Modeling boron dose loss in sidewall spacer stacks of complementary metal oxide semiconductor transistors

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1. Introduction

Scaling transistor dimensions in complementary metal oxide semiconductor (CMOS) technologies implies an enhanced control of the physical dimensions and properties of ultra-shallow junctions (USJs) to manage device performances. In particular, the lightly doped drain (LDD) region under the sidewall spacer controls the serial resistance as well as the short channel effects (SCE) [1]. The need to limit the dopant diffusion and increase the activation in silicon, along with the introduction of new materials as well as the increased interface effects as the dimensions are reduced, have made the junction engineering a difficult challenge. In this frame, and according to the International Technology Roadmap for Semiconductors (ITRS) [2], the development of predictive models of segregation and dose loss are considered as key modeling and simulation challenges for the technology nodes after 14 nm.

Oxide nitride sidewall spacers have been introduced to control the overlap of the source-drain and LDD junctions with the gate oxide [3]. In the case of p-type metal oxide semiconductor (pMOS) transistors, several papers [4–7] have depicted the diffusion of boron from silicon to oxide during the thermal anneals performed subsequently to the sidewall spacer process steps. This effect, called out-diffusion, can lead to substantial boron dose loss from silicon into oxide, which may affect the electrical characteristics of pMOS transistors. Typically the resistance $R_{\text{ext}}$ of the LDD extension and the threshold voltage $V_{T}$ can be impacted. Fig. 1 shows a diagram of the materials and interfaces present in pMOS transistors. The boron out-diffusion phenomenon highlighted with the red arrows in Fig. 1 is modulated by the diffusion mechanisms occurring in the LDD region, into the silicon and silicon oxide materials.

Several studies of out-diffusion of boron were initially carried out on thermally grown oxides aiming to evaluate the diffusion of boron from the doped polycrystalline gate through the gate oxide into the channel. It was shown [8] that boron diffusion in

1 For interpretation of color in Fig. 1, the reader is referred to the web version of this article.
oxide is modulated by the Si—O bonds, also called peroxy-linkage defects (PLDs). Several studies [8–10] have also shown the important role played by hydrogen during thermal anneals in a H₂ ambient. It has been postulated that O—H bonds called hydrogen-related defects (HRDs) also mediate boron diffusion in silicon oxide [8].

Since the advent of the 65 nm technology node, the oxide and nitride layers use for the sidewall spacers are formed at low temperatures to limit detrimental diffusion phenomena. Different types of chemical vapor deposition (CVD), plasma enhanced CVD, and more recently, atomic layer deposition (ALD) have been used as deposition techniques. As a result of the reduced temperature, these materials are hydrogen rich compared to the previous layer deposited at higher temperatures [11–13] and are expected to further impact the boron diffusion in Si and SiO₂. The content of hydrogen, and more specifically of HRDs in oxide depends on the process parameters. A boron diffusivity modulated by the concentration of OH bonds (or HRDs) was proposed to model the enhancement of boron diffusion in grown oxide [10] and deposited [14] oxides. Although the boron diffusion depends on the initial OH concentration in the oxide, to our knowledge, the evolution of this concentration during post thermal anneal is not considered in any models. In addition to the oxide, the nitride top layer can influence the out-diffusion mechanism by injecting some hydrogen into oxide during thermal anneals subsequent to the spacer forming process, which modify the OH concentration in oxide. Moreover, the nitride can also act as a capping layer which results in substantial hydrogen retention into the pedestal oxide. Consequently, the boron diffusion in the oxide is increased [6]. Thus, to quantitatively study the boron out-diffusion mechanism in nitride/oxide/silicon spacer stacks during thermal treatment, we should monitor the physical characteristics and variation of the hydrogen-related species present in both the nitride and the oxide layers, in addition to the dependence of oxide boron diffusion with hydrogen-related species concentrations.

In this paper we have evaluated the boron out-diffusion and the corresponding dose loss mechanism modulated by the presence of different nitride/oxide capping bi-layers. To correlate the hydrogen-related species characteristics with the boron dose loss, we prepared a set of boron implanted and annealed silicon samples covered with different oxide/nitride blanket bi-layers, as described in Section 2. We used secondary ion mass spectrometry (SIMS) measurements to determine boron profiles in the multi-layer system presented in Section 3. The relationship between hydrogen content and boron diffusion and the statics and dynamics of the generation and diffusion of hydrogen in oxide and nitride are then presented in Sections 4.1 and 4.2. Based on these results, an improved boron out-diffusion model, which allowed for the reproduction of the different SIMS data, is presented in Section 4.3.

2. Experiments

We prepared five samples (S₁ to S₅) on (001)-oriented p-type silicon wafers according to the experimental plan presented in Table 1. We first performed a 1 keV 5·10¹⁴ cm⁻² BF₂ implantation step similar to the condition used for LDD in electrical lots. Four different material stacks were then deposited by combining two different oxides (OA and OB) and three different nitrides (NA, NB, and NC), which present different hydrogen characteristics.

Oxide OA was deposited at 625 °C by low pressure chemical vapor deposition (LPCVD) using a liquid tetraethyl orthosilicate (TEOS) precursor. Oxide OB is an un-doped silica glass (USG) film which was deposited at 400 °C by plasma-enhanced chemical vapor deposition (PECVD) using the reaction between SiH₄ and N₂O compounds. In addition, we determined the concentration of OH bonds in as-deposited OA and OB oxides with Fourier transform infrared (FTIR) spectroscopy [15].

NA and NC nitride layers were deposited by PECVD using a SiH₄/NH₃/N₂ chemistry at 480 °C and 400 °C, respectively. Nitride NB was obtained at 590 °C with LPCVD with hexachlorodisilane (HCD), ammonia (NH₃), and ethylene (C₂H₄) as precursors. NA, NB, and NC nitride densities were been determined by combining thickness measurement with ellipsometric spectroscopy and a high sensitivity weighing machine, resulting in an accuracy better than 2.5%. The initial hydrogen bond concentrations summarized in Table 2 were obtained with FTIR spectrometer using the methodology from Landford and Rand [16]. Hydrogen diffusion characteristics in silicon nitride were extracted with stress/TDS measurements and modeling methodology similar to those carried out by Morin et al. [17] and briefly described below. In silicon nitride films, hydrogen is incorporated by forming SiH or NH bonds [18] in the SiN lattice as a function of deposition process parameters. During a subsequent thermal anneal, hydrogen bonds can be broken, releasing free-diffusing hydrogen H atoms or di-hydrogen molecules according to various chemical mechanisms [19]. The released hydrogen species can then freely diffuse through the nitride film and eventually be transferred to adjacent materials or released in the annealing chamber atmosphere. The hydrogen release in the chamber depends not only on the kinetics of chemical hydrogen dissociation but also on the diffusion of released hydrogen through the layer. In addition, it has been shown that PECVD nitrides are mechanically meta-stable [17]. When submitted to post-thermal treatment, mechanical stress increases and hydrogen is released, as both mechanisms are related and follow similar kinetic behavior. Accordingly, measuring in parallel the hydrogen release and the stress variation on meta-stable PECVD silicon nitride layer subjected to a thermal cycle allows for a determination of hydrogen diffusion coefficients according to the following set of equations [18].

\[
\frac{\partial H_{\text{nat}}}{\partial t} = D(H_{\text{nat}}) \frac{\partial^2 H_{\text{nat}}}{\partial x^2} + K(H_{\text{nat}}) \text{SiNH} \tag{1}
\]

\[
\frac{\partial \text{SiNH}}{\partial t} = -K(H_{\text{nat}}) \text{SiNH} \tag{2}
\]
Table 1
Description of the samples used in this study. $S_1$ to $S_2$ are made of silicon substrates implanted with 1 keV 3 $10^{14}$ cm$^{-2}$ BF$_2$ capped with nitride/oxide blanket stacks and subsequently annealed at 1000 °C during 2 min. A reference sample $S_5$ similar to $S_2$ is kept un-annealed for the reference.

<table>
<thead>
<tr>
<th>Process</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_4$</th>
<th>$S_5$</th>
<th>Deposition</th>
<th>Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_2$ implant</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>LPCVD, 625 °C</td>
<td>TEOS</td>
</tr>
<tr>
<td>Oxide OA</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
<td>PECVD, 400 °C</td>
<td>SiH$_4$/N$_2$D</td>
</tr>
<tr>
<td>Nitride NA</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>PECVD, 480 °C</td>
<td>SiH$_4$/N$_2$H$_4$</td>
</tr>
<tr>
<td>Nitride NB</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
<td>LPCVD, 590 °C</td>
<td>H$_2$/SiH$_4$/C$_2$H$_4$</td>
</tr>
<tr>
<td>Nitride NC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PECVD, 400 °C</td>
<td>SiH$_4$/N$_2$H$_4$</td>
</tr>
<tr>
<td>Anneal (1000 °C, 2 min)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIMS</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
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</tr>
</tbody>
</table>

Table 2
Summary of physical parameters used in this study for the different materials. $K(H_{init})$ and $D(H_{init})$ were obtained following a coupled stress/TDS methodology [15] for nitrides NA to NC. The initial H bonds concentration in nitride SiNH$_0$ and in oxide OH$_0$ were extracted from FTIR measurements for nitrides NA to NC and oxides OA and OB. Nitride density $\rho$ was obtained by using a weighing machine. The values of the parameters calculated at 1000 °C are given in italics.

<table>
<thead>
<tr>
<th></th>
<th>$K(H_{init})$ (s$^{-1}$)</th>
<th>$D(H_{init})$ (cm$^2$.s$^{-1}$)</th>
<th>SiNH$_0$ (cm$^{-3}$)</th>
<th>OH$_0$ (cm$^{-3}$)</th>
<th>$\rho$ (g.cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>5.71 $10^{-14}$</td>
<td>2.37 $10^{-3}$</td>
<td>1.05 $10^{-14}$</td>
<td>9.59 $10^{-15}$</td>
<td>$\sim10^{23}$</td>
</tr>
<tr>
<td>NB</td>
<td>Extrapolation 9.0 $10^{-4}$</td>
<td>9.53 $10^{-1}$</td>
<td>1.05 $10^{-14}$</td>
<td>5.02 $10^{-11}$</td>
<td>$\sim10^{21}$</td>
</tr>
<tr>
<td>NC</td>
<td>6.34 $10^{-15}$</td>
<td>9.53 $10^{-3}$</td>
<td>4.07 $10^{-10}$</td>
<td>5.02 $10^{-11}$</td>
<td>$\sim10^{21}$</td>
</tr>
<tr>
<td>OA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\sim10^{21}$</td>
</tr>
<tr>
<td>OB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\sim10^{21}$</td>
</tr>
</tbody>
</table>

Here, $H_{init}$ and SiNH are, respectively, the released hydrogen species (atomic or molecular) concentrations that diffuse within the nitride and the hydrogen bonded to either Si or N, assuming that no free species were present in nitride before annealing. $D(H_{init})$ is the hydrogen diffusivity in nitride, in cm$^2$.s$^{-1}$, and $K(H_{init})$ the H desorption reaction constant in s$^{-1}$. Both $D(H_{init})$ and $K(H_{init})$ at 1000 °C have been extrapolated from coupled stress/TDS measurements carried out between 20 and 850 °C similarly to the technique detailed in Ref. [17] assuming a similar mechanism up to 1000 °C. This methodology applied to nitride NA and NC yield to the diffusion coefficient at 1000 °C given in Table 2. As catalogued in this table, hydrogen effective diffusivity in NC nitride is much higher than in NA nitride, which can be explained by the respective densities of NA and NC nitrides of 2.65 and 2.15 g.cm$^{-3}$, respectively. These results are in agreement with literature results [20–22] and highlight the increase of hydrogen diffusivity as the nitride density decreases. Nitride NB was deposited with LPCVD and is therefore almost thermally stable, preventing the need for similar methods to determine hydrogen diffusion [19]. Given NB density of 2.52 g.cm$^{-3}$ which is near NA density (2.65 g.cm$^{-3}$), we assumed that the hydrogen effective diffusivity in NB equals 9.59 $10^{-15}$ cm$^2$.s$^{-1}$, the same as for NA (on the same order of magnitude as those observed in literature at 1000 °C for similar LPCVD nitride at 5 $10^{-14}$ cm$^2$.s$^{-1}$) [23]. Given the diffusivity value for NB, the reaction constant $K(H_{init})$ at 1000 °C was inferred from hydrogen desorption profiles obtained with TDS measurements [24] using Eqs. (1) and (2) and is presented in Table 2.

Samples $S_1$ to $S_5$ were then subjected to an anneal at 1000 °C for 2 min by using a rapid thermal annealing (RTA) tool in a N$_2$ atmosphere at the atmospheric pressure, under a controlled oxygen atmosphere (radiance chamber from Applied Materials). The annealing duration, longer than the standard processes used after sidewall spacer integration, has been chosen to enhance the diffusion phenomena and facilitate the analysis. The boron profiles have been measured after anneal on all samples with secondary ion mass spectrometry (SIMS) using a 1 keV 45° tilted O$_2$ beam. The SIMS signals have been post-treated to account for the difference of SIMS characteristics in silicon and silicon oxide, to obtain quantitative boron concentration in both materials.

3. Results

Boron SIMS profiles for samples $S_1$ to $S_2$ are given in Fig. 2a. We observed first a substantial boron diffusion in silicon after anneal compared to the un-annealed reference sample $S_5$. In addition, boron has diffused in the oxide whereas any boron was detected within the nitride cap layers. Qualitatively, the higher the boron dose in oxide the lower it is in silicon. Two main different behaviors are observed: samples $S_1$ and $S_2$, with the same oxide layer OA (LPCVD TEOS oxide), showed a higher boron dose loss in the oxide and a shallower diffusion in silicon. Conversely, samples $S_3$ and $S_4$ made with oxide OB (PECVD USG) exhibited a higher dose and diffusion depth in silicon as well as a lower boron out-diffusion in silicon oxide. We also observe on every sample boron segregation at the oxide surface ($z < 30$ nm) generated during the growth of oxide, even without the presence of silicon nitride (see sample $S_5$ for example). For the sake of simplicity, this phenomenon is neglected in the following.

Some conclusions can also be drawn concerning the impact of the spacer nitride layer. For the same OA oxide, the NA/OA bilayer exhibits slightly higher out-diffusion than the NB/OA stack, which suggests on first order a higher initial hydrogen concentration in NA in comparison to NB nitride. These results are in agreement with out-diffusion literature, which has demonstrated the impact of a nitride cap on the loss of boron in oxide during anneal [4–6].

As mentioned above, the boron profiles in silicon oxide exhibit an exponential tail, equivalent to a straight line in a log scale, whereas the classical resolution of Fick’s second law diffusion equation [25] should lead to shaped profiles of classical complementary error functions (erfc). The exponential diffusion behavior suggests that oxide boron diffusion could be mediated by intermediate mobile species. This will be discussed in the following section.

4. Analysis and discussion

SIMS analyses emphasized in Fig. 2a the boron dose loss phenomena from silicon into oxide as function of the stacks. In Sec-
the following reaction\[6–8\]:

\[ \text{diffusion mechanism typically implies } O - H \text{ in grown and deposited oxides in presence of OH defects:} \]

been proposed to account for the enhancement of boron diffusion process parameters. A specific expression for boron diffusivity has mechanisms through fixed and mobile chemical traps, boron diffusion in Sub-section 4.3, using two different diffusion
cicies content in oxide and nitride. Finally, we present models of
diffusion in static mode. Then we discuss hydrogen-related

\begin{align}
\frac{\partial \text{H}_{\text{ox}}}{\partial t} &= D(\text{H}_{\text{ox}}) \frac{\partial^2 \text{H}_{\text{ox}}}{\partial x^2} - K_{\text{a}}(\text{H}_{\text{ox}})\text{H}_{\text{ox}} + K_{\text{d}}(\text{H}_{\text{ox}})\text{OH} \\
\frac{\partial \text{OH}}{\partial t} &= K_{\text{a}}(\text{H}_{\text{ox}})\text{H}_{\text{ox}} - K_{\text{d}}(\text{H}_{\text{ox}})\text{OH}.
\end{align}

Here, $$D_{\text{B}}$$ is the boron diffusivity in a reference oxide in which the diffusion is not mediated by the presence of silanol bonds and OH$_{\text{ref}}$ the concentration of OH defects in the reference oxide. $\text{OH}$ is the effective OH concentration, i.e. the part of silanol bonds involved in boron diffusion, i.e. the difference between the total silanol concentration and OH$_{\text{ref}}$ whereas. Exponent $n$ is a fitting parameter. It is important to notice that although the boron diffusion depends on the initial OH concentration in the oxide, the variation of OH concentration during thermal anneal, in particular in presence of nitride capping layer [4–6] is not considered when using Eq. (5) alone.

4.2. Dynamics of hydrogen-related species in oxide

In this section we set out the relations of hydrogen dynamics in oxide. We apply the methodology to the study of samples $S_1$ to $S_4$. In the deposited oxides of this study, hydrogen is mainly incorporated as SiH and OH bonds [11–13], the latter corresponding to HRDs already seen in reaction (4), which enhances the boron diffusion in oxide. Various chemical reactions can lead to the formation of HRDs [26,27]. The characteristics of hydrogen-related species in oxides OA and OB have been post-determined from the boron SIMS profiles in silicon and oxide shown in Fig. 2a by using the diffusion models of both hydrogen and boron species as detailed later in Section 4.3. For the sake of simplicity we consider in this study that the free hydrogen-diffusing species form a single group called H$_{\text{ox}}$. Hydrogen can only be chemically trapped by oxygen atoms to form one type of hydrogen bond (OH that corresponds to the HRDs) and this process is reversible. We also assume that no free diffusing H$_{\text{ox}}$ species are contained in the oxide before anneal (in fact H$_{\text{ox}}$ will be released during the first temperature ramp up along the silicon nitride deposition). Accordingly, hydrogen is only present in oxide before anneal under its trapped form OH with an initial concentration OH$_0$. We modeled H$_{\text{ox}}$ and OH concentrations in the oxide using the following equations considering a one-dimensional (1D) system along x direction:

\[ D(\text{H}_{\text{ox}}) \frac{\partial^2 \text{H}_{\text{ox}}}{\partial x^2} - K_{\text{a}}(\text{H}_{\text{ox}})\text{H}_{\text{ox}} + K_{\text{d}}(\text{H}_{\text{ox}})\text{OH} \]  
\[ \frac{\partial \text{OH}}{\partial t} = D(\text{H}_{\text{ox}}) \frac{\partial^2 \text{H}_{\text{ox}}}{\partial x^2} - K_{\text{a}}(\text{H}_{\text{ox}})\text{H}_{\text{ox}} + K_{\text{d}}(\text{H}_{\text{ox}})\text{OH}. \]

Fig. 2. (a) Experimental boron SIMS profiles for samples $S_1$ to $S_4$ (Table 1) with different nitride/oxide/silicon spacer stacks after annealing at 1000 °C for 2 min, in addition to a NB/OA $S_5$ reference sample without anneal. (b) Experimental boron SIMS profiles compared to TCAD simulation for samples $S_1$ to $S_4$ (Table 1) using (10) for boron diffusivity in oxide, and (6)–(9) for hydrogen-related species temporal evolution. The final percentages of boron dose maintained in silicon (experimental/simulated) are the following for $S_1$: 31/42%, $S_2$: 48/45%, $S_3$: 64/51% and $S_4$: 79/65%. (c) Experimental boron SIMS profiles compared to TCAD simulation for the same samples using (11) and (12) for boron diffusivity in oxide with the long hop mechanism, and (6)–(9) for hydrogen-related species temporal evolution. The final percentages of boron dose maintained in silicon (experimental/simulated) are the following for $S_1$: 31/36%, $S_2$: 48/43%, $S_3$: 64/55% and $S_4$: 79/69%.

4.1. Statics of hydrogen-related species and their impact on boron diffusivity

As mentioned in the introduction, boron diffusion in oxide is mediated by the Si–O bonds (or PLDs) following:

\[ \text{B}^{+} = \text{Si} - \text{O} - \text{O} - \text{Si} \equiv \cdots \equiv \text{Si} - \text{O} - \text{B} - \text{O} - \text{Si}, \]

with an activation energy for the diffusion mechanism through PLDs $E_A^{\text{PLD}} = 3.56$ eV [6]. The role played by hydrogen in the boron diffusion mechanism typically implies O–H bonds (or HRDs) with the following reaction [6–8]:

\[ \text{B}^{+} = \text{Si} - \text{O} \cdots \text{H} - \text{O} - \text{Si} \equiv \cdots \equiv \text{Si} - \text{O} \cdots \text{H} - \text{B} - \text{O} - \text{Si}, \]

with an activation energy for the diffusion mechanism mediated by HRDs $E_A^{\text{HRD}} = 3.12$ eV [8]. Spacer oxide and nitride layers deposited at low temperatures are hydrogen rich [11–13] as function of the process parameters. A specific expression for boron diffusivity has been proposed to account for the enhancement of boron diffusion in grown [10] and deposited [14] oxides in presence of OH defects:

\[ D(\text{B})_{\text{SiO}_x} = D(\text{B}) \left( 1 + \frac{\text{OH}}{\text{OH}_{\text{ox}}} \right)^n. \]
estimated the coefficients of absorption and desorption $K_a(H_{ox})$ and $K_d(H_{ox})$ for free hydrogen from the boron SIMS profiles presented in Fig. 2a for samples $S_1$ to $S_4$ using the coupled hydrogen and boron diffusion models described in the following section.

4.3. Boron dose loss modeling

After the presentation of the model driving the hydrogen dynamics in oxide and nitride, we addressed the boron diffusion by introducing a diffusion mechanism first through fixed traps and then with mobile traps.

4.3.1. Boron diffusion in oxide through fixed chemical traps

We consider here that boron diffusion in oxide depends on OH bonds using (5), in which B diffusivity depends on the OH bonds' concentration. This relation yields to the following Fick's-based boron diffusion equation in oxide:

$$\frac{\partial B_{\text{ox}}}{\partial t} = D_{\text{B}}(B) \left( 1 + \frac{\text{OH}}{C_{\text{OH,ref}}} \right)^n \frac{\partial^2 B_{\text{ox}}}{\partial x^2}. \tag{10}$$

For the description of boron diffusion in silicon, we used the set of advanced models of Synopsys Sentaurus Process simulator [28]. We implemented the equations for the hydrogen-related species in the simulator using Alagator scripting language. We described the boron transfer from silicon to oxide with a three-phase segregation model at the oxide/silicon interface [29,30], the three phases being oxide, silicon, and oxide/silicon interface.

From the data plotted in Fig. 2a for samples $S_1$ to $S_4$, a set of model parameters for OH and boron was inferred to reproduce the SIMS boron profiles in silicon (see Table 3). All OH and boron parameters used in Eqs. (6), (7), and (10) are similar for both OA and OB oxides, except for the hydrogen desorption constant $K_d(H_{ox})$ which is higher for OA oxide (0.8 s$^{-1}$) than for OB oxide (0.6 s$^{-1}$). We compare in Fig. 2b the experimental boron profiles with the optimal simulation for the different stacks using the parameters for hydrogen and boron given in Tables 2 and 3. By combining (10) describing the boron diffusion [12] with the evolution of hydrogen species concentration provided by Eqs. (1), (2), (11) and (12), we obtain the following equation:

$$\frac{\partial B_{\text{ox}}}{\partial t} = D_{\text{B}}(B) \left( 1 + \frac{\text{OH}}{C_{\text{OH,ref}}} \right)^n \frac{\partial^2 B_{\text{ox}}}{\partial x^2}. \tag{10}$$

In Eqs. (11) and (12) as in (10), BOH diffusivity is driven by OH concentration through the multiplying factor $1 + \text{OH}/C_{\text{OH,ref}}$ in front of the first right-hand side (r.h.s.) of (12). After a diffusion step with characteristic length $L_B$, BOH is captured and forms an immobile boron atom B. To account for the steep dependence of the recombination with OH concentration in (11) and (12) we evaluate various expressions. A consistent result is obtained with a recombining factor like $K_{r0}(\text{OH}/C_{\text{OH,ref}})$ present in the first and second r.h.s. terms of Eqs. (11) and (12). This term depends on the OH concentration in oxide and on the two fitting parameters $r_0$ (in s$^{-1}$) and $g$, (in cm$^{-3}$). In fact the numerical optimization provides a proportionality factor that is decomposed in prefactor $r_0$ and dimensional parameter $L_B$. Note that OH$_r$, different from $C_{\text{OH,ref}}$, the threshold silanol concentration above which boron diffusion is impacted by OH concentration. Similarly to the kick-out mechanism for BI pairs in silicon, we assume that BOH can be generated following the reaction between B and OH [3] with a generation constant $g$ (in cm$^{-3}$ s$^{-1}$) following the second and third r.h.s. terms of Eqs. (11) and (12), respectively. In addition to absorption and desorption constants $K_a(H_{ox})$ and $K_d(H_{ox})$, it should be noted that the boron diffusion expressed in oxide with (11) and (12) has five different calibration parameters ($D(B)$, $g$, $C_{\text{OH,ref}}$, $r_0$ and OH$_r$, finally $g$). Given the number of experimental conditions (only four spacer stacks $S_1$ to $S_4$), the set of parameter values found in the simulations, and even the formulation for the recombination constant might not be unique. However, we demonstrate that using a long hop mechanism reproduce accurately the boron exponential tails observed experimentally in silicon oxide (Fig. 2c), which was not the case with a classical Fickian diffusion law as shown in Fig. 2b. The different model parameters of Eqs. (11) and (12) are given in Table 4. With the long hop mechanism, the fit with SIMS data yields to absorption constant $K_a(H_{ox})$ decreased from 0.01 to 0.008 s$^{-1}$ for oxide OB, and a desorption constant $K_d(H_{ox})$, modified from 0.8 to 3.8 s$^{-1}$ and 0.6 to 3.6 s$^{-1}$, respectively, for OA and OB as visible in Table 4. With this set of parameters, the estimation of the loss of boron dose from silicon is improved compared to previous case with only slight differences remaining that could be attributed to SIMS artifacts at the oxide/silicon interface.

The calibration enables to determine for each nitride/oxide/silicon system the hydrogen and boron dynamics during anneal based on Eqs. (1), (2), (11) and (12). We compare in Fig. 3 the behavior of samples $S_1$ and $S_2$, which exhibit respectively the highest and the lowest boron dose loss. The variation of SiNH bonds is shown in Fig. 3a. The variation of hydrogen concentration in both nitride and oxide shown in Fig. 3b. Fig. 3c plots the variation of OH in oxide while the boron dose in silicon and oxide is shown in Fig. 3d. As plotted in Fig. 3a, SiNH bonds dissociate by emitting free hydrogen which are not re-trapped in nitride yielding to an exponential SiNH variation. We focus our interest on sample $S_2$ (NC nitride and OB oxide). Given the high desorption reaction...
constant $K_\text{Hox}$ ($9.53 \cdot 10^{-1}\text{s}^{-1}$), we should have expected the hydrogen concentration in nitride to quickly reach a maximum. However, the hydrogen diffusivity in NC nitride $D_\text{Hox}$ at 1000°C equals $5.02 \cdot 10^{-11}\text{cm}^2\text{s}^{-1}$ which is almost four orders of magnitude higher than for NA and NB nitrides, at $9.59 \cdot 10^{-15}\text{cm}^2\text{s}^{-1}$. Consequently both hydrogens dissociated from the SiNH bonds or originated from oxide segregate from oxide to nitride and are eventually released into the anneal chamber, inducing a complete desorption of OH bonds from oxide. In other words, nitride in $S_2$ (NC) does not exert any capping effect to H and facilitates the instantaneous hydrogen degas from the bilayer. The release of hydrogen results in a limited boron out-diffusion from silicon into oxide [6]. The fast OH decrease (Fig. 3c) is directly correlated to the reduced loss of boron from silicon displayed in Fig. 3d. Conversely, the continuous increase of OH in $S_1$ is correlated to the substantial transfer of B from Si to SiO2 during anneal.

Finally we used the model to evaluate the behavior of a sample formed by a simple oxide layer deposited on silicon after implantation and subjected to a similar post anneal. We assume that the air/oxide interface boundary condition is similar to the air/nitride boundary condition of Eq. (9). Thus, for an oxide directly in contact with the chamber atmosphere, hydrogen can almost instantaneously degas resulting in a reduced concentration of OH bond in oxide and a limited boron dose loss. We compare in Fig. 4a the simulated boron profiles for $S_1$ (NA/OA), $S_2$ (NB/OA), and a simple oxide/silicon stack OA. The corresponding variation of OH bonds is shown in Fig. 4b. The oxide/silicon case OA produces a reduced boron dose loss compared to $S_1$ and $S_2$ due to a massive degassing of hydrogen from the oxide.

5. Conclusion

We have studied the impact of silicon oxide/silicon nitride capping bilayer on boron junctions in silicon. This structure typically mimics the practical case of the sidewall spacers in CMOSFET technologies formed before the dopant activation anneal. We observe a substantial dose loss induced by the out-diffusion of boron from the silicon into the oxide. The dose loss is driven by the segregation...
at the interface and the boron diffusivity in oxide modulated by the hydrogen content. To reproduce and predict the boron profiles in silicon and in silicon oxide in such configuration, we have developed a model to describe on one hand the hydrogen dynamics in the samples and on the other hand the boron diffusivity as function of the hydrogen content. We have postulated that boron diffuses in oxide through long hop mechanism, considering mobile and immobile boron species. With this model, we obtained a good consistency with the experimental profiles and in particular with the exponential-shaped boron-profiles measured in oxide. The model can emulate the capping effect of dense nitride which prevents the release of hydrogen from the oxide, as observed experimentally in literature. We also confirm the possibility of other types of hydrogen-rich nitride to inject some hydrogen into the oxide. Both phenomena tend to enhance the boron out-diffusion and impact the junction profiles in silicon.

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