

# Modeling of a Hydrogenation Process of GaAs in an Atomic Hydrogen Flow

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**Abstract** – A theoretical model describing hydrogenation process of GaAs samples in atomic hydrogen is presented. The equations set including seven differential equations describes diffusion transfer processes of hydrogen atoms and ions, formation and dissociation of hydrogen molecules and hydrogen–shallow center complexes, electrical field onset and ions and charge-carriers drift in it. Calculation results of concentration profiles evolution of hydrogen atoms, ions and molecules, active impurity, free charge-carriers, as well as concomitant variation of electric field distribution in crystal are presented. An electric field occurred during process of charge exchange between the subsystems of free charge-carriers and hydrogen atoms appear to be a reason for hydrogen ions extension in GaAs crystal depth. A complicated shape of the simulated profile of total hydrogen does qualitatively match with the experimentally obtained profiles occurred resulting from superposition of profiles of hydrogen particles of all kinds.

## 1. Introduction

The purposeful hydrogenation of GaAs structures in hydrogen plasma or atomic hydrogen flow results in passivation of shallow and deep-centers providing in a number of case an improvement of electrophysical properties of material and semiconductor devices parameters [1]. On the other hand, hydrogen penetration and dissolving in the near-surface layers of GaAs associated with etching of GaAs structures in liquid solutions or plasma-chemical deposition of dielectric layers results in degradation of characteristics of semiconductor devices [2]. One might increase hydrogenation process efficiency and avoid unwanted degradation of semiconductor structures being grounded only on correct interpretation of the mechanisms of hydrogen penetration and extension in GaAs crystal. Therewith, there is no doubt that development of theoretical models of GaAs hydrogenation is topical.

The profiles of hydrogen distribution in GaAs are known to have a complicated shape, for which interpretation several models of hydrogen diffusion in a crystal were suggested. A simplified modeling of hydrogen diffusion in GaAs was made in a number of works. So, in [3, 4] solutions of an equations set including three equations describing diffusion transfer

of hydrogen atoms as well as formation and decomposition processes of hydrogen molecules and hydrogen–shallow defect center complexes were studied. In [5], simulation of evolution of hydrogen atoms profiles, hydrogen molecules and hydrogen–shallow defect center complexes based on an analogous equations set but taking into account an influence of a diffusion barrier formed from interstitial hydrogen molecules was done. In the same work, it was suggested that hydrogen particles charge states and built-in electric field were taken into account for the more correct modeling of hydrogenation process.

In this work, on hydrogenation process modeling, the processes of formation of hydrogen ions and electric field occurrence were taken into account. Hence, the equations set occurred to be more complicated but it allowed to present the pattern of processes comprehensively at the initial stage of hydrogenation and to describe hydrogen extension in GaAs properly.

## 2. Equations Set

Concentrations  $N_i$  of the following particles are considered in the model:  $H^0$  (a hydrogen atom),  $H^+$  (positively charged hydrogen ion),  $L^-$  (negatively charged ion of active impurity),  $h^+$  (charge carrier – hole),  $HH^0$  (a hydrogen molecule),  $HL^0$  (a complex hydrogen–impurity). Equations describing changing of concentration of such particles determined by their diffusion-drift transfer and interaction have the following general form:

$$\frac{\partial N_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i \frac{\partial N_i}{\partial x} + q_i \mu_i N_i \frac{\partial \varphi}{\partial x} \right) - P_{(i \rightarrow jk)} N_i + \sum_{m=1}^n P_{(m \rightarrow ik)} N_m + \sum_{j=1}^n \sum_{k=1}^n R_{(i \leftarrow jk)} N_j N_k, \quad (1)$$

where indexes  $i, j, k$  determine particle type;  $t$  is time counted off from hydrogenation start;  $x$  is a coordinate counted off from the crystal surface;  $D_i, \mu_i, q_i$  are diffusion coefficient, mobility and charge of a particle  $i$ ;  $\varphi$  is electric field potential;  $P_{(i \rightarrow jk)}$  is a rate coefficient of generation of particles  $j$  and  $k$  under dissociation of a complex particle  $i$ ;  $R_{(i \leftarrow jk)}$  is a rate coefficient of generation of complex particles  $i$  under junction of the particles  $j$  and  $k$ .

Similarly to [5], the coefficients of hydrogen atoms and ions are supposed to be dependent on con-

centration of all the  $n'$  particles capable to occupy crystal interstitials to be blocked for transportation of other particles:

$$D_i = D_{i0} \exp\left(-\frac{E_i}{kT}\right) \left(1 - \frac{1}{N_1} \sum_{j=1}^{n'} N_j\right), \quad (2)$$

where  $N_1$  is concentration of all crystal interstitials, which could be potentially occupied by diffusing atoms;  $D_{i0}$  is preexponential factor corresponding to diffusion of particle  $i$  ( $H^0$  or  $H^+$ ) on the assumption  $N_{H0} + N_{H+} + N_{HH0} + N_{L-} + N_{HL0} \ll N_1$ ;  $E_i$  is the activation energy of diffusion of particle  $i$ ;  $k$  is Boltzmann constant;  $T$  is absolute temperature.

The coefficients  $P_{(m \rightarrow ik)}$  are determined by a characteristic complex oscillatory frequency  $\nu_m$  and activation energy of its dissociation  $E_{(m \rightarrow ik)}$ :

$$P_{(m \rightarrow ik)} = \nu_{ik} \exp\left(-\frac{E_{(m \rightarrow ik)}}{kT}\right). \quad (3)$$

The coefficients  $R_{(i \leftarrow jk)}$  are determined by using the formula

$$R_{(i \leftarrow jk)} = 4\pi r_{(i \leftarrow jk)} D_{jk}, \quad (4)$$

where  $r_{(i \leftarrow jk)}$  is a characteristic radius of interaction of particles  $j$  and  $k$  with the following formation of a particle  $i$  in their diffusion motion;  $D_{jk} = D_j + D_k$  is effective diffusion coefficient of interacting particles. With expression (2) taken into account, all coefficients  $R_{(i \leftarrow jk)}$  also become functions of particles concentrations.

The full equations set is obtained by addition Poisson equation to the equations (1):

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{1}{\varepsilon} \sum_{i=1}^n q_i N_i = 0, \quad (5)$$

where  $\varepsilon$  is semiconductor permittivity.

**Boundary and initial conditions.** Suppose that in the initial moment of time the particles of only two types have nonzero concentration, these are holes and acceptors:  $N_{h+}(x,0) = N_{L-}(x,0) = L_1 = \text{const}$ . The electric field potential in  $t=0$  is anywhere supposed to be equal to zero.

The boundaries are supposed to be impenetrable for all particles types, i.e.

$$D_i \partial N_i / \partial x(0,t) = D_i \partial N_i / \partial x(l,t) = 0,$$

except for neutral hydrogen atoms:

$$D_{H0} \partial N_{H0} / \partial x(0,t) =$$

$$= j_0 [N_{H0}(0,t) + N_{H+}(0,t) + N_{HH0}(0,t) + N_{HL0}(0,t)]$$

for the point  $x=0$ . Here the parameter  $j_0$  is density of hydrogen flow penetrating material from the outside on the condition that all the interstitials are free. The size of total calculation coordinate domain  $l$  was se-

lected equal to  $10 \mu\text{m}$ , being rather greater than characteristic size of hydrogen penetration area and electric field. The conditions laid down for electric field potential are  $\varphi(0,t) = \partial \varphi / \partial x(l,t) = 0$ .

**Equations parameters.** In the presence of a lot of the formal parameters in the equations (1) one ought define their significance allowing presence of no more than two free parameters. A part of parameters are supposed to be equal to zero due to absence of the corresponding processes. Other coefficients were taken from the literature data available.

In accordance with [7], hydrogen molecules formation is supposed to occur by three reactions  $H^0 + H^0 \rightarrow HH^0$ ,  $H^0 + H^+ \rightarrow HH^0 + h^+$  and  $H^+ + H^+ \rightarrow HH^0 + 2h^+$ , and formation of impurity-hydrogen complexes by the reactions  $L^- + H^+ \leftrightarrow HL^0$  and  $H^0 + L^- + h^+ \leftrightarrow HL^0$ .

In GaAs, active impurity particles and hydrogen-impurity complexes are considered immobile, and hydrogen molecules immobile and thermostable (under typical hydrogenation temperatures the reactions of molecules dissociation are absent) [3, 4]. That is why the values  $D_{L-}$ ,  $D_{HH0}$ ,  $D_{HL0}$ ,  $P_{(HH0 \rightarrow H0 H0)}$ ,  $P_{(HH0 \rightarrow H0 H+)}$  and  $P_{(HH0 \rightarrow H+ H+)}$  were supposed to be equal to zero.

Due to major mobility of charge-carriers the reaction  $H^+ \leftrightarrow H^0 + h^+$  is hardly accented to ions formation. In these conditions selection of degradation parameters  $\nu_{H h+}$  and  $E_{(H+ \rightarrow H0 h+)}$  in a wide range of values does not effect on the end result that is confirmed by calculations.

Important parameters for calculation of active impurity profiles are  $P_{(HL0 \rightarrow L- H+)}$  and  $R_{(HL0 \leftarrow L- H+)}$ . In our calculations were used the data on acceptor  $Zn_{Ga}$ :  $\nu_{ZnH} = 5 \cdot 10^{13} \text{ s}^{-1}$  and  $E_{(ZnH \rightarrow Zn, H+)} = 1.25 \text{ eV}$  [8]. Characteristic radii of interaction of all the particles forming complexes just like in [3, 4] were supposed to be equal to  $r_{(HL0 \leftarrow L- H+)} = r_{(HH0 \leftarrow H0 H0)} = r_{(HH0 \leftarrow H0 H+)} = r_{(HH0 \leftarrow H+ H+)} = r_{(H+ \leftarrow H0 h+)} = 10^{-8} \text{ cm}$ , that by order of magnitude corresponds to interatomic distances.

Parameters of hydrogen atoms diffusion are mostly ambiguous. According to theoretical estimation of [6], an effective barrier for  $H^+$  particle motion in p-type GaAs is equal to  $0.46 \text{ eV}$ . Experimentally, there are values of activation energy of diffusion coefficient in p-GaAs from  $0.37 \text{ eV}$  [6] to  $1.13 \text{ eV}$  [3]. These parameters were assumed as free parameters in the equations set, and as initial values  $D_{H0} = 0.01 \text{ cm}^2 \cdot \text{s}^{-1}$  and  $E_H = 1.12 \text{ eV}$  were accepted. Diffusion coefficients of neutral and charged hydrogen were supposed to be equal. Drift mobility of hydrogen ions was found from Einstein ratio  $\mu_{H+} = q_{H+} D_H / kT$ .

For definition of holes mobility in GaAs a dependence  $\mu_{H+} = \exp(18.45 - 2.2 \cdot \ln(T)) \text{ cm}^2 / (\text{V} \cdot \text{s})$  approximating the known experimental data [10] was used, and the Einstein ratio was taken for definition of holes diffusion coefficient.

Theoretical studies, in particular the studies of [6], testify that hydrogen in a doped semiconductor ap-

appears as a compensating impurity but not a trap for charge-carriers. Since recombination time for the majority charge-carriers in semiconductors and charge-carriers released by hydrogen is negligible, charge acquisition by a hydrogen atom may be considered as hole capture. The corresponding coefficient in this process defined by the formula (4) was received as  $R_{(H+\leftarrow H_0 h+)} = 4\pi r_{(H+\leftarrow H_0, h+)} D_{h+}$ .

### 3. Calculation Results and Discussion

Aimed at comparative analysis of behavior of various particles,  $N_i$  particles profiles in depth, values of doze

$$S_i = \int_{x=0}^l N_i(x, t) dx,$$

for  $l_i$ , particles corresponding to  $L_l/2 = 5 \cdot 10^{15} \text{ cm}^{-3}$  concentration were calculated.

**Hydrogen.** Fig. 1,a presents the plots of the early stage of concentration profiles evolution for hydrogen atoms, ions and molecules ( $t = 300 \text{ s}$ ). The summarized calculated profiles of the total hydrogen and experimentally obtained profiles by SIMS [11, 12, 13] are similar. This testifies that all three types of hydrogen particles take part in hydrogen profile formation. The molecules containing the main hydrogen amount are mainly concentrated in the near-surface crystal area. Since the first seconds of hydrogenation the surface layers of crystal appear to be saturated utterly with molecules, and the molecules profile is rather slowly moving in material depth. Of all the hydrogen particles mostly dynamic are ions – the rapid extension of such particles in crystal depth is determined not only by diffusion but also by drift in electric field. The hydrogen atoms stand intermediately both by the maximal concentration value and by movement rate of the profile edge.

In the most of experimental works it is noted that movement of hydrogen profile edge corresponds to diffusion transfer being dependent on  $t$  as  $l_{H^+} \sim t^{1/2}$ . From Fig. 2,a it is seen that in the course of the total calculated time of hydrogenation a coordinate of profile edge of hydrogen ions (which is by essence is the profile edge of the total hydrogen) is displaced in accordance with the same law  $l_{H^+} \sim t^{1/2}$ . Nevertheless the ratio  $(l_{H^+})^2/t$  appears to be by an order of magnitude more than hydrogen diffusion coefficient taken for calculations. That means that despite diffusion-like movement of profile edge of hydrogen concentration the basic contribution in hydrogen transfer during the early hydrogenation is given by ions drift under electric field but not diffusion of ions or atoms.

With the given flow density of penetrating hydrogen atoms saturation of the near-surface interstitials by molecules occurs within fractions of a second. At that, entry of atoms from the external flow is sharply reduced, and atomic hydrogen doze in GaAs becomes decreased (Fig. 2,b). A decrease in the doze of neutral atoms may be explained by practically irreversible

reactions turning them in ions and molecules in the conditions, when interstitial molecules block entry of atoms through the surface of crystal.

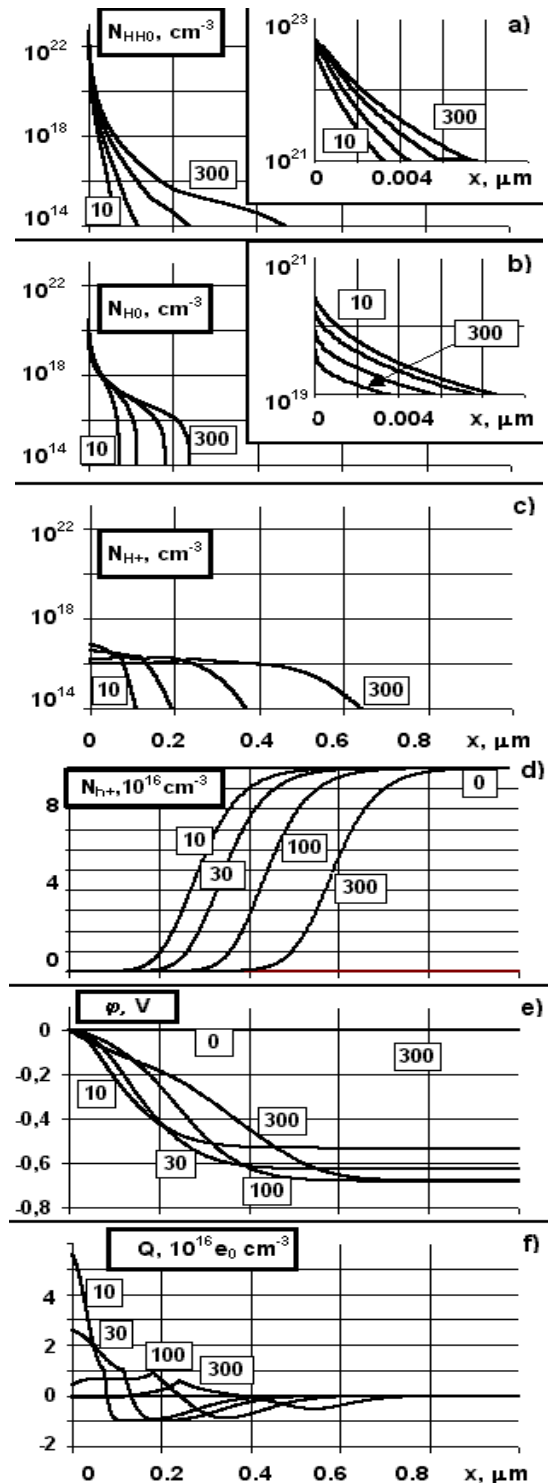


Fig. 1. Development of profiles concentration of hydrogen molecules (a), hydrogen atoms (b), hydrogen ions (c), holes and passivated impurity (d), and variation of electric field potential distribution (e) and charge density (f) for the instants of 10, 30, 100, and 300 s. Temperature is 250 °C. Doping level is  $L_1 = 10^{16} \text{ cm}^{-3}$ . The initial density of atomic hydrogen flow is  $j_0 = 10^{15} \text{ cm}^{-2} \cdot \text{s}^{-1}$ .

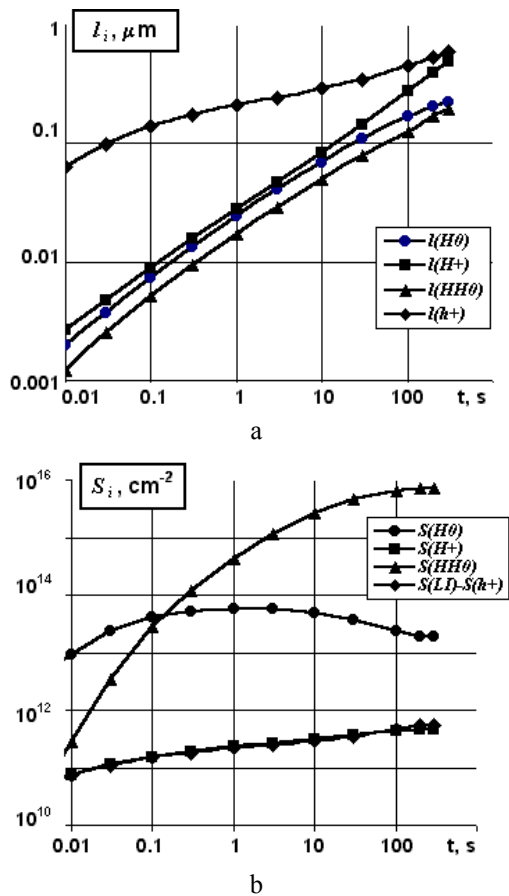


Fig. 2. A dependence of position of concentration profile edge (a) and particles specific doze (b) on hydrogenation time

**Holes and electric field potential.** Distributions of holes concentration (Fig. 1,b), charge density (Fig. 1,d) and electric field potential (Fig. 1,c) are interconnected. At the first instants the atoms entered a crystal they actively capture the holes to form a dense layer of positive ions and zone of holes depletion with an excessive negative charge of acceptors (double layer). Since the profile edge of holes concentration is shifted in crystal depth at the rate somewhat less than that of ions transfer, the profiles of holes and ions concentration gradually become closer, that results in compensation in negative space charge of acceptors and a decrease in electric field strength in a double layer. The corresponding shift and degradation of the double electric layer boundary is shown in Fig. 1,d). The gradual decrease in electric field strength leads to decreasing of the average velocity of ions motion and graded junction from drift to diffusion transfer of particles.

**Hydrogen-impurity complexes.** The calculations made with the use of the parameters taken from the literature available have shown that in the process of hydrogenation formation of hydrogen-acceptor do not occur, i.e. concentration of the active impurity keeps everywhere at the level close to the initial concentration  $L_1$ . However, a decrease in holes concentration in the near-surface layer of a semiconductor is observed.

The resulting profile of holes is similar to the profiles of charge-carriers being measured experimentally by using C-V method and which are often identified with active impurity profiles. From the analysis of calculation results it follows that the reason for impurity passivation absence is low probability of hydrogen ions and atoms trapping by acceptors as well as the high probability of dissociation of hydrogen-acceptor complexes.

The calculations have shown that it is possible to observe efficient passivation of acceptors at hydrogenation temperature of about  $250^\circ\text{C}$  and hydrogenation time of  $\sim 10^3$  s only at the parameters  $r_{H+L^-} \geq 5 \cdot 10^{-7}$  cm and  $E_{HL0} \geq 1.7$  eV. With the lower values of activation energy, achievement of concentration of hydrogen-impurity complexes at the level of  $\sim L_1$  is impossible at any duration of hydrogenation process.

Figures 3 and 4 show calculation results obtained at artificially increased values of trapping radii  $r_{H+L^-} = 5 \cdot 10^{-6}$  cm and activation energy of complex degradation  $E_{HL0} = 3$  eV. It is important to note that even at such great values of parameters corresponding to fully appropriate conditions for complexes hydrogen-impurity to form, the primary factor making effect on formation of holes profile keeps to stay ions formation process. After some time passed only accumulation and extension of hydrogen-impurity complexes in the crystal depth does occur. Formation process of complexes  $H^+ + L^- \rightarrow HL0$ , in the course of which ions do vanish, does not lead to charge transfer, and that is why it does not effect much on the field distribution and evolution of profiles of another particles, holes profile including. If in the early hydrogenation the vanished holes doze was equal to the doze of hydrogen ions, in the course of passivation process development such a doze approaches to the value of complexes doze (Fig. 4,b).

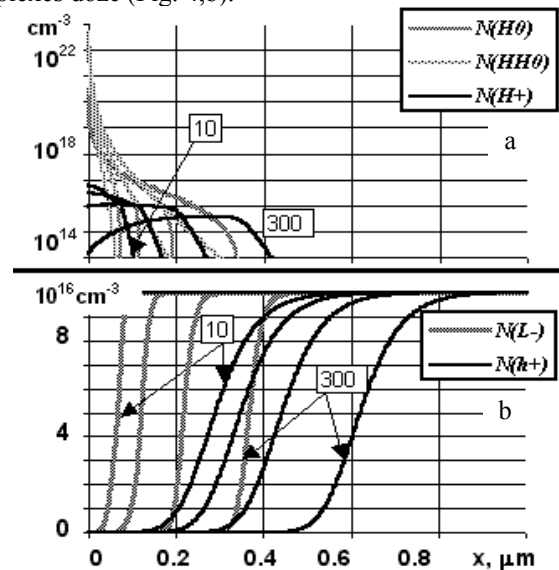


Fig. 3. Evolution of concentration profiles of molecules, atoms, and ions of hydrogen (a), holes and passivated impurity (b) under the parameters:  $r_{H+L^-} = 5 \cdot 10^{-6}$  cm and  $E_{HL0} = 3$  eV

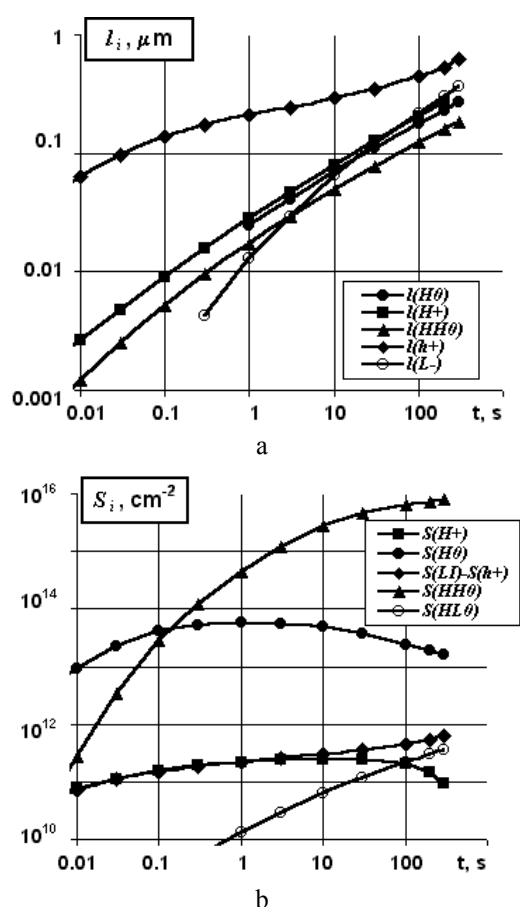


Fig. 4. Evolution of concentration profiles of molecules, atoms, and ions of hydrogen (a), holes and passivated impurity (b) under the parameters:  $r_{H+L-} = 5 \cdot 10^{-6}$  cm and  $E_{HL0} = 3$  eV

The phenomena described above which relates to formation of electric field and movement of charged particles under it, take place at temperature of 250 °C within the time of  $\sim 10^3$  s (Fig. 2,a), that is commensurable with the typical values of hydrogenation time. At the lower temperature values and/or lower densities of atomic hydrogen flow, that period of time becomes essentially increased. The given calculation shows that during this time it is impermissible to identify distribution profiles of holes and active impurity. This ought to be taken into account on interpretation of experimental data obtained by using the method of C-V-measurements.

#### 4. Conclusions

1. Taking into account of ions drift, diffusion of hydrogen ions and atoms, as well as formation of a near-surface layer having a high concentration of interstitial molecules of hydrogen allows obtaining of calculated profiles of the total hydrogen in GaAs similar by their form to the experimentally obtained profiles.

2. In the course of a long hydrogenation time the built-in electric field has an active influence on distribution profile of particles concentration.

3. In the first stages of hydrogenation formation of holes is determined by formation of hydrogen ions. In the course of time formation of holes profiles is joined by impurity passivation process.

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