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ANALYTICAL MODELLING AND SIMULATION OF THE SELF-LIMITATION PROCESS DURING THE CHEMICAL ETCHING OF THE BORON-DOPED SILICON LAYERS FROM BN SOLID SOURCES FOR MICROMECHANICAL APPLICATIONS

Florin GAISEANU[1]

Abstract. *An analytical model of the boron diffusion in silicon from the solid boron nitride (BN) sources is presented and is applied to simulate the chemical etching rate and the etching time for the achievement of the silicon micromechanical elements within the bulk micromachining technology. It is shown that the diffusion profile obtained under such conditions is a consequence of a diffusion mechanism by electrically charged vacancies within the high concentration region, where the diffusion coefficient is proportional with the diffusion concentration, and by neutral vacancies in the "tail" (intrinsic) region, where the diffusion coefficient does not depends on concentration. Analytical relations were deduced to express the boron diffusion profile in the high-doping region and in the tail (intrinsic) region. Such relations permitted to express in an analytical way the chemical etching rate and the etching time during the chemical etching process used within the bulk micromachining technology to obtain micromechanical elements, particularly silicon membranes, under well controlled technological conditions.*

Keywords: Analytical modeling; boron diffusion in silicon; boron nitride sources: high concentration profile; diffusion tail; etching rate simulation: etching time simulation.

1. Introduction

The bulk micromachining technology is mainly based on the specific property of the highly boron-doped silicon layers, consisting in a drastic reduction of the chemical etching rate of the silicon. Such property allows to fabricate micromechanical elements by chemical etching process of the silicon layers after the application of a selective boron doping technique [1-3]. It was shown that boron-doped silicon layers with doping levels exceeding values of the order of 10^{20} cm^{-3} become effective stop-layers during the chemical etching of silicon in alkaline type solutions (KOH, NaOH, LiOH) [2] or in EDP (ethylene-diamine-pyrocatechol) [1]. A chemical solution based on the tetramethyl ammonium hydroxide (TMAH) with isopropyl alcohol (IPA), showing similar etching properties was also earlier proposed [2]. The boron-doped silicon layers are used as the most convenient etch-stop technique, based on the capability to control not

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[1] PhD, Solid State Physics (University of Bucharest), Principal Senior Researcher (Professor), Science and Technology of Information Bucharest (Romania) and Barcelona (Spain) - (e-mail: fgtext@yahoo.es).

only the junction depth of the boron diffusion in silicon [3], but also the distribution of the diffusion concentration into the silicon bulk, i.e. the diffusion profile [4,5].

An indispensable objective of the technological engineering in the bulk micromachining technology is the effective and efficient control of the chemical etching process to obtain a very well defined thickness of the micro-mechanical elements, according to the designed requirements, as it is the case for instance for the fabrication of the sensitive elements (silicon membrane) of the silicon capacitive pressure sensors for biomedical applications [5]. As the boron diffusion profile in silicon at high concentration depends not only on the concentration itself but also on the doping source [6,7], it is therefore of great interest to find adequate solutions to control the characteristic parameters not only of the etching process, but also of the boron diffusion and the associated processing conditions. The boron diffusion profile in silicon presents a continuous decrease of the concentration from the silicon surface to the bulk, that depending on the diffusion conditions, i.e. diffusion time, temperature and doping technique [8, 9]. It is therefore expected that such a decrease would determine a continuous variation of the etching rate and a consequent variation of the etching time with the diffusion depth. To obtain reproducible thickness of the silicon membrane and to eliminate the stress gradient induced by the high variation of the high doping concentration of the diffusion profile, it is necessary to control therefore strictly the technological parameters of the self-limitation process.

A general analytic expression of the boron diffusion profile after the diffusion from a solid boron nitride (BN) source was not published up to date. In this paper we present an analytical model which allows to control the self-limitation process of the chemical etching, taking into account a correct shape of the boron diffusion profile including, besides the high-doped region of the profile where the boron concentration C>ni (ni - the intrinsic carrier concentration at the diffusion temperature), the contribution of the diffusion in the range of the boron concentration where C < ni. On this basis the chemical etching rate and the chemical etching time is simulated under some specified etching conditions. However, the obtained results allow to control the key parameters of the self-limitation under various technological conditions of silicon doping and etching process.

2. ANALYTICAL MODELLING AND SIMULATION OF THE BORON DIFFUSION PROFILE IN SILICON FROM BN SOURCES

The profile of the boron diffusion in silicon shows contradictory results. From one side, there are evidences that this profile would correspond on the high concentration range (C>ni) with an atomic diffusion process by a vacancy mechanism, as proposed by Fair [10]. However, Gaiseanu shown that the so called "universal" profile proposed by Fair [10], obtained by the representation of the experimental data as C/Co vs. x/x_j, where C is the boron concentration, Co the surface value Co=C(x=0), x the diffusion depth and x_j a depth value corresponding to $C=10^{18}cm^{-3}$, is actually well described by a solution of the diffusion equation with the diffusion coefficient of the form $D=Do(C/Co)^{1/2}$ instead of D=Do(C/Co) (Do=D(x=0)), which would be characteristic for such a mechanism [6].

Taking into account this discrepancy, after the gold diffusion in silicon was explained by a so called "kick-out" mechanism proposed by Gösele [11], where the silicon self-interstitial atoms seems to play a protagonist role, a dominant mechanism of boron diffusion in silicon by interstitials contribution was further proposed [12]. Trying to clarify this ambiguity, Gaiseanu determined [8, 9] and shown [7] that the boron diffusion from a solid (non-oxidizing) BN source, both chemically and electrically measured, follows a right mechanism by vacancies, proposed earlier by Fair [10]. He also shown that the discrepancy is due actually to the different distinct conditions at the silicon surface during the diffusion from various diffusion sources [7]: while during the diffusion from a liquid (oxidizing) BBr_3 liquid source the oxidation process generates additional point defects, i.e. silicon self-interstitials enhancing the diffusion, during the diffusion from a (non-oxidizing) BN source this mechanism is not significant, the dominant one being the diffusion by vacancies [13].

2.1. Experimental data

In Fig.1 it is shown the boron diffusion profile in silicon obtained after the diffusion from a BN source at 1100°C for the diffusion time t = 120min. [8], analyzed from the point of view of the diffusion mechanisms [7, 9]. As it can be seen in this figure, at concentrations higher than the intrinsic concentration (C>ni), defined as extrinsic diffusion range, useful for the micromechanical applications, the boron diffusion coefficient shows a specific variation with the boron diffusion concentration determined by the dependence D=Do(C/Co).

The main conclusions derived from this analysis are: (i) the boron diffusion profile shows a distinct behavior (D=Do(C/Co)) in the extrinsic range (C>ni) with respect to the behavior (D=Di constant) in the intrinsic range (C<ni), defined as the diffusion "tail"; (ii) the entire quantity of boron is electrically active, because not distinct differences results from the two profiling methods, allowing therefore to relate the entire boron concentration to the carrier concentration. This behavior is determinant for the doping properties of the silicon diffused layers on the high

concentration range, where the carrier concentration n is fully given in this case by the electrically charged boron atoms (C=n) and allows to define the interface between the high concentration region and the tail region by the relation C=ni (Fig. 1).

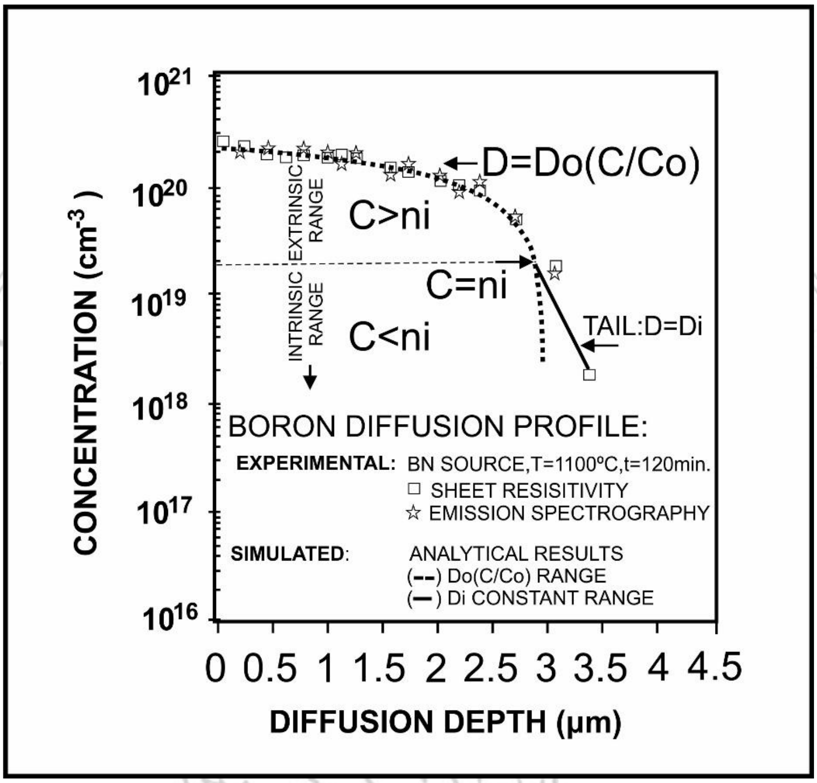

Fig. 1. Boron diffusion profile in silicon experimentally determined by electrical (sheet resistivity) method and by chemical (emission spectrography) and simulated (dashed and full line) after the diffusion from a BN source at 1100°C for 120min.

2.2 Analytical modelling and simulation

As it can be seen from Fig. 1, the high concentration region (C> ni) of the boron diffusion profile resulting from the boron diffusion in silicon from a boron nitride (BN) source shows a concentration dependence of the boron diffusion coefficient D of the form D ~ C [7]. To solve analytically such a problem of diffusion from an infinite source (permanent contact of the silicon surface with the doing source), it was used the substitution $X=x/2(Dot)^{1/2}$, which reduces the two-dimensional problem to an one-dimensional problem, with a unique variable X. Moreover, the natural behavior of the diffusion process under these diffusion conditions is that both the boron concentration and the diffusion flux should become null faraway from the surface, at a finite value of X (in this case it was deduced that this characteristic value is $\sqrt{(2/3)}$), just because of the specific dependence D ~ C [14] and as it can be also seen also from Fig. 1. This behavior is really different from that associated to a diffusion with a constant diffusion coefficient, where the diffusion problem delivers the well-known erfc-type solution, C tending to a null value only if $x \to \infty$ [15].

X is a compact variable, including both x and t. Therefore, we can approach the general diffusion problem of infinite source in two distinct, but coupled problems: one associated with the extrinsic range, where $D=Do(C/Co)$ and another one with the intrinsic range, where the interface acts as an infinite diffusion source with the same concentration ni, and the diffusion coefficient Di constant, independent of concentration. Two explicit analytical relations are in this way obtained: on the extrinsic range the concentration can be expressed by the relation:

$$C = Co[\, 1 - (2/3)^{1/2}X \; - \; (1/2)\, X^2 \,] \qquad (1)$$

and on the intrinsic range the concentration can be described by the explicit relation:

$$Ci = ni \,\mathrm{erfc}\,(rX)/\, \mathrm{erfc}\,(rXi) \qquad (2)$$

where Xi is deduced from rel. (1) with the condition $C(Xi)=ni$ as:

$$Xi = (2/3)^{1/2}\ \{ -1 + [1+3(1-ni/Co)]^{1/2} \} \qquad (3)$$

and $r = (Do/Di)^{1/2}$, Di is the intrinsic boron diffusion coefficient (which is not concentration dependent).

Rel. (1) seems to be very simple, but in spite of this simplicity, this relation was deduced under rigorous conditions from the diffusion equation. Taking into account the rapid decrease both of the concentration and of the diffusion flux far way from the surface just due to the dependence D ~ C, and searching a solution as a series form, it was found that this solution converges very rapidly, so only a few terms are sufficient (approximation <1%) to fully describe the boron profile on this range. The agreement between the theoretical profiles given by rel. (1) and (2) and the experimental data, well supports the theoretical model (Fig. 1).

In Fig. 2 are shown some simulated diffusion profiles after the boron diffusion from BN solid sources for 120min at 1100°C, 1150°C and 1200°C. As discussed above, these profiles were simulated including the diffusion both in the extrinsic and intrinsic range of concentration.

The solid solubility Co in silicon is still a controversial parameter [16] because up to date it is not clear that the diffusion characteristic parameters depends on the used diffusion source, as discussed above. However, in this paper were used for simulation the data reported earlier by Vick and Whittle [17], because within a study on the solid solubility recently reported [16], it was shown that these data are well supported by more than one documental source. Indeed, the used diffusion source in that experiments was a boron rich glass (B_2O_3) layer, pyrolytically deposited onto the silicon surface, so the experiment was performed avoiding the oxidation conditions, similarly with the diffusion from a BN source. The intrinsic values of the diffusion coefficient Di were also used from the same source [17], to assure the coherence of the data. However, we have to note that although these data have quite close values at the high diffusion temperatures shown in Fig. 2 with that of the Fair's results (obtained by the fitting of more data collected from literature [10]), at lower temperatures these data are different.

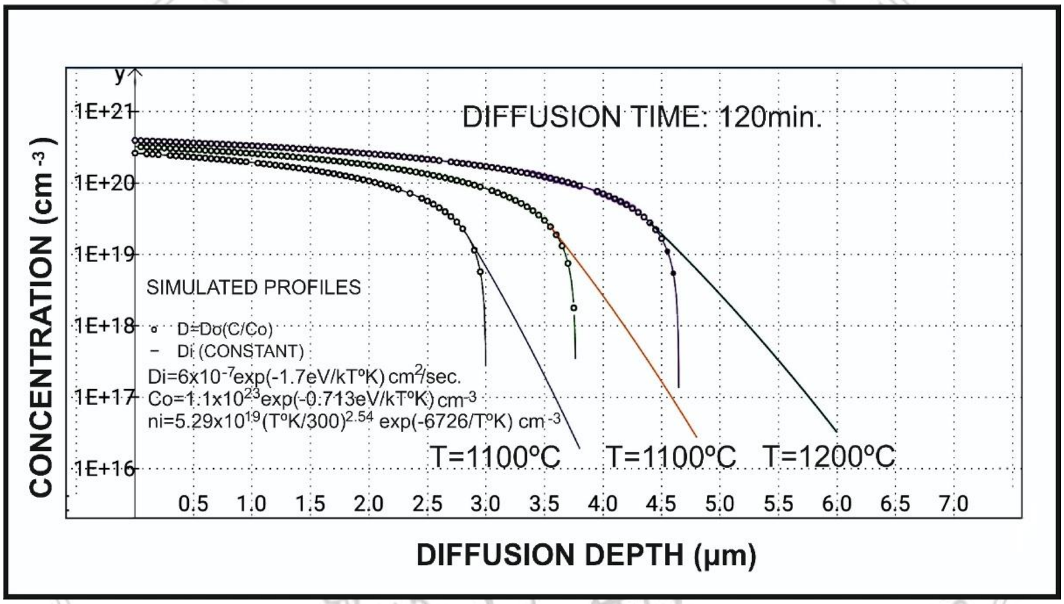

Fig. 2. Boron diffusion profiles in silicon simulated according to the analytical results after the boron diffusion from the BN source at 1100°C, 1150°C and 1200°C for 120min.

An accurate expression for ni seems to be still under debate [18], but for the diffusion purposes the used data for the intrinsic carrier concentration were calculated from a formula reported relatively recent, claiming accurate results [19]. The data of Di and Co were calculated from an Arrhenius type variation obtained by a fitting procedure on the experimental data reported earlier [17], all of them expressed as a function of the absolute temperature T°K as:

$$ni = 5.29x10^{19}\ (T°K/300)^{2.54}exp(-6726/T°K) \qquad (4)$$

$$Di = 6x10^{-7}exp(-1.7eV/kT°K) \qquad (5)$$

$Co = 1.1x10^{23}exp(-0.713eV/kT°K)$ (6)

where k is the Planck constant, the concentrations ni and Co are expressed in cm^{-3} and the diffusion coefficient Di in cm^2/sec.

3. SIMULATION OF THE SELF-LIMITATION PROCESS

The model developed above is used to describe the etching rate and the etching time necessary to process the doped silicon layer within the bulk micromachining technology. During a standard chemical etching process, the etching front starts from the back side of the silicon wafer and advances in the silicon bulk with a constant etching rate, where the silicon is uniformly doped with a very low concentration (of the order of 10^{15} – 10^{16} cm^{-3}) [4, 5].

A quantitative analysis of the etching rate as a function of the p-type doping concentration in the silicon bulk and of various types of chemical solutions was presented earlier [20], but no reference about the depth variation of the concentration in the real p-doped silicon layers was made. In such layers, when the chemical etching front attains the boron-doped region, defined by a silicon p-n junction with the depth xj, the boron doping concentration increases gradually from the low-doped substrate to the highly-doped silicon region of the diffusion profile. This increasing determines a corresponding modification of the chemical etching rate and of the chemical time, depending on the specific shape of the boron diffusion profile [4, 5], so a corresponding suitable analysis of such a real system should be actually done. Moreover, this analysis is also necessary for the fabrication of the micro-mechanical elements, because it is extremely important not only to obtain reproducible thickness of these elements, but also to remove the strong concentration gradients, in order to avoid the mechanical stress induced by the boron diffusion profile in the silicon layers, as it was discussed earlier [5].

3.1 Chemical Etching Rate

It was previously found [20] that the etching rate R of the uniformly boron-doped silicon layers depends on the boron concentration as:

$R/Ri = [1+(1+C/Cc)^a]^{4/a}]$ (7)

where Ri is the etching rate of the low-doped silicon substrate, Cc is a critical value in the range $(2\text{-}4)x10^{19}$ cm^{-3}, depending on the etching temperature Te and on the concentration of the etching solution of the alkaline type (KOH, NaOH, LiOH) or of EDP, and “a” is a shape parameter. It was found that a=4 for 10% KOH (NaOH, LiOH) and ethylene-diamine-based solution (EDP) type S, while a=2 for 24% alkaline-type solutions [20]. C in rel. (7) is the doping level, and may be expressed by the analytical relations (1) and (2), each of them on the corresponding range of variation of concentration. In such a way, in Fig.3 it was simulated the variation of the ratio R/Ri with the depth x into the silicon boron-doped layer after diffusions at 1100°C, 1150°C and 1200°C by using a chemical etching solution for which a = 4, and in Fig. 4 the corresponding variation for a=2. The values of the etching temperatures of solutions were [20]: 110°C for which $Cc=3.0x10^{19}$ cm^{-3}, 81°C for which $Cc=2.9x10^{19}$ cm^{-3} and 66°C for which $Cc=2.8x10^{19}$ cm^{-3}.

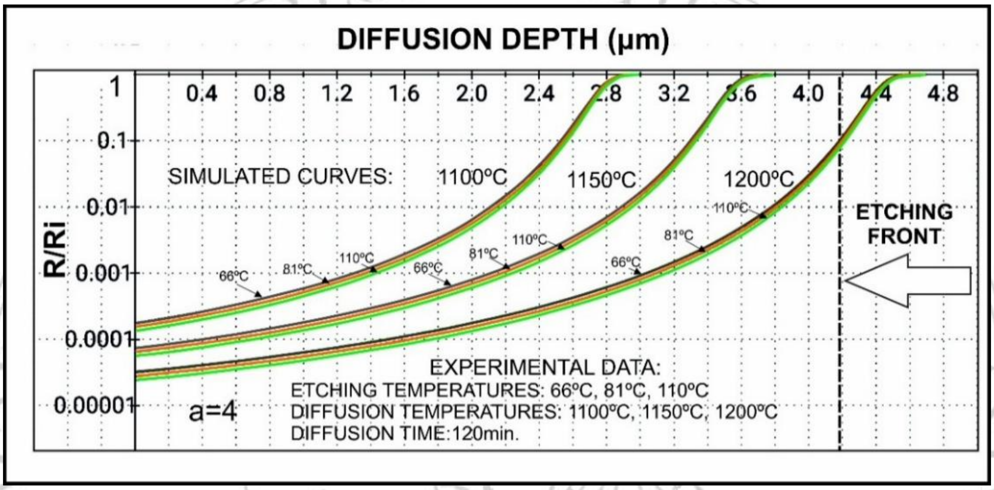

Fig. 3. The variation of R/Ri ratio during the chemical etching process of the boron diffused silicon layers in a=4 type etching solutions, simulated according to the analytical results describing the boron profile after the diffusion from a BN source at 1100°C, 1150°C and 1200°C for 120min. The temperatures of the etching solutions are: 66°C, 88°C, 110°C.

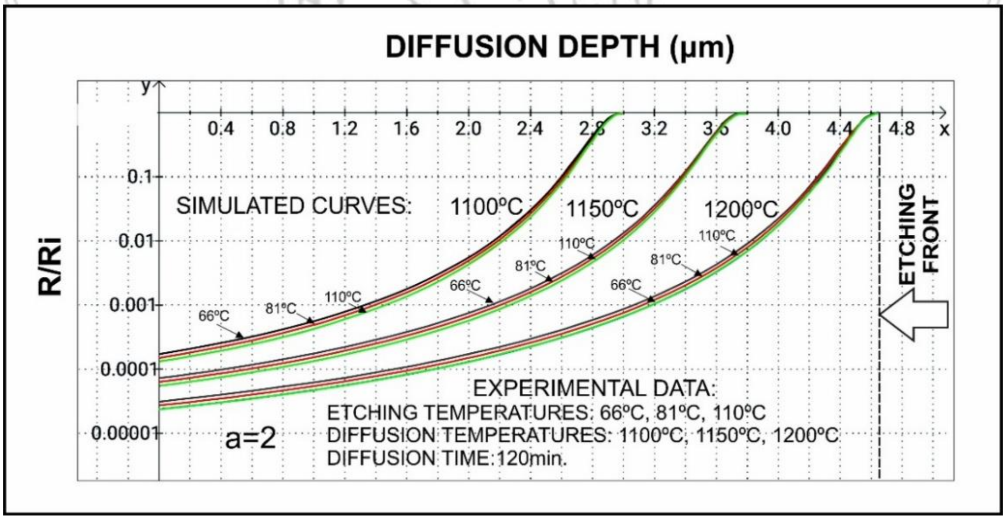

Fig. 4. The variation of R/Ri ratio during the chemical etching process of the boron diffused silicon layers in a=2 type etching solutions, simulated according to the analytical results describing

the boron profile after the diffusion from the BN source at 1100°C, 1150°C and 1200°C for 120min. The temperatures of the etching solutions are: 66°C, 88°C, 110°C.

From the experimental data reported earlier [20], we can deduce the following relation which seems to fit the experimental values of Cc:

$$Cc = 5.5 \text{ x } 10^{19} \exp(-0.025eV/kT^{o}K) \qquad (8)$$

allowing to calculate Cc (expressed in cm^{-3}) for any temperature of etching solution.

The curves represented in Fig. 3 and Fig. 4 could be used as a technological guide to design a chemical etching process. Although the variation of the etching rate as a function of the temperature of the etching solutions is not too large comparatively with that corresponding to various diffusion temperatures, the control of fine differences is very important within a technological process to sharply define the thickness of the micro-mechanical elements. Such differences are marked also by the etching time, which is a cumulative parameter controlling actually the etching process.

As it can be seen from Fig. 3 and Fig. 4, the doping level strongly influences the chemical etching rate, especially starting from the concentration around ni value, which is of the order of 10^{19} cm^{-3}. This value can be calculated in terms of depth from rel. (4), taking into account the definition of $X=x/2(Dot)^{1/2}$. Fig. 3 and 4 allow to evaluate the efficiency of the etching process as a function of the diffusion depth. The criteria concerning a certain efficiency could be established according to the graphs represented in these figures. If a low remained concentration gradient inside of the diffusion layer is requested, then the etching process should be also continued (not limited to) the region of the high boron concentration.

Low concentration gradients after the diffusion from BN sources can be obtained in a region near the silicon surface. The width of these regions depends on the diffusion time and on the diffusion temperature. As it can be seen from Fig. 3 and 4, if membranes or micro-mechanical elements with a large thick are necessary, then a higher diffusion temperature should be used. This permits to choose a certain depth on the region near the surface where the etching process should stop, with a certain corresponding rate ratio value.

From Fig. 3 and 4 can be evaluated the thickness of the doped layer where the gradient is lower. If it is necessary for instance to obtain a membrane or a micro-mechanical element with a thickness of 2µm, this could be performed by processing the boron doped layers at 1100°C, 1150°C, 1200°C or any other temperature, but the boron diffusion gradients will be different, depending on the applied diffusion temperature. From the graphs represented in Fig. 3, it can be seen that a R/Ri efficiency of $6.4x10^{-3}$ after diffusion at 1100°C, $7.9x10^{-4}$ after a diffusion at 1150°C and $1.7x10^{-4}$ after a diffusion at 1200°C result by using an a=4 type etching solution at Te=110°C. The corresponding values for a=2 are $5.5x10^{-3}$, $7.4x10^{-4}$ and $1.7x10^{-4}$ respectively, as deduced similarly from the graphs represented in Fig. 4. In each case however the gradient of the boron concentration is different, the optimal (smaller) one corresponding to higher processing diffusion temperature.

A comparison between the ratio R/Ri associated with a=4 and a=2 type solutions for Te=110°C after the boron diffusion from BN source at T=1100°C, 1150°C and 1200°C is shown in Fig. 5. From this figure it can be seen that the difference is really significant for moderate or low etching efficiency (R/Ri $\leq$ 0.01), corresponding with the diffused region of concentration lower than about 10^{20} cm^{-3}. However, as it was already remarked above, a fine "tuning" of the conditions of the etching process is necessary to take into account when a certain solution, either a=4 or a=2 type, would be used in the low or high concentration range, for a correct monitoring of the chemical etching process, as shown in Fig. 3 and Fig. 4.

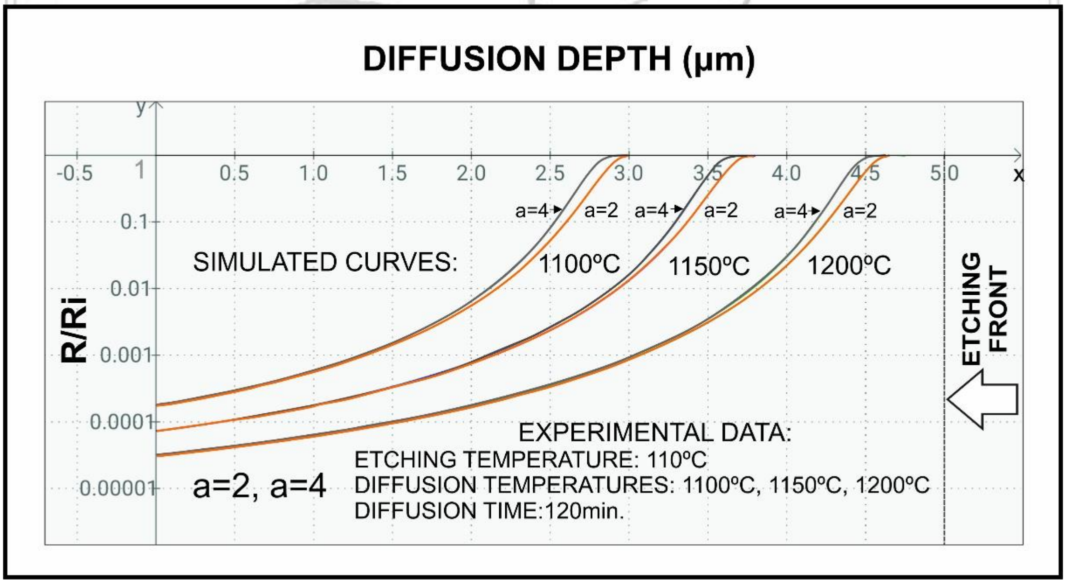

Fig. 5. Comparative analysis of R/Ri ratio during the chemical etching process of the boron diffused silicon layers in a=2 and a=4 type etching solutions, simulated according to the analytical results describing the boron profile after the diffusion from the BN source at 1100°C, 1150°C and 1200°C for 120min. The temperature of the etching solutions is Te =110°C.

3.2 Chemical Etching Time

In the planar technology, the etching process refers to the same surface which advances in an Ox direction. Therefore, starting from the definition of R in the planar processing technology (R=dx/dt) [21], the chemical etching time t necessary to etch a boron diffusion layer from the low-doped silicon bulk to the highly boron-doped region can be deduced as:

$$t = -\int_{xj}^{x} (R/Ri)^{-1}(dx/Ri) = \int_{x}^{xj} (R/Ri)^{-1}(dx/Ri) \qquad (9)$$

where the negative sign of the integral comes from the contrary direction of the etching boundary on the Ox axis with respect to the diffusion process.

With this definition and taking into account the relations of R and of the boron concentration with respect to the depth x into the silicon bulk, the etching time could be expressed as:

$$\Delta t/\tau = (1/xj)[\int_{o}^{x} (1+ (C(x)/Cc)^{a})^{4/a})\, dx|_{x\in[0,xi]} + \int_{xi}^{x} (1+ (Ci(x)/Cc)^{a})^{4/a})dx|_{x\in[xi,xj]}] \qquad (10)$$

where xj is the junction depth, used in rel. (10) as a normalizing parameter, $\Delta t = t-t_o$ (t_o – the initial moment – in this case $t_o=0$ at xj boundary), and τ is defined as the necessary time period that the thickness of the boron doped layer be etched with the rate Ri, so: τ=xj/Ri. The variation range of the variable x is indicated in the bottom side of each term in rel. (10), corresponding to the extrinsic and intrinsic domain of the boron diffusion profile.

In Fig. 6 it is presented the variation Δt/τ for etching processes in chemical solutions of the type a=2 and a=4 at the process temperature of 110ºC, corresponding to the boron diffusion profiles obtained after the diffusion at T=1100°C, 1150°C and 1200°C. The contribution of the second term in rel. (10) on the intrinsic variation range seems to be insignificant, because Cc and ni show actually the same order of magnitude in the examined range of diffusion temperature. Therefore, in this figure it is represented only the variation in the high concentration range (C>ni), where the stopping effect becomes really important. The numerical evaluation of the etching time was possible by normalizing it to the quantity τ, depending on the value of the junction depth xj, as defined above. However, if the intrinsic range could be neglected, as it is the case for the conditions discussed above, xj could be substituted by xi.

From Fig. 6 it can be seen that the a=2 type solutions assure a slower variation that that of the a=4 solutions. However, both of them show a high self-limitation process on the high concentration region of the boron doped silicon layers, attaining near the surface values of about 10^3 times higher than the values corresponding to Ri. As it can be seen also from Fig. 6, the increasing of the diffusion temperature from T=1100°C to T=1200°C allows to obtain larger values of the thickness of the micro-mechanical elements if the same etching duration is considered, and an increasing of the stopping efficiency and thus of the etching duration if the same value of the thickness of the micro-mechanical elements is considered.

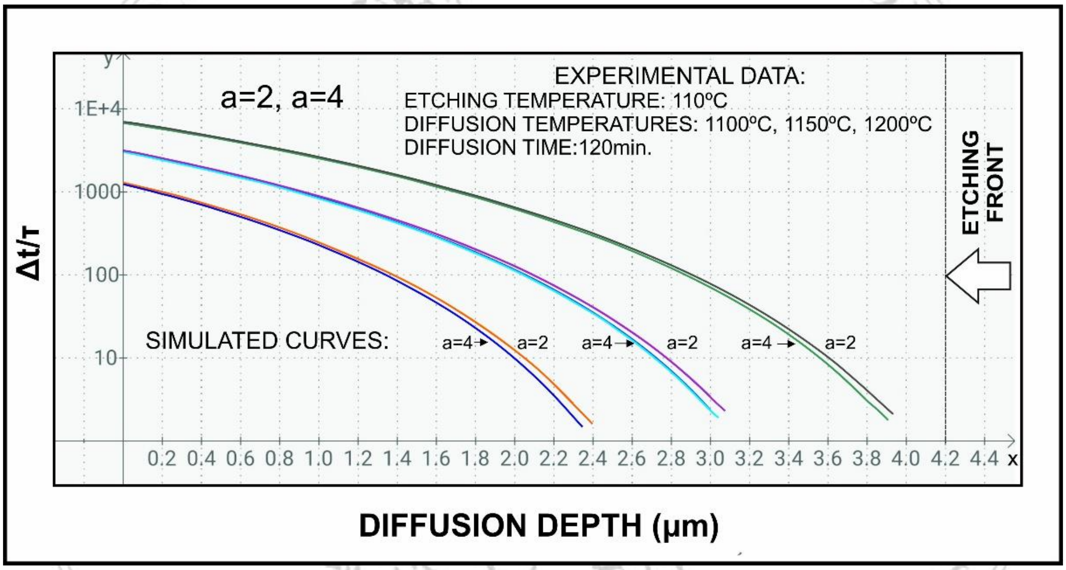

Fig. 6. Comparative variation of the etching time expressed as the ratio $\Delta t/\tau$, during the chemical etching process of the boron diffused silicon layers in a=2 and a=4 type etching solutions, simulated according to the analytical results describing the boron profile after the diffusion from the BN source at 1100°C, 1150°C and 1200°C for 120min. The temperature of the etching solutions is Te =110°C.

4. CONCLUSIONS

A suitable analytical model of the boron diffusion in silicon from a solid BN source was developed, including the highly-doped region, where the diffusion coefficient depend linearly on concentration, and the tail region of the profile, where the diffusion concentration is constant, allowing to approach correctly the simulation of the boron diffusion profile at high temperatures (1100°C), useful to control the self-limitation process during the chemical etching of silicon and to obtain reproducible thickness of membranes or micro-mechanical elements. It was shown that the agreement between the simulated profile and the experimental data after a boron diffusion from a BN source at 1100°C for 120min. was very good, well supporting the analytical modelling. Taking into account therefore that the boron diffusion profile in silicon is different if the diffusion process is performed under oxidizing conditions (BBr_3 liquid source) or not (BN or B_2O_3 oxides), the variation of the solid solubility and of the intrinsic diffusion coefficient with the diffusion temperature was deduced by a fitting procedure on some reliable data collected from literature, providing suitable values for profile simulations at 1150°C and 1200 °C after the diffusion from a BN source.

The obtained results were applied to calculate and to comparatively analyze the etching rate in chemical solutions of the type a=4 (10% KOH (NaOH, LiOH or EDP type S solution) and a=2, (KOH 24%) at the process temperature of 66°C, 81°C and 110°C. On the basis of the analytical results allowing the simulation of the boron diffusion profile at 1100 °C, 1150°C and 1200 °C, the self-limitation process of the chemical etching of the boron-doped silicon layers was simulated by the calculation of the etching rate and of the etching time as a function of the diffusion depth, resulting conclusions concerning the optimization of the fabrication of micro-mechanical elements with various values of the thickness and low concentration gradients, necessary to avoid the mechanical stress. It was shown that the use of the high diffusion temperatures is favorable for such process optimization.

The reported results presented in this work represent a powerful and indispensable tool for the suitable and accurate control both of the crucial fabrication processes (boron diffusion, chemical etching) and of the geometrical parameters of the micro-mechanical elements in silicon bulk micromachining technology.

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