Modeling of Hydrogenation Process of GaAs: Relaxation Stage

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Abstract — Relaxation processes after hydrogenation of gallium arsenide are investigated by numerical calculations. Is shown, that the level of dopant passivation and resulting profiles of passivated dopants depend not only on hydrogenation parameters, but also on a regime of decreasing of sample temperature after hydrogenation process.

In [1] we presented theoretical model describing hydrogenation process of GaAs under atomic hydrogen flow and results of numerical calculations based on this model. The evolution of profiles of hydrogen particles (atoms, ions and molecules), active impurity, free charge carriers concentrations, and evolution of electric field distribution during hydrogen penetrating into the semiconductor were studied. The calculations have shown, that the formation of complexes hydrogen — acceptor (passivation of the impurity

by hydrogen) is slight during hydrogenation. Concentration of active impurity remains at a level, close to value of its initial concentration L_I. The reason to this is that the diffusion of hydrogen in the semiconductor is activated only at those temperatures, at which the complexes impurity — hydrogen are unstable. At the same time, the literary data testify that passivated impurity contains in a large quantity in hydrogenated semiconductors [2].

The decreasing of temperature of the semiconductor after interruption of heating and exterior flow of hydrogen atoms may be realized only during some long period of time, which defined by technological features of concrete experiment. Therefore, there is a basis to assume, that stage of temperature decreasing is decisive in passivation of the basic quantity of the
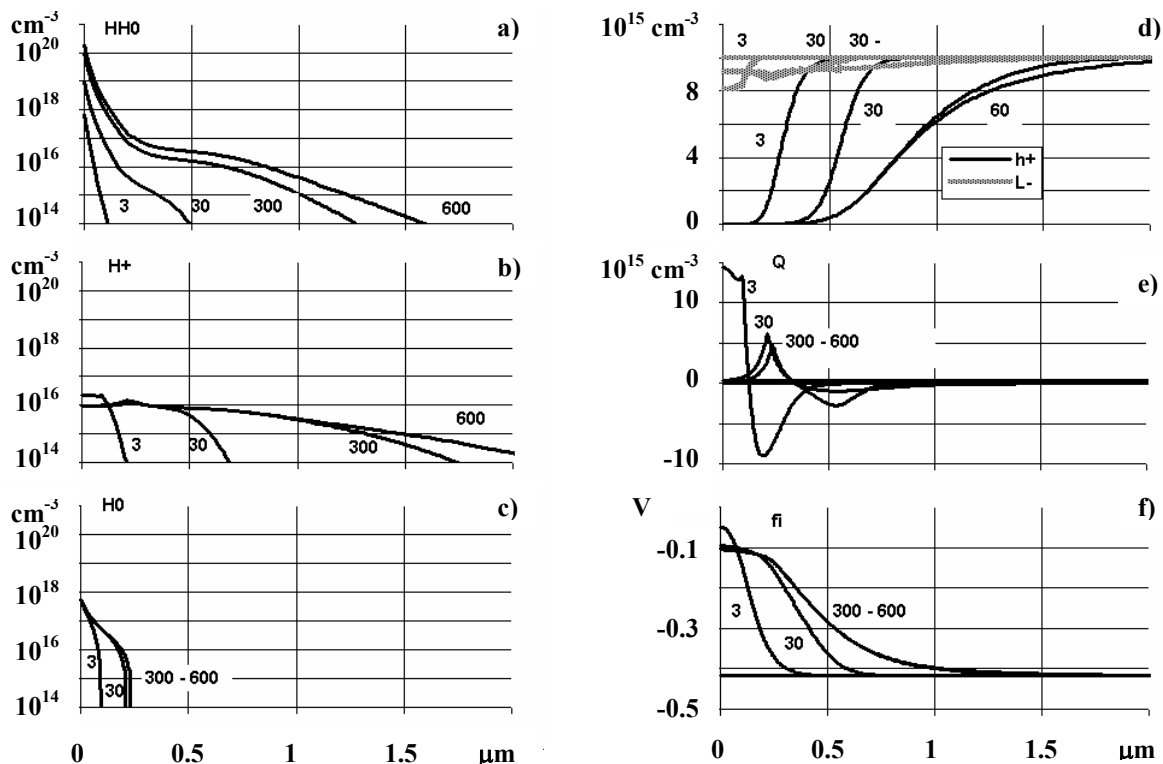

Fig. 1. The evolution of distributions of: a) hydrogen molecules, b) hydrogen atoms, c) hydrogen ions d) holes and active impurity, e) space charge (number of the elementary charge), f) electric potential. Hydrogenation stage. Temperature T=200 °C. Doping level $L_I = 10^{16}$ cm^{-3}. Density of the external atomic hydrogen flow $j_0 = 10^{12}$ cm^{-2}s^{-1}. Hydrogen diffusivity corresponds to the dependence $D_H = D_{SUP}(T)$. Numbers in plots — the time which passed from the beginning of hydrogenation process (in seconds)

impurity. For checkout of this assumption, the numerical calculations of the further evolution of concentration profiles of particles at this stage (which we named as "relaxation stage") were carried out. The external hydrogen atomic flow density j_0 was equated to zero. The cooling of the sample was imitated by a choice of constant temperature between room temperature and temperature of hydrogenation.

Fig. 1 presents the plots of concentration profiles of particles, distribution of electric field potential and distribution of space charge density at the various moments of hydrogenation stage (t=0−600 s). One can see, that the formation of complexes hydrogen-acceptor almost is insignificant, in spite of the fact that the value of radius of capture of hydrogen ion by impurity ion is choice equal to theoretically upper limit $r_{(HL^0 \leftarrow H+L-)} = q_0^2/(4\pi\varepsilon kT)$ (requirement of equality of Coulomb interaction energy and thermal energy), where q_0 − elementary charge; ε − permittivity, k − Boltzmann constant; T − absolute temperature. In other words, concentration of active impurity remains everywhere and anytime at a level closes to doping level L_1 at a stage of atomic hydrogen penetration.

In Fig. 2 and 3, results of calculations of the further evolution (t>600 s) of concentration profiles after the interruption of exterior atomic hydrogen flow for temperatures 100 and 150 °C are shown. From Fig. 2 (d) and 3 (d) it is seen, that a cooling of the sample provide appreciable intensify the formation of complexes $\mathbf{HL^0}$ (the disappearance of a active impurity $\mathbf{L^-}$).

At the first stage of the relaxation, the concentration profiles of hydrogen ions and charge carriers are rather stable. The transport of hydrogen ions deep into crystal and its transmutation to molecules and complexes are compensated by their producing from the residual undersurface reservoir of hydrogen atoms formed in hydrogenation stage. Passivation of an impurity does not exert direct influence on distributions of space charge and electric field. After some time the undersurface reservoir of atoms runs low, and this leads to rather sharp changes: to intensive exhaustion of ions, to changing in form of charge carriers concentration profiles and to reduce of electric field. For temperature 100 °C, this moment corresponds to ~1500 s (~900 s from moment of flow interruption), and for temperature 150 °C − to ~800 s (~200 s from moment of flow interruption). As hydrogen ions join into molecules, profiles of holes and active impurity are gradually equalized, and the concentration of an active impurity comes nearer to an equilibrium concentration (for given temperature).

The cooling of the sample can be presented as superposition of short exposures at various temperatures with their proper features of particles system evolution. Therefore, the various regimes of temperature reducing can lead to various finish states of particles.

Concentration profile of molecular hydrogen and actually defined by it concentration profile of the total content of hydrogen, practically do not vary during a relaxation period (see fig. 2, *a*, 3, *a*).
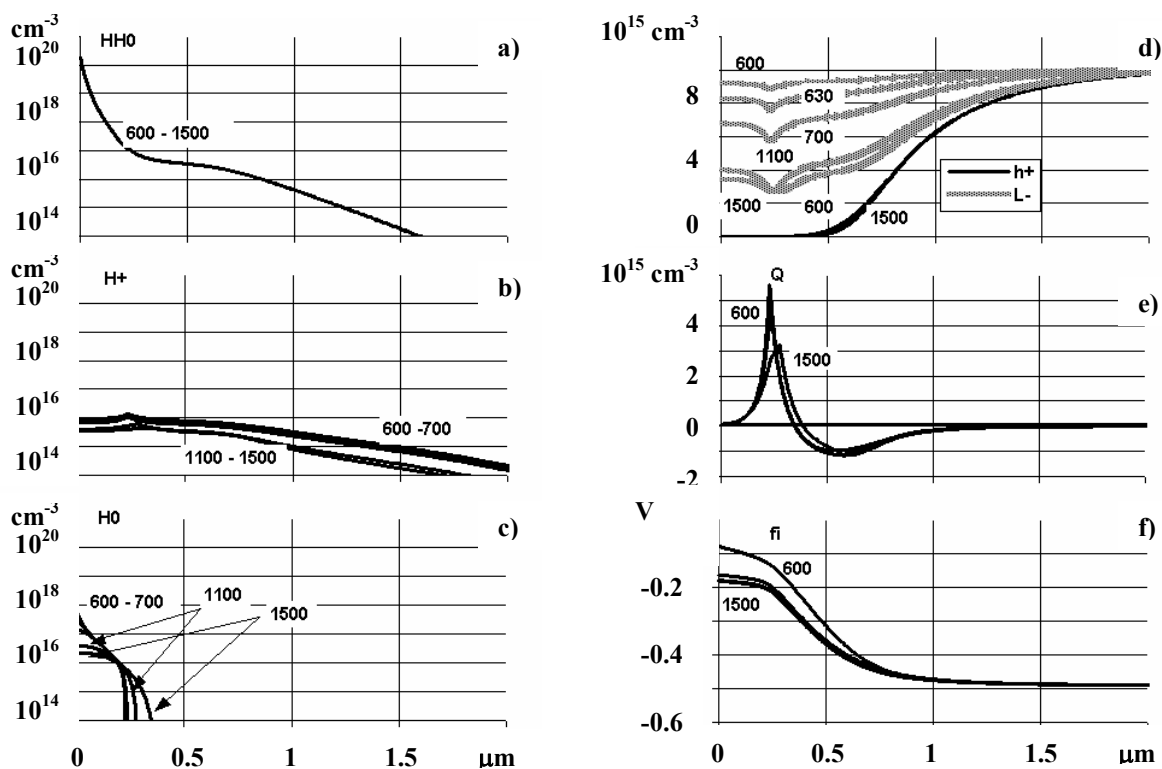

Fig. 2. The same, as in fig. 1 at subsequent relaxation stage. Temperature T=100 °C

Increase in doping level of semiconductor leads to more compact concentration profiles of particles under other identical conditions of hydrogenation (Fig. 4). This fact agrees with literary data (for example, see ref. [3]). Moreover, according calculations, at increase of a doping level, the degree of impurity passivation and rate of relaxation processes raises. The quantitative substantiation of such connections is given below.

For estimation of experimental conditions, at which optimum of impurity passivation will reached, there is no need to make numerical calculations. It is enough to examine one equation of system (1) (ref. [1]) written for concentration of complexes impurity — hydrogen, which has the most simple structure

$$\frac{\partial N_{HL^0}}{\partial t} = R_{(HL^0 \leftarrow H^+ L^-)} N_{H^+} N_{L^-} - P_{(HL_0 \rightarrow H^+ L^-)} N_{HL^0} \quad (1)$$

The first term of the right side of equation describes an interaction and disappearance of active impurity and mobile hydrogen ions under process of complexes formation. The second term describes an inverse process of complexes decay. The given equation is not unique. It is a part of many mathematical models describing hydrogenation process.

The temperature conditions must provide, on the one hand, a stability of complexes ($T < T_{MAX}$), and on the other hand must provide large diffusion mobility of hydrogen ions for intensive generation of complexes ($T > T_{MIN}$).

Therefore, one can consider that the impurity activation is appreciable, if, on the one hand, in equilibrium conditions of reactions ($\partial N_{HL0}/\partial t = 0$), condition $N_{L^-} < 0.1 N_{HL^0}$ is realized. The substitution of explicit expressions for coefficients $P_{(HL^0 \rightarrow H+L-)}$ and $R_{(HL^0 \leftarrow H+L-)}$ [1] gives an estimation of a upper bound of a temperature region, acceptable for complexes formation:

$$T_{MAX} = \frac{E_{(HL^0 \rightarrow H^+L^-)} - E_{D(H)}}{k \ln\left(\frac{v_{(HL^0)}}{0.4\pi r_{(HL^0 \leftarrow H^+L^-)} D_{(H)0} N_{H^+}}\right)}, \quad (2)$$

where $D_{(H)0}$ and $E_{D(H)}$ are parameters defining diffusivity of hydrogen atoms (ions) in expression $D_{(H)} = D_{(H)0} \exp(-E_{D(H)}/kT)$, and $v_{(HL^0)}$ and $E_{(HL^0 \rightarrow H+L-)}$ — parameters, defining the decay rate of a complexes in similar expression $P_{(HL^0 \rightarrow H+L-)} = v_{(HL^0)} \exp(-E_{(HL^0 \rightarrow H+L-)}/kT)$.

On the other hand, one can require, that the characteristic time of passivation process τ must not exceed maximal duration of experiment $\tau_{MAX} = 10^4$ s. Value of can be estimated from equation (1) too. After substitution of explicit expression for $P_{(HL^0 \rightarrow H+L-)}$ [1], one can receive an estimation of the inferior boundary of a temperature region, acceptable for complexes formation:

$$T_{MIN} = \frac{E_{D(H)}}{k \ln(4\pi r_{(HL^0 \leftarrow H^+L^-)} D_{(H)0} N_{H^+} \tau_{MAX} 0}, \quad (3)$$

Expressions (2) and (3) define boundaries of the temperature region, which provide the impurity passivation. It is possible to put an ion concentration N_{H^+} equal to a level of a doping L_I. The Table 1 re-

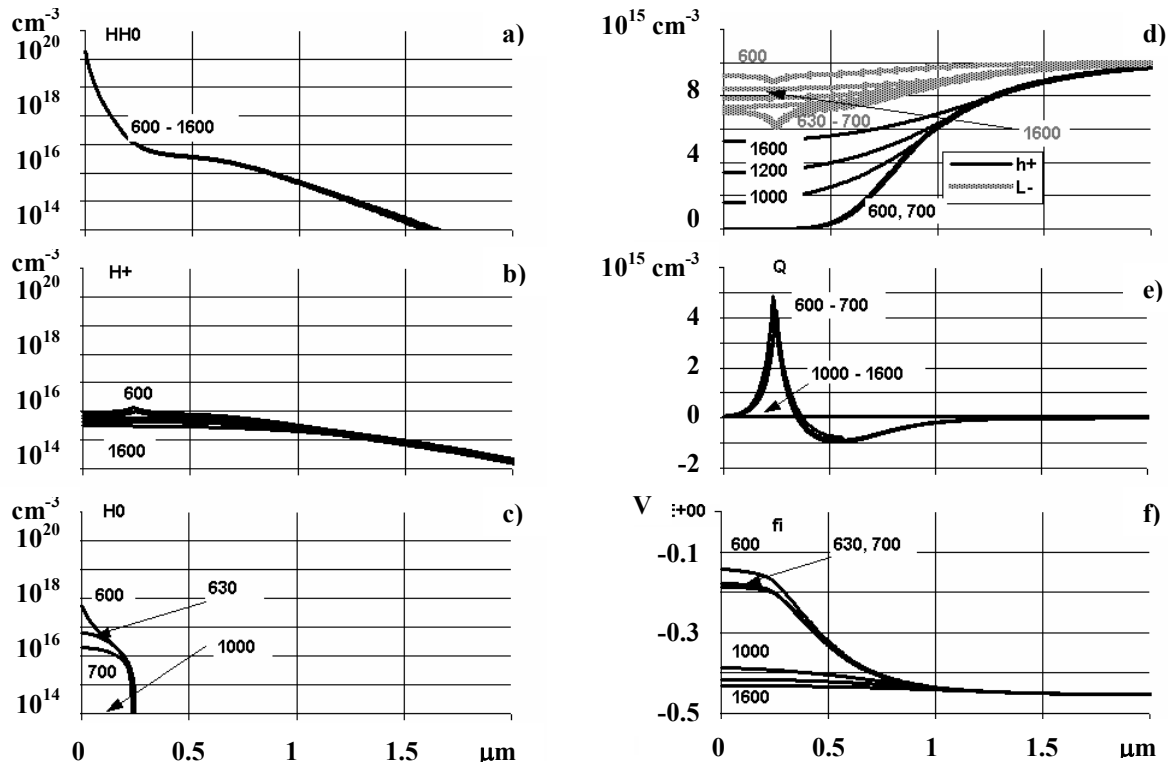Fig. 3. The same, as in fig. 1 at subsequent relaxation stage. Temperature $T = 150\ °C$
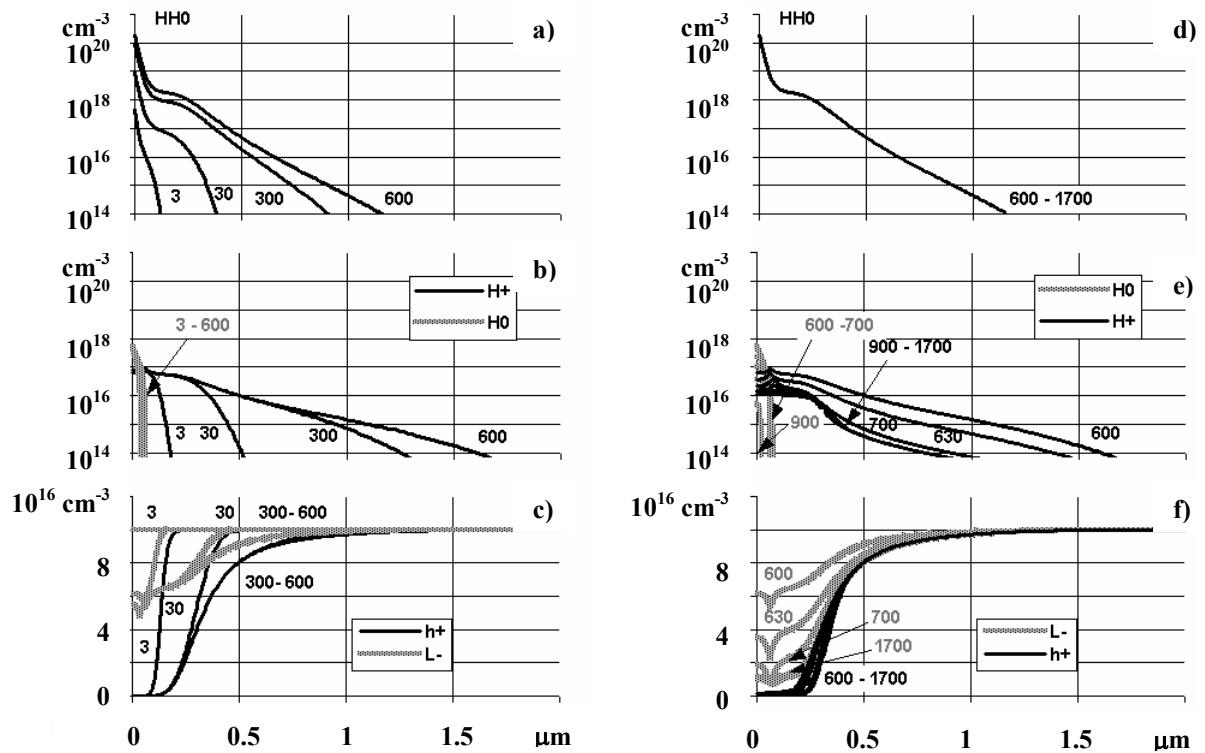
Fig. 4. The evolution of distributions of: a) hydrogen molecules, b) hydrogen atoms, c) hydrogen ions at hydrogenation stage ($L_I=10^{17}$ cm^{-3}, $T=200$ °C, $j_0=10^{12}$ cm^{-2}s^{-1}, $D_H=D_{SUP}(T)$), and same distributions d)–f) at subsequent relaxation stage at the temperature $T=100$ °C

present calculations for two published temperature dependences of hydrogen diffusivity, $D_{SUP}(T)=1.54\cdot10^{-5}$ cm^2/s·exp(-0.62 eV/kT) and $D_{INF}(T)=1.41\cdot10^{-2}$ cm^2/s·exp(1.12 eV/kT). These dependences represent, accordingly, superior and inferior limits for various experimental estimations of the hydrogen diffusivity in GaAs. Moreover two levels of doping 10^{16} and 10^{17} cm^{-3} are examined. In each cell of the table two values T_{MAX}, and T_{MIN} for each combination of parameters are given.

Table 1.

L_I		$D_H=D_{SUP}(T)$	$D_H=D_{INF}(T)$
10^{16} см$^{-3}$	T_{MAX}	364 K	113 K
	T_{MIN}	313 K	436 K
10^{17}см$^{-3}$	T_{MAX}	412 K	175 K
	T_{MIN}	284 K	378 K

From the Table 1. it is visible, that for dependence $D_H=D_{SUP}(T)$ there is a quite certain temperature region at which appreciable impurity passivation is possible. However, it is not right for dependence $D_H=D_{INF}(T)$. Thus, the dependence $D_{INF}(T)$ conflicts to the literary data (for example [2]), which confirm a possibility of appreciable passivation of active im-

purity by hydrogen. For $D_H=D_{SUP}(T)$ the table show rising of temperature region with increasing of the level of doping.

Conclusions

The numerical calculations and estimates testify that the resulting forms of concentration profiles in GaAs of particles depend not only on hydrogenation parameters, but also on regimes of decreasing of temperature after hydrogenation process. In particular, the second have strong influence on the degree of passivation of shallow impurity and on its resulting distribution.

References

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