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A Monte Carlo simulation study of boron profiles as-implanted into LPCVD–NiDoS polycrystalline thin films

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Abstract

This work presents a Monte Carlo simulation study of boron profiles obtained from as-implanted ions into thin films nitrogen doped silicon (NiDoS) thin films. These films are performed by LPCVD technique from Si_2H_6 and NH_3 gas sources, four values deliberately chosen, of the ratio NH_3/Si_2H_6 to obtain samples, differently in situ nitrogen-doped. Taking into account the effect of the codoping case, and the structure specificity of these films, an accurate Monte Carlo model based on binary collisions in a multi-atomic target was performed. Nitrogen atoms present in the target is shown to affect the boron profiles and confirms clearly a reduction penetration effect which becomes more significant at high nitrogen concentrations. Whereas, the fine-grained polysilicon structure, and thus the presence of grains (G) and grain boundaries (GB), is known to enhance the opposite phenomenon by assuming an effective role played by GB's in the scattering calculation process of the incident ions. This role is represented by the change in direction of the incident ion after interaction with GB without corresponding loss in its energy.

The results obtained show an enhancement of the stopping parameter when nitrogen concentration increases, while the GB interaction remains very important. This behavior is due to a great number of GB's interactions with boron atoms which gave low deflection angles. So that, the average positions described by the sequences of trajectories took place farther than what expected with channeling effect in crystal silicon materials.

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Keywords: Monte Carlo simulation; LPCVD; NiDoS; Boron implantation; Codoping

1. Introduction

Ion implantation of dopants is one of the most used techniques for controlled ion introduction into semiconductor materials [1,2]. In down-scaled device regime, the dopant profiles inside submicron layers have to be considered as challenging if we have to enhance the IC's performances with respect to the reduced dimensions [3]. The depth–concentration profiles of ion-implantation play an important role in the physical understanding of phenomena happened at the subsequent device processes. The ion-implantation is known to induce damage and hence, for subsequent thermal annealing, to increase diffusion of dopant by impurity-vacancy and/or impurity-interstitial interactions. This case is largely treated by many authors but despite the fact that a huge interesting result has been obtained when implantation is done on crystalline materials, many other points need to be clarified with random materials, where the structure presents an important degree of disorder. For instance, a particular interest is focused on polysilicon layers which are widely used as interconnections, load resistors, emitter contacts in bipolar technologies, and gate MOS transistors. Among the recent applications, this material is successfully used to perform thin film transistors (TFT) [4–6]. Especially, in VLSI/ULSI area, where both smaller and faster devices are required, it is

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necessary to perform not only the shortest junctions but also to deal with regions heavily doped and easily processed. However, it is known that after implantation, boron diffuses quickly in the polysilicon film during thermal annealing. This behaviour causes a considerable degradation of the electrical characteristics of MOS transistors (increased offset, short-circuit between drain and source, and enhanced electron capture in the gate of the silicon oxide). To reduce boron penetration, polysilicon is first, in situ nitrogen-doped, and second, boron as-implanted. For a prior achievement of this aim it is of prime necessity to know all key parameters of dopant profiles before and after annealing processes. Nowadays, the SIMS measurement experienced on implanted samples remains the existing reliable mean, with which we can obtain accurate dopant profiles, despite the destructive nature of a such technique. With the SIMS measurements, each time the examined sample is sacrificed because destroyed during the analysis process. That means, if the initial profile before annealing treatments may be known with a good accuracy, the sample on which this profile is done cannot be used subsequently for fabricating devices after the annealing process. At the same time, if we use this technique for knowing the post-annealing profile, the initial one remains always unknown because modified by the thermal treatment. Thus, it is clear that it is impossible to get these profiles together (before and after annealing) each time when we use a destroying technique. For this reason, the appropriate alternative to solve this dilemma may be by coupling simulation approach (for determination for example of the as-implanted profiles) with the SIMS experimental data (for determination of profiles after annealing treatments). So, in attempting to find mathematical models, both analytical and numerical methods have been extensively explored by several authors [1–8].

In the case of the analytical method (AM), the first model, more cited in the literature was the well-known Gaussian-like distribution parameterized with its two moments, the projected range R_p, and the standard deviation (the straggle) ΔR_p [9]. To improve this model, a third moment μ was suggested by Gibbons et al. [10] leading to have the 'Joint Half–Gaussian' (JHG) model. Later on, other authors have reported the general relationship of the Pearson-IV distribution characterized by an expression with higher moments μ_i [11,12].

On the other hand, the numerical models (NM), such as Monte Carlo methods (MC) have been successfully used to simulate a great number of phenomena inside various materials. MC methods can be divided into two major groups. The first one consists in reproducing directly the microscopic dynamics of the physical process studied, which are already statistical in its nature [13]. In this case, we used the term of 'MC simulation' and the most tools suitable to this kind of applications are basically the TRIM [14–16], MORELOVE [17], and UT-MARLOWE [18–22] codes. The second group based on 'MC methods' was devised for the solution of well-defined mathematical equations [23].

This work deals with an MC simulation study of boron profiles into as-implanted LPCVD nitrogen-doped silicon films. It will be limited only to the calculation technique of the characteristic key parameters of dopant profiles before the annealing processes. Diffusion process is the second step which will occur after and may be concerned by other further investigations.

2. Experimental setup

Growth experiments were carried out in horizontal LPCVD hot-wall furnace. 250 nm thick nitrogen doped silicon films (NiDoS) were deposited on 4″ oxidized wafers (oxide thickness: 120 nm) from silane Si_2H_6 and ammonia NH_3. The temperature and total pressure were kept constant at 480 °C and 200 mTorr, respectively. Using this deposition process, the films obtained are simultaneously in situ nitrogen-doped. The gas ratio NH_3/Si_2H_6 allows controlling the relative N/Si composition in the solid phase (between 1 and 30 nitrogen atoms for 100 silicon atoms). According to this ratio, four values have been deliberately chosen in order to obtain four series of samples in situ nitrogen-doped. After deposition process, the film structure was stabilized by a pre-annealing at 900 °C for 20 min. The average grain size (see Fig. 1) measured by using a 200 keV Temscan microscope is estimated in the range of 20–30 nm. Then, the depth–concentration profiles were assessed by secondary ion mass spectroscopy (SIMS) CAMECA IMS 4f microanalyser. In Fig. 2, we present the nitrogen concentration level which is

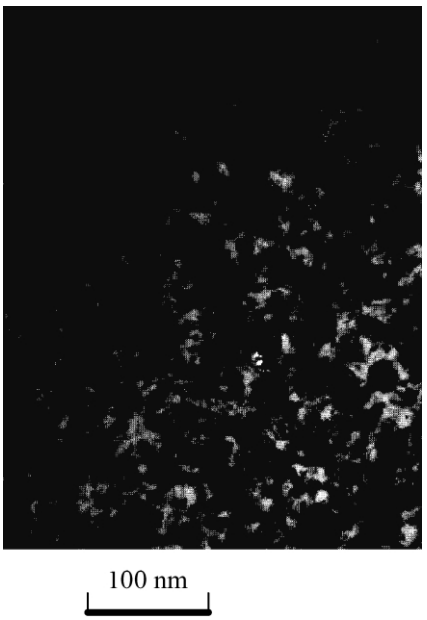


Fig. 1. TEM plan view photo of 250 nm NiDoS–LPCVD film deposited at $T_d = 480$ °C (200 mTorr) and pre-annealed at 900 °C during 20 min.

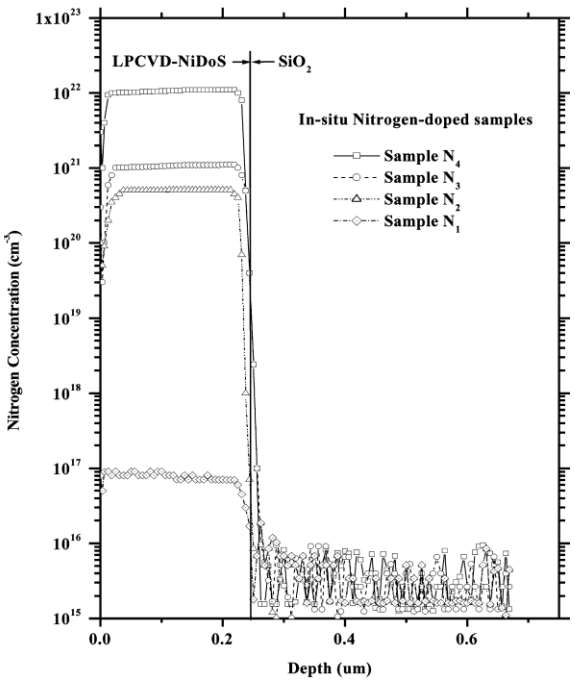


Fig. 2. SIMS profiles of nitrogen into the studied LPCVD–NiDoS samples ($N_1 = 1 \times 10^{17}$ cm^{-3}; $N_2 = 5 \times 10^{20}$ cm^{-3}; $N_3 = 1 \times 10^{21}$ cm^{-3}; and $N_4 = 1 \times 10^{22}$ cm^{-3}).

found, for the four series, equal to $N_1 = 1 \times 10^{17}$ cm^{-3}; $N_2 = 5 \times 10^{20}$ cm^{-3}; $N_3 = 1 \times 10^{21}$ cm^{-3} and $N_4 = 1 \times 10^{22}$ cm^{-3}. A complete study concerning these films have been previously reported in refs [24–26]. Then, after deposition, in-situ-doping, and pre-annealling stabilization, all these films are boron-implanted with the same implant dose $D = 5 \times 10^{15}$ cm^{-2}, at the low energy $E = 10$ keV.

3. Results and discussion

It is well-established that in penetrating the target, the energetic ions lose energy due to both the elastic collisions with atomic nuclei and the inelastic interaction with electrons. In ion-nuclei collisions (nuclear stopping), energy is transmitted to the target atoms; the ions lose velocity and change direction [27]. The interaction between ions and electrons (electronic stopping), causes the ions to lose energy without corresponding changes in the direction [27].

The first mechanism is modeled using the binary collision approximation [28]. In order to account for the nuclear scattering events between B–Si, B–N, N–Si, and Si–Si atoms, Ziegler, Biersack and Littmarck (ZBL) specific pair atom potentials for these pairs are implemented in the program [29]. For the electronic stopping, we have used the approach of calculating the stopping power for a uniform density electron gas, as it is usually done for the simulation of moving ions [30–33].

In addition to these two mechanisms just mentioned above, we have supposed that the interaction between grain boundaries (GB) and boron incident ions should happen with the change in direction without corresponding loss in energy. This fact is considered according to what is seen in single crystal targets presenting many channels that ions can follow. Along these channels, the open lattice structure offers few opportunities for ion-nuclei collisions. Ions will thus travel two or three times farther when the incident beam is aligned with a low-index crystallographic direction [27]. In random materials such as polysilicon case, GB are supposed likely acting as the same manner to these open ways. However, the total distance traveled due to the interaction between each B ion and GB is not a straight line but with random directions. Because, when crossing a GB the B ion has a larger probability to follow the open way associated to the randomness void region between grains separation areas. At the same time, this ion passing through a boundary has also a larger probability to change direction and thus, the new scattering angle may be calculated at each time. The most commonly used models which do not model the energy loss of the incoming ion are namely those of Lindhard and Scharf [30], and Firsov [31]. So, when coupling Firsov model [31] for energy determination with the classical scattering theory for angle calculation it becomes possible to simulate this kind of situation. In another manner, and just for a clear explanation of the interaction result between B ions and GB's, this behavior may be supposed to be equivalent to collisions between B ions and virtual flexible atoms. These bodies are imagined to be represented as supple rubber marbles. Even this concept contains unphysical parameter but it represents a scheme by which we can characterize the change in direction of the incident ion after collision with the virtual atoms without corresponding loss in the energy.

Moreover, if we refer to what occurred during diffusion process (post-annealing step), quite differences in diffusivity between G and GB are confirmed. As it can be seen in Fig. 3, the comparison between our SIMS profiles (case of the sample N_1) and other reported results is made. A good agreement is obtained between boron as-implanted profiles ($D = 5 \times 10^{15}$ cm^{-2}, $E = 10$ keV) of LPCVD-Si films published in Ref. [34] by Nédélec et al., and results obtained with the case of our N_1 sample which has the same dose ($D = 5 \times 10^{15}$ cm^{-2}), and the same energy ($E = 10$ keV). But, a great discrepancy is shown between these mentioned results and those published in Ref. [19] by Klein et al., and Ref. [21] of Yang et al. for boron profiles as-implanted into crystal silicon and simulated by UT-MARLOWE code. To obtain comparable penetration, implantation energy must be higher than 65 keV in the case of c-Si materials instead of 10 keV needed for LPCVD-Si materials. At least, for the same penetration value of our N_1 sample equal to 70 nm, SRIM code calculations

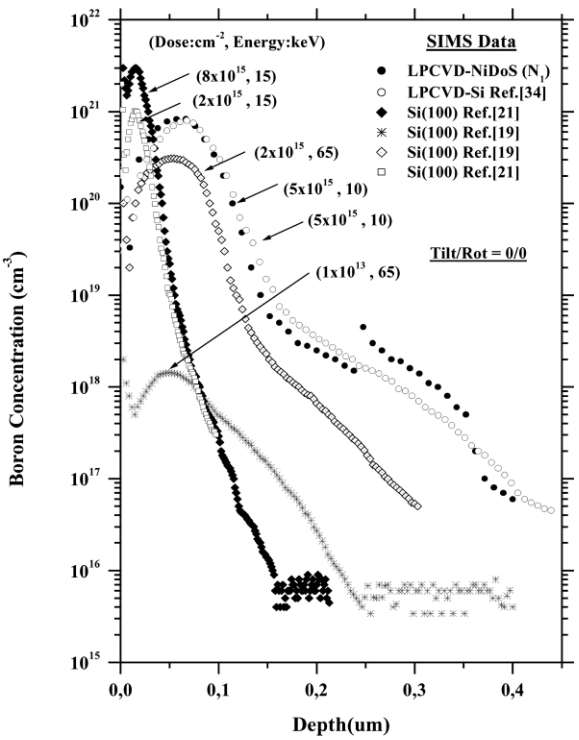


Fig. 3. Comparison between our SIMS experimental profile (case of the sample N_1) and other reported results as the LPCVD-Si films published in Ref. [34] by Nédélec et al. ($D = 5 \times 10^{15}$ cm^{-2}, $E = 10$ keV), and those published in Ref. [19] by Klein et al., and Ref. [21] of Yang et al., for boron profiles as-implanted into crystal silicon with varied dose D and energy E.

(Table 1) give 72.8 nm for an energy of 20 keV, which is, roughly two times higher than what we have used in our work (10 keV). So that, it is clear that the R_p penetration parameter in fine-grained and randomly oriented materials are more important than in monocrystalline ones. It seems clearly that a large part of these differences is attributed to the presence of G and GB structure in such materials.

Indeed, if we compare another phenomenon between these two kinds of materials which occurs during diffusion process (post-annealing step), the predicted diffusivity along the GB, with low concentration doping level, is ≈ 100 times faster than in c-Si material [1,3]. In the case of high concentration doping level, Nédélec et al. [34] have found a value of $(10D_G \leq D_{GB} \leq 100D_G)$ for boron-implanted polysilicon layers. In another publication, Losee et al. [35] have reported a value of $(D_{GB} \leq 100D_G)$ for phosphorus diffusion in polysilicon, which is significantly different from what has been reported elsewhere in the literature [3]. Therefore, in order to take into account this structure specificity, we have separated the ballistic collisions from GB interactions. For silicon and nitrogen atoms, the elastic scattering of the incident energetic ion by the target nuclei are calculated by means of classical scattering theory [36]. On the other side, it should be of great importance to calculate the scattering angle θ, in the center of mass coordinate system while there is no contribution in the total slowing down process. In this scattering calculation process based on the asymptotic scattering angle, we have implemented additional iterations issued from the test of target species. This test consists to differentiate between collisions with effective ions of the target (Si, N) and interactions with GB's. This assumption yields to introduce other supplementary random number generators. In addition to R_1, R_2, and R_3 the classical three random number

Table 1
Comparison between our results and those reported in previous references [14,16,17,19,21,34] for the projected range R_p, the standard deviation ΔR_p, the skewness γ, and the kurtosis β

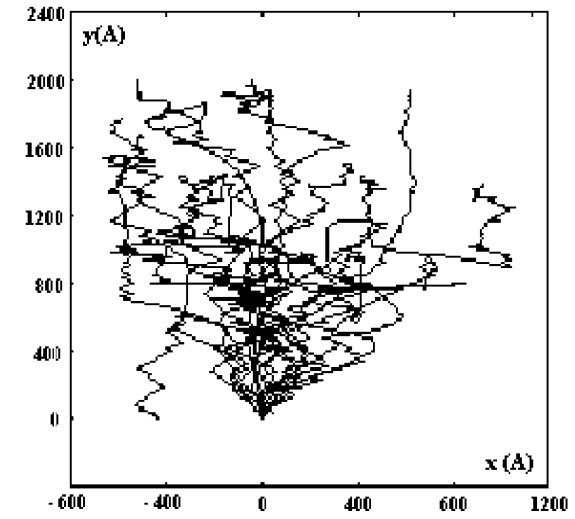
Sample	Dose (cm^{-2})	Energy (keV)	R_p (nm)	ΔR_p (nm)	Skewness γ	Kurtosis β	Ref.
B–Si (100)	8×10^{15}	15	15.4	12.1	−0.06	3.0	[19,21]
	2×10^{15}	15	14.9	12.0	−0.06	3.0	[19,21]
	2×10^{15}	65	53	69	−0.06	3.0	[19,21]
	1×10^{13}	65	49	60	−0.06	3.0	[19,21]
B–SiO_2	5×10^{15}	10	40	50	−0.08	3.5	[14]
B–Si (100):	SRIM results	10	37.4	20.3			[14,16,17]
		15	55.1	27.5			
		20	27.8	33.9			
		65	227.4	73.3			
B–LPCVD–Si	5×10^{15}	10	68	80	−0.2	2.5	[34]
B–LPCVD–NiDoS	5×10^{15}	10	N_1 67	81	−0.05	4.0	Our results
			N_2 57	71	−0.03	3.0	
			N_3 44	71	+0.02	3.5	
			N_4 41	51	+0.04	3.0	

generators, we have used R_4 with two logical states ($R_4 = 0$, or $R_4 = 1$), which allows us to separate effective ion collisions from GB interactions. Another similar random number R_5 having also two logic states ($R_5 = 0$, or $R_5 = 1$) is necessary to differentiate between silicon and nitrogen atoms. If $R_5 = 0$, an atom of a given species will act as the scatterer; if $R_5 = 1$, then an atom of another species will act as the scattering center, and so on.

Several particle histories are followed and processed taking into account n_B, n_N and n_{GB} events, where n_B, n_N are the total numbers of collisions (elastic and inelastic) with boron and nitrogen atoms, respectively, and n_{GB} is the total number of interactions with GB. A history was terminated when the ion energy decreased from 10 keV to below a predetermined energy (fixed at 5 eV). The calculation is repeated for each of the incident ions upon the target until the total number of particles in the beam has been considered. When all particles trajectories are calculated, ion positions can be determined and histograms can be generated. The final results are stored in a grid as a function of the depth, and then deliberately converted into depth-concentration profiles for prior comparison with the SIMS data. Fig. 4 shows a test trajectory plots for small input data ($n = 100$, $E = 10$ keV, and Alpha $= 90°$). A significant proportion of particles appears to have stopped between 80 and 200 nm whether those back-scattered seems to be negligible. Compared with other reported data we can observe similar results where the stopped particles are also ranged between 80 and 240 nm with no back-scattered ones. So, a good agreement is mentioned between results of this work and those published in Ref. [1].

The effect of the nitrogen atoms on the boron impurity, is seen to be different from the case when the films were boron-implanted without nitrogen (see Fig. 5). A similar effect was also observed after a subsequent annealing treatment (during diffusion) in which the boron diffusion coefficient is found to decrease. This behavior may be explained by the fact that the number of collisions and interactions with back scattered sequences increases. This enhancement is suitable with the assumption if we effectively consider a great number of collisions with the incident ion take low deflection angles, and therefore, the average of the ion positions will be seen to be stopped early as expected. The maximum of this reduction of penetration is reached at the concentration limit of C_{limit} (N) $= 1 \times 10^{22}\,cm^{-3}$. Fig. 5 shows the main results obtained with this program. In trying to ensure that effectively the N concentration has a serious impact on the reduction of boron penetration, we have used the following calculation procedure.

As the target contains two atoms Si and N, if we assume GB's equivalent to the virtual atom (mentioned above) with a flexible atomic mass, $A_v = A_N R_6$, where A_v and A_N are the mass of virtual and nitrogen atoms, respectively, and R_6 ($0 < R_6 < 1$) is an additional random number generator, the following results are obtained. Apart the two limit cases,



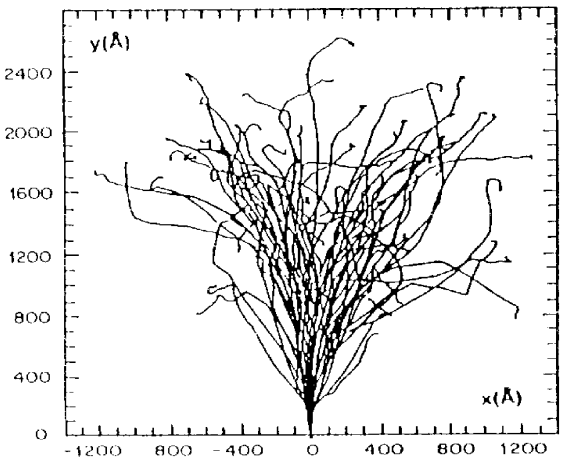


Fig. 4. Comparison between the obtained results for small input data ($n = 100$, $E = 10$ keV, and Alpha $= 90°$); in the case of this study (figure represented above) and those reported in Ref. [1] by Sze et al. (figure represented below).

when $A_v = 0$, and $A_v = A_N$, considered as rare events, and only values between these limits of the many encounters in the target cause significant deflections. Normally, deflection angles are small and account for the multiple scattering, which gradually changes the direction of the ion's motion. When $A_v = 0$ and knowing that $A_{Si} = 2A_N$, the target becomes the same case as the classical c-Si material codoped with B and N. In the other side, when $A_v = A_N$, two opposite phenomena will take place due to simultaneous presence of N and GB's. The increase of the nitrogen concentration should tend to reduce the boron penetration, whereas the increase of the 'virtual atom concentration' should act to enhance the boron penetration. At the end, and even if the nitrogen effect part is clearly

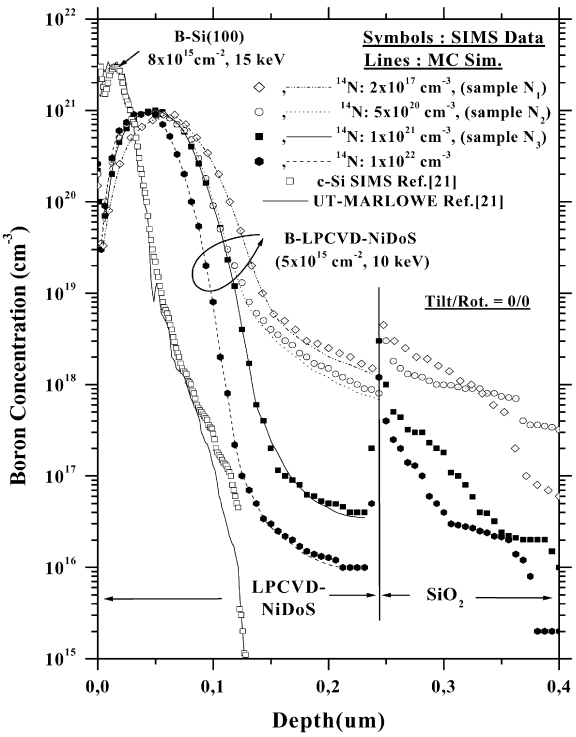


Fig. 5. MC simulation results compared to SIMS experimental data.

evidenced, the other part related to GB interactions remains more important. So, the average positions described by the final sequences of each trajectory take place too farther than what expected with channeling effect in crystal silicon materials.

Table 1 presents the results obtained using this program for the main as implanted profile parameters of boron atoms into LPCVD–NiDoS films (the projected range R_p, the standard deviation ΔR_p, the skewness γ, and the kurtosis β). For R_p values (first moment which measures the projection of the total path length on the direction of incidence), we observe clearly a decreasing behavior of the projected range with the increasing nitrogen concentration. R_p varies from 70 nm in the case of the sample N_1 (without nitrogen) to 41 nm in the case of N_4 (heavily nitrogen doped). Consequently, the top of the curves tends to become too near of the surface. On the other hand, with this decrease, is also associated a decrease in the standard deviation (second moment which measures the spread of the distribution). ΔR_p values drop from 81 to 51 nm. The diminution of both R_p and ΔR_p is related to the delay effect induced by the presence of nitrogen atoms which leads to place the peak of the distribution closer to the surface.

For the third and the fourth moments, it is well-known that the skewness characterizes the asymmetry of the distribution and the kurtosis measures the flat degree of its top. The sign of γ indicates the direction of the skewness. For $\gamma > 0$, the profile is steeper towards the surface, and for $\gamma < 0$, the profile is steeper towards the bulk side [9]. The parameters γ and β are responsible for the total skewness. Indeed, if we compare our results to those reported in Table 1, we can see that a quiet difference is visible. In the case of boron implantation into monocrystalline silicon wafers, the profiles become more and more negatively skewed because the channeling effect very important in these materials. To obtain correct and reproducible profiles, boron ions were implanted at both low energy and into fine-grained polycrystalline films. For this reason, we have used this low energy of implantation (10 keV) and, at the same time, these LPCVD–NiDoS films which can be considered as an intermediate materials between single crystal silicon (c-Si), and amorphous silicon (a-Si). The profiles of our results seem to have a changing behavior from a negative skew (-0.05 for the case of N_1) to a positive one ($+0.04$ for the case of N_4). However, although this remarkable change in the skewness values, the variations of the obtained values remain closer to zero. Knowing that the typical Gaussian distributions have in general, a skewness of 0 and a kurtosis of 3 [1], we can see that, for our case, both low energy and high nitrogen concentrations are suitable to have profiles clearly very closer to zero skewed. For high energy ($E > 100$ keV), the profiles have generally negative skew, which increases more quickly but can also become positive for sufficiently low energies and for heavier ions.

So, qualitatively, when compared to other results published previously [14,16,17,19,21,34], we believe that more comprehensive investigations in this way may open other perspectives to a better understanding of specific phenomena concerned by these materials.

As indicated in Fig. 5, the improvements of the model combined with the codoping effects, present a good agreement between simulated profiles and experimental ones obtained by the SIMS technique.

4. Conclusion

The SIMS technique associated with Monte Carlo simulations have been used to analyze the boron implantation/diffusion mechanisms into LPCVD nitrogen-doped silicon films. Nitrogen doping is often used to impede boron diffusion occurring during thermal annealing processes. Boron profile parameters are quite different before and after thermal annealing processes. For this reason, the results of these Monte Carlo simulations should be considered as the input data needed for a prior simulation of diffusion mechanisms concerned by the next step occurring after the annealing processes.

Thus, in order to explain what has happened during the first stage, Monte Carlo simulations have been developed to predict these results. In such models, the specificity of the

film structure has been taken into account by introducing random interactions between GB's and incident ions. These interactions, in one hand, are considered to influence effectively the scattering angle in the center of mass coordinate system but, on the other hand, they have no contribution for the energetic slowing down process. With this approach, it becomes not only enabling to extract boron profiles parameters issued from any ion implantation process but also from processes containing, first, in situ nitrogen doping, and second, boron ion implantation. The results show that all of boron profile parameters are quite different as a function of nitrogen concentration. Consequently, these results will have a key role for the later steps process when the thermal diffusion of boron atoms into doped silicon films is dependent of those done before.

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