Simulation of hydrogen diffusion and boron passivation in crystalline silicon

O I Velichko¹, Yu P Shaman² and A P Kovaliova¹

¹ Department of Physics, Belarusian State University of Informatics and Radioelectronics, 6, P. Brovki Street, Minsk, 220013 Belarus
² Scientific-Manufacturing Complex ‘Technological Center’ MIET, 5-4806, Street, Zelenograd, Moscow, 124498, Russia

E-mail: velichkomail@gmail.com (Oleg Velichko)

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Abstract
The previously developed model of hydrogen migration and reactions of hydrogen atoms with electrically active impurity is applied to simulate the hydrogen diffusion and passivation process during plasma deuteration of silicon substrates doped with boron. The calculated deuterium concentration profiles agree well over the length of the passivated region with the experimental data obtained upon treatment in hydrogen plasma at a temperature of 200 °C for 5, 10 and 15 min. On the other hand, to achieve a good fit to the abruptness of the calculated profiles between the passivated and unpassivated regions, it is necessary to suppose that the values of the parameters that describe the absorption of hydrogen interstitials by electrically active dopant atoms decrease with increase in the depth of the passivated region. For example, nonuniform spatial distributions of nonequilibrium point defects generated during plasma treatment can lead to a spatial dependence of hydrogen absorption.

Keywords: diffusion, passivation, interstitial, hydrogen, boron, silicon, solar cell

1. Introduction
The increase in the cost of traditional energy resources has been a worldwide trend over the past years. Therefore, investigation and implementation of alternative renewable energy sources are particularly urgent now. Solar cells provide such a type of promising alternative energy sources. Here, new modules based on silicon layers constitute a reliable, proven, sustainable and environmentally friendly source of energy. It is worth noting that the best crystalline silicon photovoltaic modules are 5% more efficient than the best modules based on polysilicon films [1, 2]. This is especially important for solar cells used in outer space. The treatment of
silicon photovoltaic layers in a hydrogen-containing gas plasma results in a further increase in the solar energy-to-electricity conversion ratio. All of the above-mentioned factors demonstrate the importance of elucidating the role of hydrogen in the evolution of defect-impurity systems in the near-surface region of silicon layers including passivation of dangling bonds, undesirable defects and dopant atoms. The main goal of this work is to analyze theoretical models and carry out calculations of hydrogen diffusion and hydrogen passivation of electrically active impurity atoms in silicon crystals doped with boron.

2. Model

It is well known that the hydrogen concentration profiles in silicon crystals intrinsic or low-doped with electrically active impurities have two characteristic regions: (i) a narrow high-concentration region in the vicinity of the surface and (ii) an extended ‘tail’ in the low-concentration diffusion zone (see, for example, the deuterium concentration profiles in the review of Herring and Johnson [3]). Such a form of the hydrogen concentration profiles can be explained by assuming that two different diffusion species, namely ‘slow’ and ‘fast’ diffusing species, provide hydrogenation of silicon crystals [4, 5].

In silicon uniformly doped with boron, a ‘plateau’ with a constant hydrogen concentration is formed during hydrogenation between the high-concentration region (near-surface region) and the bulk of the semiconductor [6–14]. The hydrogen concentration in the ‘plateau’ region is approximately equal to the boron concentration [6–9, 11–14]. A similar behavior of hydrogen and boron concentrations is observed after hydrogen treatment of layers implanted with boron [9, 15]. However, when a large number of hydrogen atoms are introduced into a silicon substrate due to plasma treatment, the hydrogen concentration exceeds the concentration of boron atoms [9, 15]. On the other hand, it follows from the experimental data that a distinct ‘plateau’ usually is not formed in phosphorus-doped silicon [9, 12, 13, 16]. However, the change of the deuterium concentration profile is also observed for phosphorus-doped substrates with an impurity concentration such as $1 \times 10^5 \mu \text{m}^{-3}$ and above. It is worth noting that the hydrogen penetration depth is reduced in phosphorus-doped silicon compared with intrinsic silicon [10, 13, 16] and silicon doped with boron [9]. These facts provide direct evidence that diffusivities and trapping efficiency are different for positively and negatively charged mobile species participating in hydrogen diffusion. In addition, from analysis of the experimental data [7, 9, 16], it can be concluded that precisely ‘fast’ diffusing species interact with dopant atoms and provide their passivation.

A number of models have been developed to explain hydrogen diffusion in crystalline silicon (see, for example, [3–5, 17–28]). It is supposed in the majority of the papers that hydrogen diffusion in the ‘tail’ region occurs due to migration of monatomic hydrogen species. These hydrogen interstitials are considered to be nonequilibrium and a separate equation is used to describe the diffusion of neutral (or charged) hydrogen atoms. The most comprehensive models [3, 5, 19, 22, 28] account for the simultaneous diffusion of interstitial hydrogen species in different charge states and the drift of charged hydrogen interstitials in a built-in electric field. The effective diffusion coefficient of hydrogen interstitials obtained in [3, 19, 22] is similar to the effective diffusion coefficient for impurity interstitials proposed in [29]. Various mechanisms for trapping hydrogen atoms are also taken into account. However, it is commonly supposed that one hydrogen atom passivates one boron atom because the hydrogen concentration in the passivated region is equal to the concentration of boron atoms.

The model of hydrogen diffusion which accounts for the passivation of electrically active impurity atoms that is used in this investigation was developed in [30, 31]. It is worth noting
that in contrast to other models of hydrogen diffusion (see, for example, [22]), in the model of Velichko et al [30, 31] as well as in the model of Zhang [5], the values of hydrogen diffusivity are approximated from high-temperature experimental diffusivity data obtained in [32]. Thus, the contradiction between the diffusivity data obtained for low- and high-temperature treatments (see [5] and references therein) is eliminated. References [30, 31] suppose that there are two fluxes of hydrogen atoms: 'slow' diffusing hydrogen species, responsible for diffusion in the near-surface region with a high hydrogen concentration, and 'fast' diffusing species, responsible for hydrogen diffusion into the bulk of the semiconductor in the low-concentration region of the hydrogen concentration profile. It was supposed that fast diffusion occurs due to the long-range migration of nonequilibrium interstitial hydrogen atoms in singly negative (H\(^-\)), neutral (H\(^\times\)) and singly positive (H\(^+\)) charge states. Due to the high mobility of electrons (holes), the mass action law is valid for conversions between different charge states of hydrogen interstitials. The long-range migration of hydrogen interstitials results in the supersaturation of the bulk of the semiconductor with hydrogen atoms. Therefore, it is supposed in [30, 31] that these fast diffusing species are responsible for the passivation of electrically active boron atoms due to the following reactions:

\[
\begin{align*}
A^- + H^+ & \rightarrow (AH)^\times, \\
A^- + H^\times & \rightarrow (AH)^+ + e^-, 
\end{align*}
\]

where A\(^-\) is the acceptor atom in the substitutional position, (AH\(^\times\)) is the neutral immobile ‘boron-hydrogen’ complex and e\(^-\) is the electron. Then, to calculate the total hydrogen concentration profile and the concentration profile of the electrically active boron, the following system of equations can be used:

1. the conservation law for trapped hydrogen atoms:

\[
\frac{\partial C_{\text{HTR}}}{\partial t} = \frac{k_{\text{HIC}}(\chi)}{\tau_{\text{HI}}} C_{\text{HI}}^\times(x, t) + k_{\text{HIA}}(\chi) C_{\text{HI}}(x, t) + S_{\text{HT}}(x, t) - G_{\text{HT}}(x, t),
\]

2. the conservation law for substitutionally dissolved dopant atoms:

\[
\frac{\partial C(x, t)}{\partial t} = -k_{\text{HIA}}(\chi) C_{\text{HI}}(x, t),
\]

3. the stationary diffusion equation for nonequilibrium hydrogen interstitials:

\[
-\frac{d}{dx} \left[ d_{\text{HI}}(\chi) \frac{\partial C_{\text{HI}}^\times(x, t)}{\partial x} \right] - \frac{k_{\text{HIC}}(\chi)}{\tau_{\text{HI}}} C_{\text{HI}}^\times(x, t) - k_{\text{HIA}}(\chi) C_{\text{HI}}(x, t) + G_{\text{HI}}(x, t) = 0
\]

4. the diffusion equation for slow migrating hydrogen species:

\[
\frac{\partial C_{\text{HD}}}{\partial t} = D_{\text{HD}} \frac{\partial^2 C_{\text{HD}}}{\partial x^2} + G_{\text{HD}},
\]

where

\[
\begin{align*}
d_{\text{HI}}(\chi) &= \frac{\beta_{\text{HI}} - 1 + \beta_{\text{HI}}^+}{\beta_{\text{HI}}^+ - 1 + \beta_{\text{HI}}}, \\
k_{\text{HIC}}(\chi) &= \frac{\beta_{\text{HIC}} - 1 + \beta_{\text{HIC}}^+}{\beta_{\text{HIC}}^+ - 1 + \beta_{\text{HIC}}}, \\
k_{\text{HIA}}(\chi) &= \frac{1 + \beta_{\text{HIA}}}{1 + \beta_{\text{HIA}}}.
\end{align*}
\]
\[ \chi = \frac{C - C_B + \sqrt{(C - C_B)^2 + 4n_i^2}}{2n_i}, \quad (10) \]

\[ C_{HT} = C_{HTR} + C_{HD} + C_{HI}. \quad (11) \]

Here \( C_{HT} \) is the total concentration of hydrogen atoms; \( C_{HTR} \) is the total concentration of hydrogen atoms trapped by immobile sinks and boron atoms; \( C \) and \( C_B \) stand for the concentration of electrically active dopant atoms which undergo passivation and the concentration of charged species with the opposite type of conductivity, respectively; \( C_{HI} \) and \( C_{HI^\pm} \) represent the total concentration of interstitial hydrogen atoms and the concentration of hydrogen interstitials in a neutral charge state, respectively; \( C_{HD} \) is the concentration of the slow diffusing hydrogen species; \( \chi \) is the concentration of charge carriers (holes \( p \) or electrons \( n \) for passivation of acceptor or donor impurities, respectively) normalized to the concentration of intrinsic charge carriers \( n_i \); \( S_{HT} \) and \( G_{HT} \) are, respectively, the rates of direct trapping and detrapping of hydrogen atoms introduced into the near-surface region of silicon substrate by platelets or other extended defects; \( G_{HI} \) is the generation rate of nonequilibrium hydrogen interstitials in the surface region due to the plasma treatment and dissolution of platelets or other defects which incorporate hydrogen atoms; \( G_{HI^\pm} \) is the generation rate of hydrogen atoms participating in slow diffusion; \( d_{HI} \) and \( d_{HI^\pm}(\chi) \) are the diffusivity of hydrogen interstitials in an intrinsic semiconductor and normalized concentration dependence for diffusivity of this species in a doped semiconductor, respectively; \( D_{HI} \) is the diffusivity of the slow migrating hydrogen species; \( \tau_{HI} = (k_{HI})^{-1} \) is the average lifetime of nonequilibrium hydrogen interstitials in an intrinsic semiconductor; \( k_{HI} \) and \( k_{HI^\pm}(\chi) \) are the coefficients of the absorption of hydrogen interstitials in an undoped semiconductor and the normalized concentration dependence of this coefficient in a doped semiconductor, respectively; \( k_{HI^\pm}^{\pm} \) are the coefficients of absorption of nonequilibrium hydrogen interstitials when passivation of impurity atoms occurs in the near-intrinsic silicon and the normalized concentration dependence of this coefficient in a doped semiconductor, respectively.

The empirical parameters \( \beta_{HI^-} \) and \( \beta_{HI^+} \) describe the relative contribution of negatively and positively charged hydrogen interstitials, respectively, to the total hydrogen diffusion compared with the contribution of neutral interstitials. The empirical parameters \( \beta_{HI}^{-\pm} \) and \( \beta_{HI^\pm}^{\pm} \), respectively, describe the relative absorption of negatively and positively charged hydrogen interstitials due to unsaturated traps compared with the absorption of neutral interstitials. Finally, the empirical parameter \( \beta_{HI^\pm} \) describes the relative absorption of positively charged hydrogen interstitials during the passivation of electrically active boron atoms compared with the absorption of neutral interstitials.

It is important to note that the concentration dependences \( d_{HI^\pm}(\chi) \), \( k_{HI^\pm}(\chi) \) and \( k_{HI^\pm}^{\pm}(\chi) \) are smooth and monotone functions of \( \chi \) [29]. In addition, these functions assume the form traditionally used for the presentation of effective diffusivity of substitutionally dissolved dopant atoms in processing simulation codes (see, for example, [33]). Due to these features, the system of equations (3), (4), (5) and (6) is very convenient for numerical solution. It is also worth noting that the concentration of charge carriers \( \chi \) can be calculated either from the assumption of local charge neutrality (10) or, more exactly, from the Poisson equation for electrostatic potential \( \varphi \).

The coefficient \( k_{HI^\pm}^{\pm} \) and normalized concentration dependence \( k_{HI^\pm}^{\pm}(\chi) \) describe the process of impurity atoms passivation. We consider these quantities in detail. In the paper of Velichko [29], the expression for the absorption rate of impurity interstitials \( S_{AI} \) due to their interaction with the immobile traps distributed uniformly in the bulk of the semiconductor was
obtained as follows:

\[ S_{AI} = k_{AI}^{c} C_{AI}^{\times}, \]  

(12)

where

\[ k_{AI}^{c} = \sum k_{AI}^{k} h_{AI}^{k} \chi_{AI}^{-z_{AI}^{k}}. \]  

(13)

Here \( k_{AI}^{c} \) is the effective absorption coefficient of the impurity interstitials; \( C_{AI}^{\times} \) is the concentration of interstitial impurity atoms in the neutral charge state; \( k_{AI}^{k} \) is the partial coefficient of absorption of impurity interstitials in the charge state \( k \) by immobile traps; \( z \) and \( z_{AI}^{k} \) are, respectively, the charge of the impurity atom in the substitutional position and the charge of the impurity interstitial in the charge state \( k \) in terms of the elementary charge. To obtain the effective coefficient of the absorption of hydrogen interstitials due to passivation of the electrically active boron, it is necessary to take into account that in this case, the value of the absorption rate is also proportional to the concentration of the electrically active boron \( C \) (substitutionally dissolved boron atoms represent immobile traps in the passivation process) and the negatively charged hydrogen interstitials do not interact with the substitutionally dissolved boron atoms due to the Coulomb repulsive force. By writing down expressions (12) and (13) for reactions (1) and (2) and taking into account that for the boron doped layer \( z = -1 \), \( z_{AI}^{k} = 0, +1 \), one can obtain the rate \( S_{HIA} \) and the effective coefficient of the absorption of nonequilibrium hydrogen interstitials by electrically active dopant atoms \( k_{HIA}^{c} (\chi) \) in the following form:

\[ S_{HIA} = k_{HIA}^{c} (\chi) C_{HI}^{\times} C, \]  

(14)

where

\[ k_{HIA}^{c} (\chi) = k_{HIA}^{+} + k_{HIA}^{+} h_{HIA}^{+} \chi \]  

(15)

or

\[ k_{HIA}^{c} (\chi) = k_{HIA}^{\times} (1 + \beta_{HIA}^{c} \chi), \]  

(16)

where

\[ \beta_{HIA}^{c} = \frac{k_{HIA}^{+} h_{HIA}^{+} \chi}{k_{HIA}^{\times}}. \]  

(17)

Here the empirical parameter \( \beta_{HIA}^{c} \) describes the relative contribution of positively charged hydrogen atoms to boron passivation compared with the contribution of neutral ones.

We consider the case of near-intrinsic silicon \( C < n_{i} \). In that case, \( \chi \approx 1 \) and

\[ k_{HIA}^{c} (\chi) = k_{HIA}^{\times} + h_{HIA}^{+} \chi = k_{i}^{HIA}, \]  

(18)

where \( k_{i}^{HIA} \) is the coefficient of absorption of nonequilibrium hydrogen interstitials by electrically active dopant atoms in the low-doped (near-intrinsic) silicon.

Using the quantity \( k_{i}^{HIA} \), we can present the effective coefficient of absorption of nonequilibrium hydrogen interstitials due to passivation of boron atoms in the more convenient form (9).

3. Simulation of hydrogen diffusion and boron passivation

To illustrate the efficiency of the model developed in [30, 31] for describing the hydrogen diffusion and passivation of boron atoms, the simulation results for the experimental data of
Tong et al. [11] are shown in figures 1–5. In [11], deuteration was carried out in a theta-pinching plasma or a neutral atom gun. Deuterium profiling was carried out using SIMS with a cesium-ion source. The lower limit of the measurable concentration of deuterium was 10^4 \mu\text{m}^{-3}. The deuteration temperature was chosen to be 200 °C and the surface treatment durations were 5, 10 and 15 min. In the passivation processes investigated in [11], silicon substrates uniformly doped with boron to a concentration of 1.3 × 10^9 \mu\text{m}^{-3} were used. The value of boron diffusivity for a temperature of 200 °C is equal to 5.67 × 10^{-31} \mu\text{m}^2\text{s}^{-1} [34]. This means that the characteristic length of boron diffusion is approximately equal to 4.5 × 10^{-12} \mu\text{m} for 15 min of plasma treatment, even for diffusion enhancement due to nonequilibrium point defects such as 10^4 times. It is clear that one can neglect boron diffusion during hydrogenation.

To obtain the calculated deuterium concentration presented in figures 1–5, we used an analytical solution of equation (6) for the case where the source provides permanent time-independent generation of a slow diffusing hydrogen species in the thin surface layer of the silicon substrate. Thus, the flux of the slow component is approximated analytically. The reflecting boundary condition on the semiconductor surface is imposed on the low diffusing silicon substrate. Thus, the flux of the slow component is approximated analytically. The independent generation of a slow diffusing hydrogen species in the thin surface layer of the semiconductor is imposed on the low diffusing species with concentration \( C_{\text{HD}} \). It can be seen from the experimental profiles that this type of boundary condition is in agreement with the shape of the hydrogen distribution in the near-surface region. On the other hand, the finite-difference method [35] is applied to find a numerical solution for the system of equations (3), (4) and (5). It is supposed that the generation of nonequilibrium interstitials occurs due to the plasma immersion ion implantation of hydrogen in the thin surface layer. In addition, the hydrogen interstitials can be generated by the rearrangement or dissolution of platelets which incorporate hydrogen atoms. Unfortunately, the energy of hydrogen ions was not mentioned in [11]. However, the thickness of the layer where generation occurs is negligible compared with the average migration length of hydrogen interstitials and the character dimensions of the passivation region. Therefore, to obtain a numerical solution, the Dirichlet boundary conditions in the surface and in the bulk of the semiconductor are imposed on the rapidly diffusing neutral nonequilibrium deuterium interstitials with concentration \( C_{\text{HI}} \). Numerical computations were carried out on a 1D simulation domain \([0, x_B]\), where \( x_B \) and the mesh point number were equal to 1.4 \mu\text{m} and 7001, respectively. Also, the time grid with 5000 equal steps was used to obtain a numerical solution.

As can be seen from figure 1, the calculated deuterium concentration profile is in good agreement with the experimental data of [11]. The following values for the simulation parameters were used to fit the calculated curve to the experimental deuterium concentration profile: \( Q_{\text{HD}} = 1.2 \times 10^{15} \text{cm}^{-2} \); \( D_{\text{HD}} = 2.0 \times 10^{-6} \mu\text{m}^2\text{s}^{-1} \); \( d_{\text{HD}} = 7.251 \mu\text{m}^2\text{s}^{-1} \); \( \beta_{\text{HI}} = 4.2 \mu\text{m} \); \( \beta_{\text{HI}} = 1.02 \times 10^7 \mu\text{m}^{-3} \); \( \beta_{\text{HI}} = 0 \); \( \beta_{\text{HI}} = 1.0 \times 10^{-6} \); \( \beta_{\text{HI}} = 0 \); \( \beta_{\text{HI}} = 0 \); \( \beta_{\text{HI}} = 0 \); \( \beta_{\text{HI}} = 0.21 \times 10^{-3} \mu\text{m}^3\text{s}^{-1} \); \( \beta_{\text{HI}} = 0.4 \). Here \( Q_{\text{HI}} \) is the dose of hydrogen atoms that are responsible for slow diffusing species; \( C_{\text{HI}} \) is the concentration of deuterium interstitials in the neutral charge state at the surface; \( \beta_{\text{HI}} \) is the average migration length of hydrogen interstitials in an intrinsic silicon; \( C_{\text{HI}} \) is the concentration of uniformly distributed boron atoms in a substitutional position before hydrogenation.

The analysis of the experimental data of Van Wieringen and Warmoltz [32] clearly shows that diffusivity of the fast diffusing species is measured exactly due to the hydrogen permeation. Therefore, in this paper, the diffusivity of hydrogen in intrinsic silicon \( d_{\text{HI}} = 7.251 \mu\text{m}^2\text{s}^{-1} \) for a temperature of 200 °C was calculated using the data of Van Wieringen and Warmoltz [32]. According to [32], the temperature dependence of hydrogen diffusivity is described by the
The following expression:

\[ D = D_0 \exp \left( -\frac{Q}{k_B T} \right), \tag{19} \]

where the pre-exponential factor \( D_0 = 9.4 \times 10^5 \mu m^2 s^{-1} \) and the activation energy \( Q = 0.48 \text{ eV} \). It is worth noting that the hydrogen diffusivity calculated from the dependence given in [32] was used in the work of Zhang [5]. This dependence was also used in [19]. However, in a later paper [22], lower values of the hydrogen diffusivity were used. For example, the pre-exponential factor \( D_0 = 8.4 \times 10^8 \mu m^2 s^{-1} \) and activation energy \( Q = 1.12 \text{ eV} \) were extracted for the diffusivity of the neutral hydrogen in [22]. For diffusion of positively charged hydrogen atoms the pre-exponential factor \( D_0 = 1.2 \times 10^4 \mu m^2 s^{-1} \) and activation energy \( Q = 0.6 \text{ eV} \) were found.

Unfortunately, it is difficult to compare the obtained value \( D_{\text{HD}} = 2.0 \times 10^{-6} \mu m^2 s^{-1} \) of the slowly diffusing species with the published data because it is often supposed that the near-surface maximum of the hydrogen concentration is formed due to the trapping of hydrogen atoms in the layer damaged by plasma treatment [19]. However, the value of \( D_{\text{HD}} \) obtained in this paper is smaller than the diffusivities obtained in various investigations of hydrogen diffusion, including the data of Capizzi and Mittiga [17]. Using the value \( D_{\text{HD}} = 6.42 \times 10^{-7} \mu m^2 s^{-1} \) for 150 \( ^\circ \text{C} \) from our previous work [31], we can obtain the pre-exponential factor \( D_0 = 4.66 \times 10^{-2} \mu m^2 s^{-1} \) and activation energy \( Q = 0.41 \text{ eV} \) for the slowly diffusing species. However, the mechanism underlying the hydrogen maximum formation and hydrogen diffusion in the narrow high-concentration region requires further investigation.

It follows from the fitting procedure that the increase of \( k_{\text{HIA}} \) or \( \beta_{\text{HIA}} \) results in a more abrupt deuterium profile between the passivated and unpassivated regions. Because the average migration length of deuterium interstitials in an intrinsic silicon \( l_{\text{HI}} \) is greater than 1 \( \mu m \) (it can be seen from figure 1 that the thickness of intrinsic silicon to the end of the passivation process is greater than 0.4 \( \mu m \), and the thickness of the hydrogenated layer is approximately equal to 0.6 \( \mu m \)), in the simulation procedure we use the value \( l_{\text{HI}} = 4.2 \mu m \). Then, the average lifetime of the nonequilibrium hydrogen interstitials in an intrinsic silicon \( \tau_{\text{HI}} \) is equal to 2.43 s.
Figure 2. Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 15 min. The experimental data (black circles) are taken from Tong et al [11].

i.e. $\tau_1^{HI}$ is significantly smaller than the duration of hydrogenation (5 min). This value of $\tau_1^{HI}$ confirms the correctness of the assumption about the quasistationary distribution of hydrogen interstitials due to their high mobility.

In figure 2, the calculated deuterium concentration profile after thermal treatment for 15 min is presented. The same values for the diffusion of hydrogen interstitials and the same passivation parameters were used in these calculations. As can be seen from figure 2, the calculated deuterium concentration profile is in good agreement with the experimental data of [11], as concerns the length of the passivated region. On the other hand, the abruptness of the calculated profile at the boundary between the passivated and unpassivated regions is very high and disagrees with the experimental data. Similar calculations of the deuteration distribution for 10 min show that in this case, the profile abruptness is also greater compared with the experimental one.

It is rather difficult to explain the obtained disagreement at the boundary between the passivated and unpassivated regions after plasma treatment for 10 and 15 min. Indeed, to reduce the abruptness of the calculated deuterium profile, one can decrease the value of $k_1^{HIA}$ and/or $\beta^{HIA}$. In figures 2, 4 and 5, the calculated deuterium concentration profiles with $k_1^{HIA} = 0.2 \times 10^{-4} \mu m^3 s^{-1}$ and $\beta^{HIA} = 0.12$ a.u. after thermal treatment for 5, 10 and 15 min are presented. It can be seen from figures 3, 4 and 5 that the deuterium concentration profile calculated for the decreased values of $k_1^{HIA}$ and $\beta^{HIA}$ agrees well with the experimental data if plasma treatment lasts for 10 and 15 min, whereas for the 5 min duration the slope of the experimental profile is steeper. Currently, we do not know the physical reasons for the decrease in $k_1^{HIA}$ and $\beta^{HIA}$ with the increase in the duration of deuteration and, respectively, in the depth of the passivated region. Indeed, the reactions between the hydrogen and boron atoms are independent of the distance from the surface. The analysis of the experimental data presented in [3, 7, 16] shows that the slow diffusion is a characteristic feature of the narrow high-concentration region in the vicinity of the surface. Therefore, it is difficult to explain the change in the abruptness of the hydrogen profile at the boundary between the passivated and unpassivated regions due to a fraction of ‘slow’ hydrogen diffusion because this boundary is far from the surface. Perhaps there is an error in the measurements of the deuterium concentration
profile, or it is possible that the nonequilibrium point defects generated in the near-surface region due to plasma treatment change the conditions for passivation. For example, generated silicon self-interstitials can kick out boron atoms from their substitutional position (Watkins effect). Indeed, due to ion bombardment of the surface, vacancies and silicon self-interstitials are generated in the narrow surface layer. It is widely accepted that the mobility of silicon self-interstitials is very high. We can assume that diffusion of this species occurs due to the high mobility even at low temperatures, such as 200 °C, and their migration length is sufficient for reaching the boundary between the passivated and unpassivated regions shifted from the surface approximately to 1.0 μm for 15 min hydrogenation. Thus, the character of passivation

Figure 3. Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 5 min. The decreased values of $k_{\text{HIA}} = 0.2 \times 10^{-4} \mu\text{m}^3\text{s}^{-1}$ and $\beta_{\text{HIA}} = 0.12 \text{a.u.}$ are used in the simulation of hydrogen diffusion. The experimental data (black circles) are taken from Tong et al [11].

Figure 4. Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 10 min. The decreased values of $k_{\text{HIA}} = 0.2 \times 10^{-4} \mu\text{m}^3\text{s}^{-1}$ and $\beta_{\text{HIA}} = 0.12 \text{a.u.}$ are used in the simulation of hydrogen diffusion. The experimental data (black circles) are taken from Tong et al [11].
can be changed due to the high concentration of nonequilibrium silicon self-interstitials. This problem requires further investigation.

It is worth noting that a simulation of the experimental data of Tong et al [11] was also carried out in [5]. The model of hydrogen diffusion proposed in [5] also takes into account two different fluxes of hydrogen species. It is supposed that ‘fast’ diffusion occurs due to the migration of atomic hydrogen in the different charge states $H^-$, $H^+$ and $H^o$. To describe ‘slow’ diffusion, the mechanism of the formation and migration of hydrogen complexes with mobile traps generated during plasma treatment is used. It is supposed in [5] that silicon vacancies trap hydrogen atoms and form mobile complexes $V-H$, which are responsible for the ‘slow’ diffusion. In contrast to this paper, only one quasichemical reaction, i.e.

$$A^- + H^+ \rightleftharpoons (AH)^+,$$

(20)
is used to describe the passivation of boron atoms. It is also supposed in [5] that reaction (20), as distinct from reaction (1), is reversible, i.e. the detrapping of hydrogen atoms can occur. On the other hand, it was found in [20] that the dissociation energy of the (BH) complex is equal to $1.28 \pm 0.03$ eV, i.e. it is high enough compared with the value of $k_B T = 0.04077$ eV for a temperature of 200 $^\circ$C. Here $k_B$ is the Boltzmann constant. Therefore, in reactions (1) and (2), the process of detrapping is omitted. As can be seen from [5], a full fitting of the calculated deuterium concentration profiles to the experimental ones is not achieved because the abruptness of the calculated deuterium distributions at the boundary between the passivated and unpassivated regions also disagrees with the experimental data. We hope that new more precise measurements of deuterium distributions in silicon substrates doped with boron can solve this problem.

In addition, note that this work uses the condition of local charge neutrality (10) to calculate the charge carrier concentration in the doped semiconductor, whereas in the paper of Zhang [5], the solution of Poisson’s equation for the potential of the built-in electric field is used to calculate the drift velocity of charged species and charge carrier concentration. The simulation results obtained in this work demonstrate clearly that the condition of local charge neutrality is a good approximation in simulating passivation processes. This approximation essentially simplifies
the model of hydrogen transport and is very suitable for numerical solution of the system of reaction-diffusion equations because for this case the effective coefficients of the equations obtained depend only on the electrically active impurity concentration and on the concentrations of diffusing species.

4. Conclusions

The model of hydrogen migration and reactions of hydrogen atoms with the electrically active impurity that had been developed in [30, 31] was applied to simulate the hydrogen diffusion and passivation process during plasma deuteration of silicon substrates uniformly doped with boron. For comparison, the experimental data of Tong et al [11] for plasma treatment at a temperature of 200 °C for 5, 10 and 15 min was used. The calculated deuterium concentration profiles agree well with the experimental data for the entire time of plasma treatment if we suppose that the coefficient of absorption of hydrogen interstitials in the near-intrinsic semiconductor $k_{HIA}$ as well the empirical parameter $\beta_{HIA}$, which describes the relative absorption of positively charged hydrogen interstitials in comparison with the absorption of neutral interstitials during the passivation of electrically active dopant atoms, decrease with an increase in the duration of deuteration, and accordingly in the depth of the passivated region. It is possible that this decrease occurs due to the nonuniform spatial distribution of nonequilibrium point defects, which are generated during plasma treatment and can influence the passivation process. If the invariable values of the simulation parameters are used for different durations of plasma treatment, the calculated deuterium concentration profile is in good agreement with the experimental data of [11] as concerns the length of the passivated region. However, the abruptness of the deuterium concentration profiles at the boundary between the passivated and unpassivated regions disagrees with the experimental data either with treatment for 5, 10 or 15 min.

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