ANALYTICAL MODELING AND SIMULATION OF THE CHEMICAL ETCHING PROCESS OF THE BORON-DOPED SILICON LAYERS FROM BBr₃ SOURCE IN THE MICROMACHINING TECHNOLOGY

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Abstract: *The boron-doped silicon layers commonly used to fabricate various micro-mechanical elements, particularly silicon membranes, are efficient stop-etching barriers, so their control is crucial in the bulk micromachining technology. As the properties of the boron doped layers depends on the type of the doping source and on the diffusion depth in the silicon bulk, a particular analysis should be applied in each specific case. In this paper there are reported the results of an analytical modeling of the boron diffusion profile in silicon, which are applied to simulate the boron diffusion profile at high diffusion temperatures (1050°C, 1100°C, 1150°C and 1200°C), emphasizing a dependence of the diffusion coefficient as a square root of the boron diffusion concentration. It is shown that the comparison of the theoretical results and some experimental diffusion data after diffusion at 1050°C shows a very good agreement, well supporting the analytical modeling. On this basis, the chemical etching rate and the etching time are simulated as a function of the boron diffusion depth in silicon for various etching solutions and etching conditions, providing suitable guiding curves for practical applications in the bulk micromachining technology*

1.   Introduction

The bulk micromachining technology is based on the selective etching of silicon to obtain micro-mechanical elements, like various types of silicon sensors [1], particularly capacitive pressure sensors for biomedical applications [2] and accelerometers, actuators and other micro-mechanical structures [1]. The etching technique is based on the property of alkaline type solutions (KOH, NaOH, LiOH) or EDP (ethylene-diamine-pyrocatechol), to decrease the etching rate in the boron-doped layers, especially in layers with a doping levels exceeding values of the order of 10^{20} cm^{-3} [3]. However, as it was previously shown, the distribution of the boron concentration in silicon depends on the diffusion source and on the diffusion depth, so a distinct analysis of the etching process should be applied in each distinct case. Such an analysis was reported for boron doped layers after diffusion from solid boron nitride BN source [4] and for boron implantation

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process [5], showing particular dependences of the chemical etching rate and etching time on the depth in silicon in these cases. However, as it was highlighted recently [6], a categorical distinction between the diffusion from sources under non-oxidizing conditions (like silicon-doped (B_2O_3) oxides deposited onto the silicon surface [7] or solid BN source), and from sources which are active only under oxidizing conditions (as it is the case for the liquid BBr3 source), should be considered. This is due to the different diffusion mechanisms in each of the diffusion situation: while in the first case the diffusion is mainly carried by vacancies [8, 9], in the second case the oxidation process generates silicon-self-interstitial atoms which enhance the bulk diffusion of the boron atoms, determining a distinct type of dependence of the diffusion coefficient on the boron concentration and thus a distinct diffusion profile [10].

As a sharp definition of the geometrical parameters, particularly the thickness of the micro-mechanical elements is necessary to be obtained, a strict control of the etching rate and etching time during the chemical etching process should be considered. This is possible if the boron diffusion process necessary to dope the etching-stop silicon layers is also strictly controlled. In this paper it is presented an analytical model of the boron diffusion in silicon from BBr3 liquid sources, which shows a very good agreement between the simulated profile and experimental data after diffusion from BBr3 source at 1050°C. On this basis and on the basis of confirmation data earlier reported [10], the boron diffusion profiles after diffusion at the temperatures of 1100°C, 1150°C and 1200°C were simulated, and the corresponding variation curves of the etching rate and etching time in chemical solutions of 10% KOH (NaOH, LiOH) or ethylene-diamine-based solution (EDP) type S and 24% alkaline-type solutions at 110°C, each of these two categories of etching solution showing a distinct type of variation were simulated, as it will be presented below.

1.   BORON DIFFUSION PROFILE IN SILICON AFTER DIFFUSION FROM BBr3 SOURCES

The boron diffusion from BBr3 liquid source is inherently performed under oxidizing conditions due to chemical reasons concerning the necessary reaction of the oxygen atoms with the source and the growth of the suitable components on the silicon surface. An analysis of the boron diffusion previously reported has been shown that the boron diffusion profile after diffusion from BBr3 sources can be well simulated if the diffusion coefficient of the boron diffusion in silicon D depends on the square root of the boron concentration C, i.e. $D \sim C^{1/2}$ [10]. This was a surprising result with respect to the earlier proposed mechanism of the

diffusion by vacancies, which claims actually a dependence of the form D ~ C [9]. This intriguing result was clarified in some subsequent reports, showing that this is due to the different conditions of the diffusion process: the boron diffusion in silicon from BBr3 source is enhanced by the silicon self-interstitial contribution generated by the oxidation of the silicon surface [6], while the boron diffusion from non-oxidizing BN sources is mainly performed by a vacancy diffusion mechanism [8, 11, 12].   The contribution of the self-interstitial silicon atoms, proposed by Gösele to explain the kick-out mechanism during the gold diffusion atoms in silicon [13] was also observed in swirl-defect formation during crystal growth, oxygen precipitation, oxidation-induced stacking faults, and non-equilibrium effects associated with high-concentration phosphorus diffusion [14] and gettering phenomena [15]. A boron self-interstitial-boron pair-diffusion model was also proposed taking into account [16] the Gaiseanu's reported $D\sim C^{1/2}$ form [10], different from the D~C form characteristic for a standard vacancy mechanism proposed earlier by Fair [9].

No analytical results concerning the distribution of boron concentration C as a function of the diffusion depth x were reported up to date after the diffusion from a BBr3 source. An analytical model of boron diffusion under such conditions is presented below.

1.1. Experimental data

In a previous published report [10], Gaiseanu shown that the so called "universal profile" proposed by Fair [9], obtained by using various experimental data collected
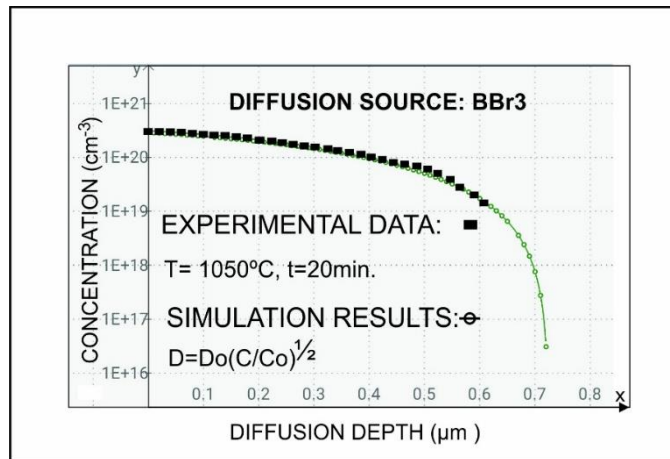

Fig. 1. Boron diffusion profile in silicon experimentally determined by electrical sheet resistivity method collected from [17] after the diffusion from a BBr3 source at 1050°C for 20min.

from literature to demonstrate the vacancy mechanism implied in the boron diffusion in silicon, represented as C/Co vs. x/xj, where Co is the surface concentration and xj a diffusion depth at $C=10^{18}cm^{-3}$, is actually well described not by the specific form of the diffusion coefficient D~C, but rather by a $D\sim C^{1/2}$ form.

To demonstrate this correspondence, in Fig.1 it is shown the experimental boron diffusion profile in silicon after the diffusion from a liquid BBr3 source at 1050°C for the diffusion time t = 20min. by using some experimental data collected from [17] and compared with the simulated profile according to the model presented in this work, taking into account a variation $D\sim C^{1/2}$. As it can be seen from this figure, the agreement between the simulated profile and the experimental data is very good, highly supporting the new proposed form of the boron diffusion coefficient during the diffusion process from the liquid BBr3 source.

1.2 Analytical modelling and simulation

The diffusion problem in this case consists in the following requirements:

  (i) to find a solution of the diffusion equation for continuous contact between the diffusion source and the silicon surface ("infinite source" problem), with the following consequences: C(x=0)=Co (constant) during the time, given by the solid solubility of the boron in silicon, so (C(x=0)/Co)=1;

  (ii) to consider the diffusion coefficient D depending on concentration C on the form:

  $$D=Do(C/Co)^{1/2} \qquad (1)$$

  where Do is the diffusion coefficient at the silicon surface (Do=D(x=0));

  (iii)to deduce a suitable condition for concentration faraway from the surface (if the diffusion coefficient would be independent of concentration, then this condition would be C(x→∞)→0).

The condition stated in (iii) provides specific results when the diffusion coefficient depends on concentration as given by rel. (1). These results refers to the fact that a finite depth could be defined, where the boron concentration is actually null, just because of the continuous decrease of the boron diffusion flux, becoming finaly zero [18]. With these conditions, and using the suitable substitution

$$X= x/2\sqrt{(Dot)} \qquad (2)$$

the following solution of the diffusion equation could be found:

$$C = Co \ [(1 - (\sqrt{(1/6)})X - (1/3)X^2]^2 \qquad (3)$$

which satisfies all requirements stated above. The finite normalized depth where the boron concentration and the boron diffusion flux is zero is obtained for $Xo = \sqrt{(3/2)}$, calculated with an approximation better than 2%.

The simulated profile after the boron diffusion from BBr3 source at 1050°C is shown in Fig.1, compared with the experimental data as commented above. These data correspond mainly to the extrinsic diffusion range (C>ni – the intrinsic carrier concentration) at the diffusion temperature. The experimental data in Fig. 1 does not permit an analysis of the boron concentration profile for concentration less than 10^{19}cm^{-3}. Therefore, although it can be supposed that a diffusion profile would be more extended into the bulk than the solution on the high concentration range could express, for the application purposes exposed in this paper this solution is sufficient to further express the dependence of the chemical etching rate and the diffusion time on the diffusion depth.
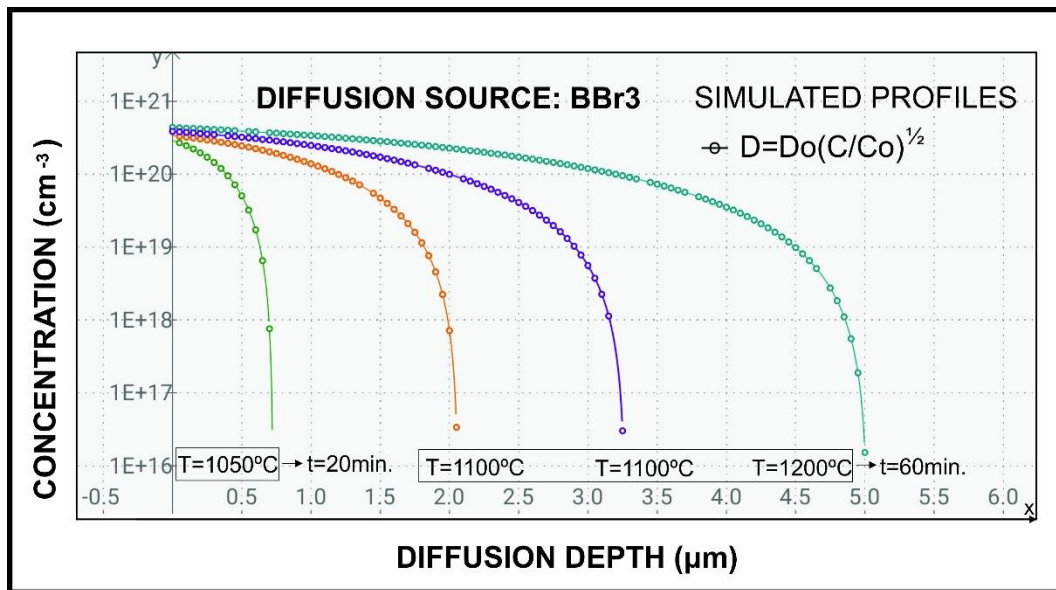

Fig. 2. Simulated boron diffusion profiles in silicon after the diffusion from a BBr3 source at 1050°C for 20min. and after the diffusion at the temperatures T=1100°C, 1150°C and 1200°C for 60min.

For this purpose, some simulated diffusion profiles after the diffusion at 1050°C, 1100°C, 1150°C and 1200°C for the time t=60min. from the liquid BBr3 source are shown in Fig. 2. The suitable data on the surface concentration and surface diffusion coefficient were taken for a previously published report [19], where a

series of diffusion data collected from literature concerning the boron diffusion from BBr3 sources were suitable fitted by an Arrhenius plots [20].

From the fitting of these data results that [19, 6]:

$$Do=0.4648exp(-3.08eV/kT°K) \qquad (4)$$

 and

$$Co=1.43x10^{22}exp(- 0.44eV/kT°K) \qquad (5)$$

where Co is expressed in cm^{-3} and Do in cm^2/sec.

Rel. (3) seems to be very simple, but it represents a solution of the diffusion equation under conditions (i) – (iii) enounced above. This relation results from the rapid convergence of the series of powers verifying the diffusion equation with a diffusion coefficient of the form (1).

2. CHEMICAL ETCHING PROCESS

The control of the chemical etching process as a function of the diffusion depth is of a crucial interest for the fabrication of the micro-mechanical elements, in order to obtain not only their designed geometrical architecture, but also to avoid the concentration gradients inside of the structure, consequently avoiding mechanical induced stress in these elements and thus their deformation.

The analytical results described above can be used to calculate the etching rate and the etching time as a function of the boron diffusion depth after diffusion from liquid BBr3 sources. In a standard chemical etching process to obtain micro-mechanical elements, the etching front advances to the doped silicon layer starting from the silicon substrate with a very low impurity concentration (of the order of 10^{15} – $10^{16}cm^{-3}$). In this region the etching rate is Ri, independent of concentration. However, as more as the etching front advances, as more important becomes the influence of the doping on the chemical etching rate. Results on the dependence of the etching rate on the boron concentration in the silicon doped layers for various chemical solutions were reported earlier [3], but no reference on the depth dependence of the etching rate was given.

2.1   Chemical Etching Rate

As it was previously found [3] the etching rate R of the uniformly boron-doped silicon layers can be expressed as a function of the boron concentration as:

$$R/Ri = [1+(1+C/Cc)^a]^{4/a} \qquad (6)$$

where Ri is the etching rate of the low-doped silicon substrate, Cc is a critical value in the range $(2-4) \times 10^{19}$ 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, with the value a=4 for 10% KOH (NaOH, LiOH) and ethylene-diamine-based solution (EDP) type S, or a=2 for 24% alkaline-type solutions [3]. By fitting the experimental results reported in [3] with an Arrhenius type variation, it can be deduced that Ce could be properly express by the relation: $Cc = 5.5 \times 10^{19} \exp(-0.025eV/kT^{o}K)$, particularly providing the value $Cc=3 \times 10^{19}$cm^{-3} if the etching process is performed at the temperature of the etching solution Tc = 110°C.
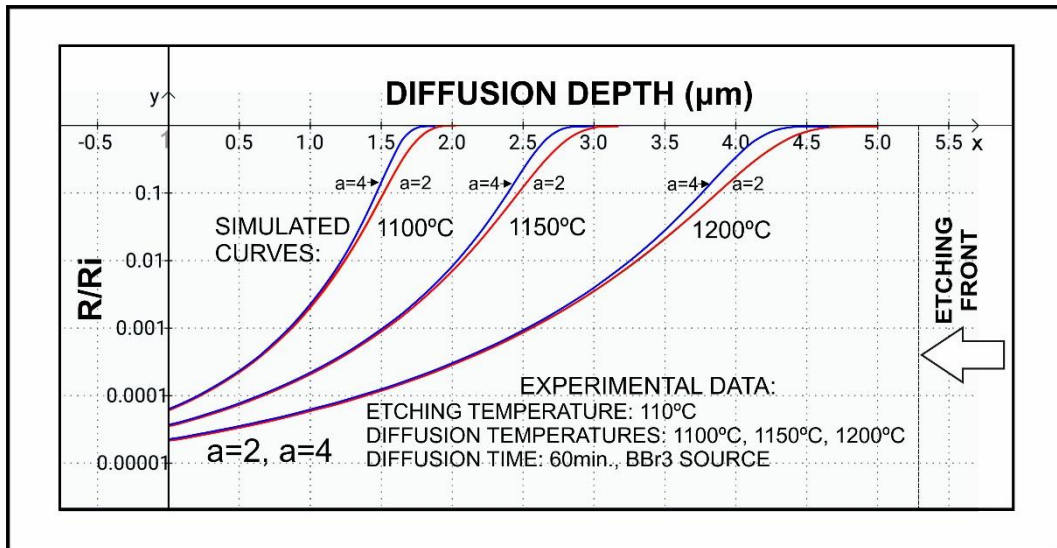

Fig. 3. The variation of R/Ri during the chemical etching process of the boron doped silicon layers, simulated according to the analytical results of the boron profile after the diffusion from a BBr3 source at 1100°C, 1150°C and 1200°C for 60min, in a=4 and a=2 type etching solutions at Te=110°C.

Introducing rel. (3) into rel. (6), the general relation allowing to calculate the dependence of the etching rate on the diffusion depth it is obtained, allowing to simulate the etching rate for various process conditions. Particularly, in Fig. 3 is shown the variation of the etching rate as a function of the boron diffusion depth in a=4 and a=2 type solutions at Te=110°C after boron diffusion from BBr3 liquid sources at T= 1100°C, 1150°C and 1200°C for 60min.

As it can be seen from Fig. 3, the doping level strongly influences the chemical etching rate. The curves represented in Fig. 3 could serve as a technological guide to design an etching process, allowing to evaluated the efficiency of the etching process as a function of the required diffusion depth. The criteria concerning a

certain efficiency could be established according to the graphs represented in this figure. The comparison between the ratio R/Ri associated with a=4 and a=2 type solutions for Te=110°C after the boron diffusion from BBr3 source at T=1100°C, 1150°C and 1200°C shows that the difference is really significant for moderate or low etching efficiency (R/Ri ≤ 0.01), corresponding approximatively with the diffused regions with concentration values C ≤ Cc. It is important to note however, that a fine control of the conditions of the etching process is necessary when a certain solution a=4 or a=2 type would be used in the low, moderate or high concentration range, for a correct monitoring of the chemical etching process, as shown in Fig. 3, when special requirements on the final thickness or on the level of the diffusion-induced stress are to be imposed.

Indeed, if low concentration gradients after the diffusion from BBr3 sources are required, the etching process should be continued even within the high concentration region. The width of these regions depends on the diffusion time and on the diffusion temperature, so if micromechanical elements with a large thick are necessary, then a higher diffusion temperature should be applied, as it can be seen from Fig. 3. If it is necessary for instance to obtain a membrane or a micro-mechanical element with the thickness of 1.5 μm, from the graphs represented in Fig. 3 will result an efficiency R/Ri = 0.14 after diffusion at 1100°C during an etching process in an a=4 type solution, while in a solution with a=2 the efficiency R/Ri=0.084 is higher. The same type of comparison shows no practical differences between the efficiency after diffusion at 1150°C and 1200°C, so R/Ri=9×10^{-4} after diffusion at 1150°C and R/Ri=1×10^{-4} in the both cases a=4 or a=2 type solutions under the same process conditions. However, the remained gradient of concentration is really more favorable after the diffusion at 1150°C and much more favorable after diffusion at 1200°C that that after a diffusion at 1100°C.

2.2   Chemical Etching Time

In the planar technology the etching process refers to the same surface which advances in an Ox direction, as it is shown in Fig. 3. Therefore, taking into account the definition of R in the planar processing technology (R=dx/dt) [5], the chemical etching time t necessary to etch a boron-doped layer by diffusion from BBr3 sources, starting from the low-doped silicon bulk to the highly boron-doped region, can be deduced as:

$$t = - \int_{x_j}^{x} (R/R_i)^{-1}(dx/R_i) = \int_{x}^{x_j} (R/R_i)^{-1}(dx/R_i) \qquad (7)$$

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. The general expression to

calculate therefore the etching time t of the boron doped layers after boron diffusion from BBr3 sources is obtained introducing rel. (3) in rel. (7), obtaining:

$$\Delta t/\tau = (1/xj)[\int_{xj}^{x} (1+ (C(x)/Ce)^a)^{4/a}) \, dx|_{x\in[xj,0]}] \qquad (8)$$

where xj is the junction depth, used in rel. (8) 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 to be etched with the rate Ri, so: τ=xj/Ri. The variation range of the variable x is indicated in the bottom side of the integration term in rel. (8).
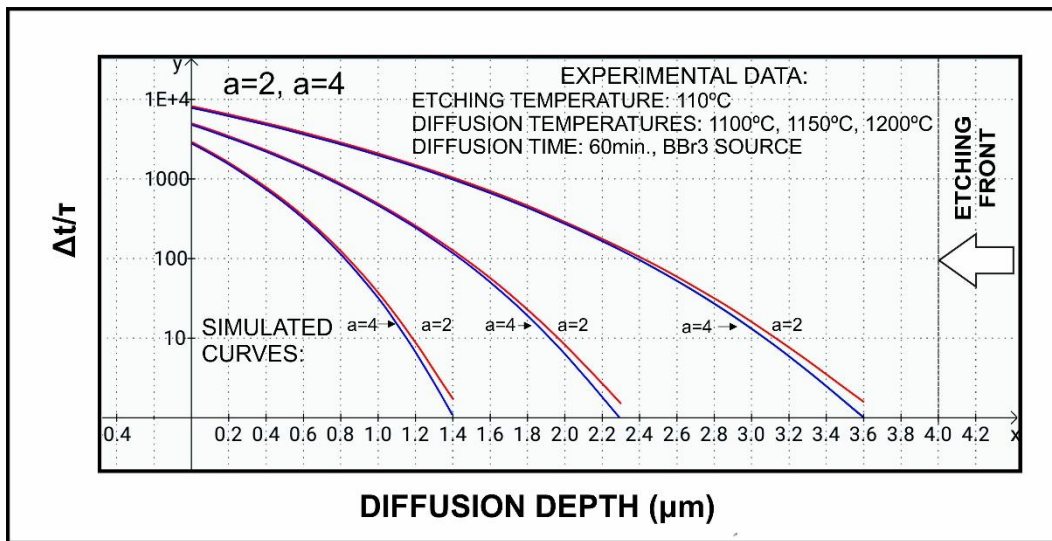

Fig. 4. Comparative variation of the etching time expressed as the ratio $\Delta t/\tau$ during the chemical etching process of the boron diffused silicon layers in a=2 and a=4 type etching solutions, simulated according to the analytical results describing the boron profile after the diffusion from the BBr3 source at 1100°C, 1150°C and 1200°C for 60min. The temperature of the etching solutions is Te =110°C.

In Fig. 4 is presented the variation $\Delta t/\tau$ for etching processes in chemical solutions of the type a=2 and a=4 at the process temperature of 110°C, corresponding to the boron diffusion profiles obtained after the diffusion at T=1100°C, 1150°C and 1200°C. Although the resulted curves represented in Fig. 4 were obtained by numerical calculation, the integral could be also solved analytically. The general form of the expression (8) including only normalized parameters allows the both evaluation possibilities under various process conditions of diffusion and etching process.

From Fig. 4 it can be seen that in order to etch a silicon layer with a certain width, the a=4 type solution is more efficient, the necessary etching time is less than the time for a=2, but this latter solution is more sensitive with respect to the boron doping concentration in the low and moderate range of concentration. However, in both cases the etching time is increased up to values of about 8×10^3 near the doped silicon surface.

4. CONCLUSIONS

Starting from the analysis of the boron diffusion from two main categories – oxidizing and non-oxidizing sources, it was shown that the boron diffusion from BBr3 source (inherently performed under oxidizing conditions) can be described by a diffusion coefficient depending on the square root of the concentration.

Taking into account this specific variation, a suitable analytical model of the boron diffusion in silicon from a liquid BBr3 source was developed and compared with some experimental data after diffusion at the temperature of 1050°C for 20min., the very good agreement between the simulated profile and experimental data well supporting the theoretical modelling. The experimental data, limited to a range $C > 10^{19}$ cm^{-3}, did not permitted to evaluate the variation of concentration on the intrinsic range. However, for the practical purposes concerning the evaluation of the etching rate and etching time on this high concentration range, it was simulated the diffusion profile after the diffusion from BBr3 sources at the temperatures of 1100°C, 1150°C and 1200°C.

The analytical expression obtained by the solving of the diffusion equation (approximation better than 2%), was used to simulate the chemical etching rate in chemical solutions of the type a=4 (10% KOH (NaOH, LiOH) and EDP type S solution) and a=2, (KOH 24%) at the etching process temperature of 110°C. From the resulted simulated curves it was concluded that a=2 type solution is more slow than the solutions of a=4 type, but more sensitive with respect to the doping concentration of the boron doped layers. It was also shown that the increasing of the diffusion temperature is favorable to obtain both thick micro-mechanical elements and lower concentration gradients, avoiding their deformation or incorrect behavior with respect to the application purposes, because of the residual diffusion-induced stress.

Taking into account the explicit analytical relation of the boron concentration on the diffusion depth after the diffusion from BBr3 liquid sources, a general expression for the etching time was obtained, suitable to calculate accurately either in an analytical or numerical way the necessary etching time as a function of the diffusion depth under various conditions of diffusion or etching temperature and of distinct categories of etching solutions (a=4, a=2). The results of the

modeling and simulation presented in this paper concerning the critical process parameters to fabricate silicon micro-mechanical elements in the micromachining technology represent a powerful and indispensable tool to accurately control both the process and structure required parameters.

Acknowledgements

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