) | (1 0 0) | (1 0 0) | (1 1 1) | (1 1 0) |
| Treatment in UH Vacuum | Thermocleaning | Ion bombardment | Cleavage |
| $N_e$, $10^{18}$ cm$^{-3}$ | 6.59 | 4.53 | 8.92 | 5.97 | 5.45/5.29** | 5.45/7.05** |
| $R_0$(P=0), Ohm | 21.7 | 3.92 | 21.8 | 20.3 | n/a | 12 |
| $N_d/N_e$ | 1.21 | 1.03 | 1.33 | 1.45 | - | 1.49 |
| Crit. Field, $10^5$ V/cm | 6.2 | Out of validity | 8.2 | 7.9 | - | 9.2 |
| Barrier Height, eV | 0.656 | 0.653 | 0.814 | 0.666 | 0.83*/0.81** | 0.93*/0.75** |

* By C-V measurement for similar samples with $N_e=1.45\cdot10^{15}$ and $1\cdot10^{17}$
** Recalculated with our technique

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![Image of graphs showing experimental $dI/dV$ curves versus bias voltage at different pressures. Theory trends to smooth out the fine structure near zero bias occurring at the highest pressures. The numbers over the lines represent pressure in GPa.](image)

Figure 1: Experimental $dI/dV$ curves versus bias voltage at different pressures. Theory trends to smooth out the fine structure near zero bias occurring at the highest pressures. The numbers over the lines represent pressure in GPa.
Figure 2: The reduced distributions of Coulomb potential, free Γ-valley electrons and ionized impurity density in Schottky barrier self-consistently calculated for two values of the bias voltage $V = 0$ (solid lines) and $V = -0.3 \, \text{V}$ (dashed lines). The density of positive charge in the depletion layer changes abruptly at some point inside the depletion layer, reflecting the possibly changing charge state of the impurity atoms owing to tunnel ionization process at high enough electric field. The shape of the barrier is obtained from the solution of the Poisson equation with the account for the exchange interaction. The inset shows the sample assembly.
Figure 3: The variation of the barrier height $\Delta \Phi_s$, calculated from the experimental $I(V)$ curves does not follow the pressure dependence of the band gap $\Delta E_\Gamma$, dropping down after 2 GPa. *(see Table 1 for the legend).*

Figure 4: The measured differential resistance at zero bias also depends on pressure differently than it would be if one assumes $d\Phi_s/dP = dE_\Gamma/dP$.
Figure 5: Fermi level calculated with the account for exchange interactions for electron densities obtained from the experiment. $L - X$ band crossing seems to come into play. Dashed line represents the Fermi level for $N_e = 6 \cdot 10^{18} cm^{-3}$ for reference.