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CONTRIBUTIONS TO THE MODELLING AND SIMULATION OF THE ATOMIC TRANSPORT PROCESSES IN SILICON AND POLYSILICON AND APPLICATIONS*

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In the context of the efforts of modelling and simulation of the impurity diffusion and other transport phenomena in silicon and in polysilicon, there are presented our results concerning the boron, phosphorus, antimony, arsenic and gold diffusion in silicon and its influence on the forward characteristic of the p-n junction, the critical conditions for the generation of the misfit dislocations, the gettering process of metallic impurities, the self-limited etching process of silicon boron doped layers and the doping-restructuring of polysilicon during the phosphorus diffusion in polysilicon for the membrane achievement.

Key words: impurity diffusion, modelling and simulation, misfit dislocations, gettering, etching, silicon and polysilicon, doping-restructuring model.

1. INTRODUCTION

The technological processes in the microelectronic industry necessaries to modify the properties of the semiconductor material to obtain the microelectronic devices act at atomic level on well defined surface areas and semiconductor bulk regions and are based on intimate atomic transport phenomena. The knowledge of the material properties of the semiconductor in those regions both before and after processing is one of the fundamental tasks for the achievement of the microelectronic and microsystem devices in order to accurately design their configuration and to control on this way the desired useful parameters. The fulfilment of these fundamental requirements explains the considerable efforts to investigate the material properties at the atomic scale [1] and to formulate in physical and mathematical terms the intimate atomic processes in the semiconductor lattice [2].

In this paper there are presented the main contributions that we obtained for the description of the atomic diffusion in silicon of boron as a p-type impurity in silicon and of phosphorus, antimony and arsenic as n-type impurities, by using conventional (thermo-chemical) and non conventional (doped polysilicon, multilayer systems, implantation, laser-assisted annealing) techniques, as well as the gold diffusion and its influence on the forward characteristic of p-n junction and the gettering phenomena induced by the diffusion in silicon wafers. As a related process during the phosphorus and boron diffusion in silicon at high concentrations, the generation of the misfit dislocations, defined in terms of the critical conditions and the corresponding variation of the characteristic parameters (critical diffusion time and temperature) is calculated and expressed in analytical form. There are presented also the main investigations results concerning the chemical etching of boron doped layers and doping – restructuring of polysilicon layers during the phosphorus diffusion, as a key processes in bulk and surface micromachining technology respectively, for the fabrication of the silicon membranes.

2. MODELLING AND SIMULATION OF BORON DIFFUSION IN SILICON

Representing the distribution along the depth x of the boron concentration C in silicon after the diffusion from infinite source as so called universal profile, i.e. C/C_o (C_o being the surface value of C) as a function of a quantity $x/2\sqrt{(D_o t)}$, where D_o is the surface value of the diffusion coefficient and t the diffusion time, it was shown for the first time [3] that this one can be suitably described on the concentration range

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$C > n_i$ (extrinsic region), where n_i represents the intrinsic carrier concentration, by a solution of the diffusion equation

$$\partial C / \partial t = \partial / \partial x[D(C)\partial C / \partial x)], \tag{1}$$

with a diffusion coefficient D depending on the boron concentration as:

$$D=D_o(C/C_o)^{1/2} \tag{2}$$

instead of a simple linear dependence, which would be typical for diffusion by a vacancy mechanism [4], as it can be seen in Fig.1. The depth x_1 in Fig.1a corresponds to a concentration of 10^{18}cm^{-3}, taken as a reference limit value in order to analyse the experimental data only on the extrinsic range.

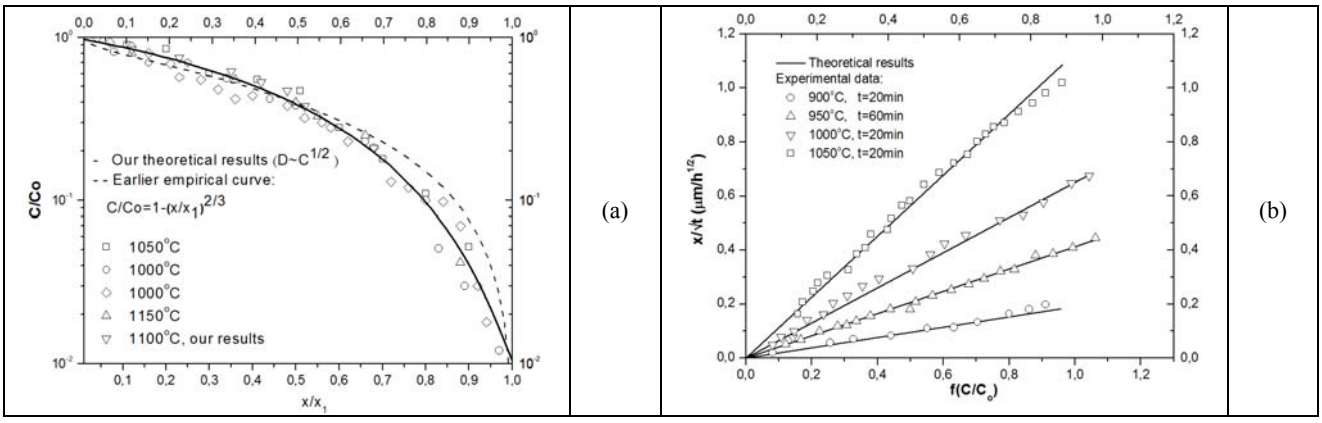


Fig.1 – Boron diffusion profile represented as: (a) normalized quantity C/Co *vs*. x/x_1 (universal profile) [3]; (b) variation of $x/\sqrt{t}$ vs. $f(C/C$o), which is the right side of the solution of the diffusion equation (rel. (3)), depending only on C and Co [5] (the experimental data were collected from [6]).

A proper solution of the diffusion equation (1) with the diffusion coefficient described by the relation (2) it was deduced as [7]:

$$x / 2.33\sqrt{D_o t} = 1 - 0.737(C / C_o)^{1/2} - 0.181(C/C_o) - 0.082(C/C_o)^{3/2}, \tag{3}$$

which express the diffusion depth as a function of the impurity concentration with accuracy better than 3%. A very good agreement between the experimental data and our theoretical results can be noticed from Fig. 1, allowing the accurate simulation of the boron diffusion profile by means of rel. (3) on the extrinsic range. Moreover, the form (3) represented by $x/\sqrt{t}$ vs. $f(C/C_o)$ as a right line in Fig. 1b permits an accurate evaluation of the surface diffusion coefficient D_o and of the surface concentration C_o by an adequate extraction procedure of the interest parameters [5], resulting: $D_o = 0.4648\exp(-3.08\text{eV/kT})$ and $C_o = 1.43\times10^{22}\exp(-0.44\text{eV/kT})$ over the experimental data on the range 900°C–1050°C collected from [6]. By using relation (3) it was possible also to express the boron atom amount $Q(t,T) = 0.9\ C_o\sqrt{D_o t}$ diffused in silicon from a BBr_3 source [7, 8], in agreement with the experimental data from [8].

Relation (3) permits to calculate also in an explicit way the sheet resistivity R_s of the boron doped silicon layers [9], which is a material parameter measurable by using the four point method. This is practically one of the most commonly used parameter not only to control the doping after diffusion but also to design the silicon semiconductor devices, so that its predictability as a function of the diffusion conditions is of major practical interest in the silicon semiconductor technology. Taking into account rel. (3), R_s was calculated on the high concentration range [9] as $R_s = [qC_o\mu_m(D_o t)^{1/2}]^{-1}$, where μ_m represents an average value of the hole mobility on the variation range of concentration, between C_b, which is the bulk concentration, corresponding to the junction depth and C_o (in the most common cases $C_b << C_o$). In a similar way it was calculated [10] the average conductivity σ_m of the boron doped layer as $\sigma_m = 0.39q\mu_o C_o + 0.59\ qC_o^{1/4}N_{ref}^{3/4}\Delta\mu \equiv \sigma_{om} + \sigma_{cm}$, where $\Delta\mu$ is the difference between the maximum and minimum value of the hole mobility on the C variation range in the empirical formula used in SUPREM process simulator [11], σ_{om} is a fundamental term earlier deduced [4] considering that the average conductivity would be entirely represented by a layer near the surface concentration ($C > 5\times10^{19}$cm^{-3}) and σ_{cm} represents our correction term, contributing to the full description of σ_m on the entire concentration range (Fig. 2b).

The full diffusion profile, including the variation of C in the intrinsic range ($C < C_i = n_i$) was simulated taking into account that $D=D_i$ (D_i is a temperature dependent quantity only for a certain impurity), so that extrinsic profile it was obtained [12]:

$$C = C_i \left[\operatorname{erfc}\left(x / 2\sqrt{D_i t} \right) \right] / \left[\operatorname{erfc}\left(x_i / 2\sqrt{D_i t} \right) \right]. \tag{4}$$

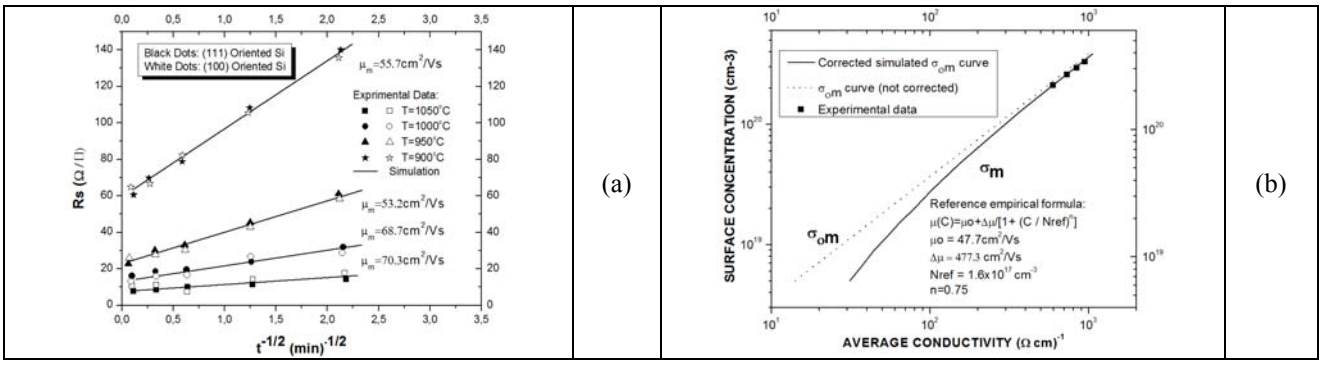


Fig. 2 – a) Simulated R_s as depending on the reverse of the square root of the diffusion time, compared with experimental data from [6]; b) our theoretical curve C_o vs. average conductivity σ_m compared with the curve C_o vs. σ_{om} earlier proposed [4] and with experimental data [6].

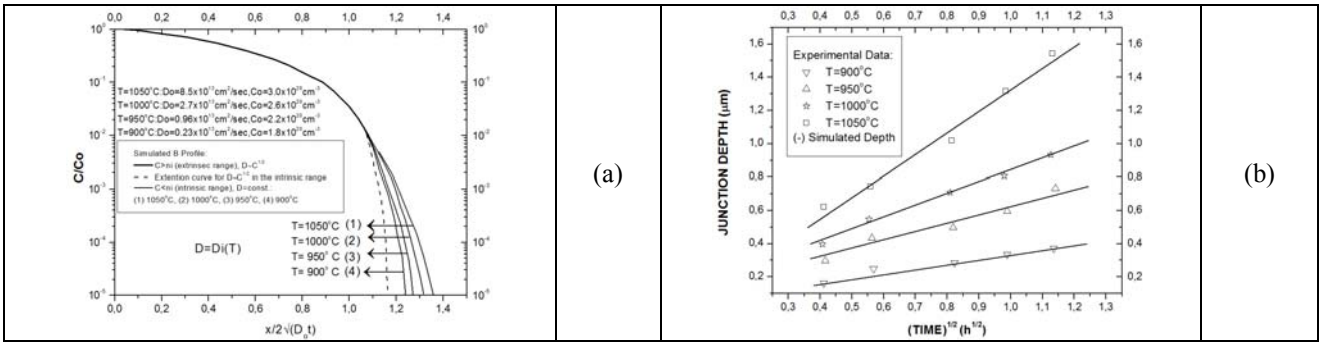


Fig. 3 – a) Simulated boron diffusion profile in silicon both on the extrinsic (universal curve) and intrinsic region for various diffusion temperatures; b) the corresponding junction depths described by rel. (4), well supported by the experimental data [6].

Whereas the boron diffusion from a BBr_3 source system (including a reactive component (oxygen) into the furnace tube) can be accurately described considering a dependence $D \sim C^{1/2}$, it was shown [13] that the boron diffusion from a boron nitride (BN) source (non oxidizing conditions) is suitably described by $D \sim C$ (Fig. 4a and b) and a corresponding solution of the diffusion equation on the extrinsic range as follows:

$$x / 1.6\sqrt{D_o t} = 1 - 0.78(C / C_o) - 0.152(C/C_o)^2, \tag{5}$$

which can be extended in the intrinsic range on a similar way as in the previously discussed case.

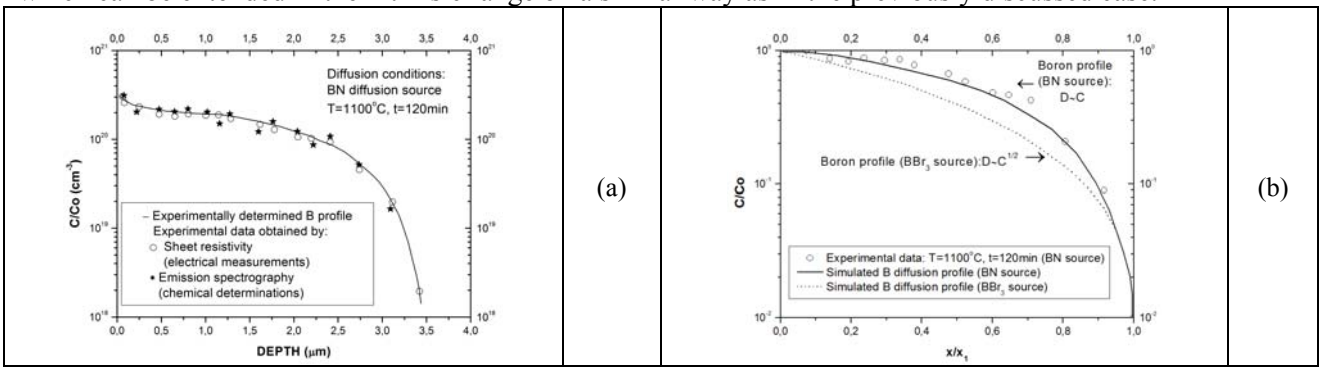
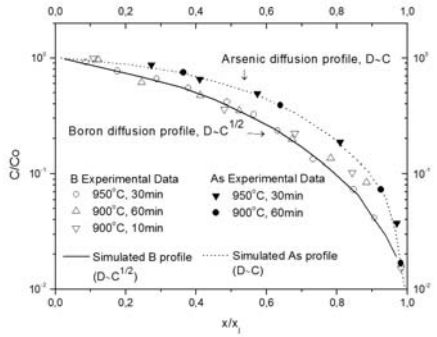


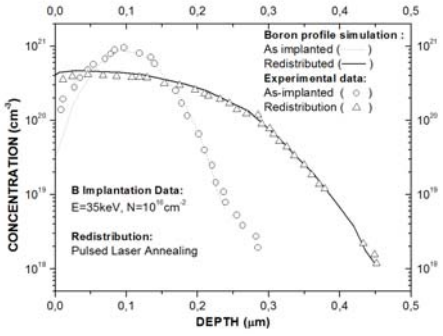
Fig. 4 – a) Experimental boron diffusion profile in silicon after diffusion from BN source (non oxidizing conditions); b) simulated profile corresponding to D~C (rel. (5)) compared with the profile after the diffusion from a BBr3 source.

Our reported results [13] suggests that the surface atomic processes (oxidation, as a generator of self-interstitial atoms [14]) during the boron diffusion from BBr_3 source should be responsible for the modification of the profile shape observed after the diffusion from the BN source (under non oxidizing conditions), which is typical for a vacancy mechanism. These results were taken as a reference to develop a new diffusion model including the self-interstitials as a co-participating transport current for B atoms [15] and successfully contributed to B diffusion modelling according both to Fair´s concepts on the transport agent (vacancies) [4] and to Gösele's ones (self-interstitials) [14].

Extending our researches to the diffusion by non conventional techniques, it was shown that a suitable analytical description of the boron diffusion profile in silicon after the diffusion from polysilicon doped sources [16] is obtained [17] taking into account rel. (2) and (3) (Fig. 5a). We succeeded also to analytically describe [19] the impurity redistribution after ionic implantation and laser post implantation annealing (pulsed laser melting and re-crystallization process) [18], by surpassing of some theoretical complications coming from the time dependence of the pulsed laser temperature and corroborating with an approached form for the post implantation redistribution [20], so that a very good agreement with the experimental data represented in Fig. 5b it was obtained.



(a)



(b)

Fig. 5 – a) Experimental B and As profile in silicon after diffusion from polysilicon doped source [16] simulated with rel. (3) and rel. (5) respectively [17]; b) simulated B profile [19, 20] after the pulsed laser post-implantation annealing [18].

2. SIMULATION OF GROUP V IMPURITY DIFFUSION IN SILICON

Considering the previous results [21] on the three distinct regions of the phosphorus diffusion profile, $D \sim C^2$ on the flat region near the surface, $D \sim C^2$ on the next transition region and $D=D_i$ in the bulk (intrinsic) region after the diffusion by thermo – chemical technique ($POCl_3$ source), an analytical solution on each range of three coupled diffusion equations were found [22], able to accurately describe the phosphorus profile, as it is shown in Fig. 6a and b.

We demonstrated also that Sb diffusion profile after the conventional diffusion [23] and As profile after the diffusion from polysilicon sources (Fig. 5a), show a dependence $D \sim C$ [17], which is characteristic for a vacancy diffusion mechanism and can be accurately described by rel. (5).

The profiles of P and As after the post implantation laser annealing [18], of Sb after the thermal post implantation annealing [24] and after the laser assisted annealing with and without impurity losses through the external silicon surface were also well described by suitable analytical approximations [19], showing a similar behaviour as B profile presented in Fig. 5b.

Versatile analytical results able to describe the impurity diffusion from [25, 26] and through [27] a multilayer system on silicon (and on GaAs for Zn diffusion), as non conventional diffusion techniques with applications in the shallow junction technology were also obtained, useful both for further theoretical developments (simulation of diffusion in regions with $D=D(x)$, for instance near the dielectric/Si interfaces) and for the simulation of the diffusion from a SiO_2/Doped-SiO_2 source in silicon.

Such accurate results and those presented in the next chapters were included in process simulators or in our patents dedicated to the fabrication technologies of various types of silicon devices as J-FET transistors, electroluminescent diodes, MESA power diodes, photovoltaic devices (solar cells), phototransistors, planar epitaxial diodes and integrated circuits.

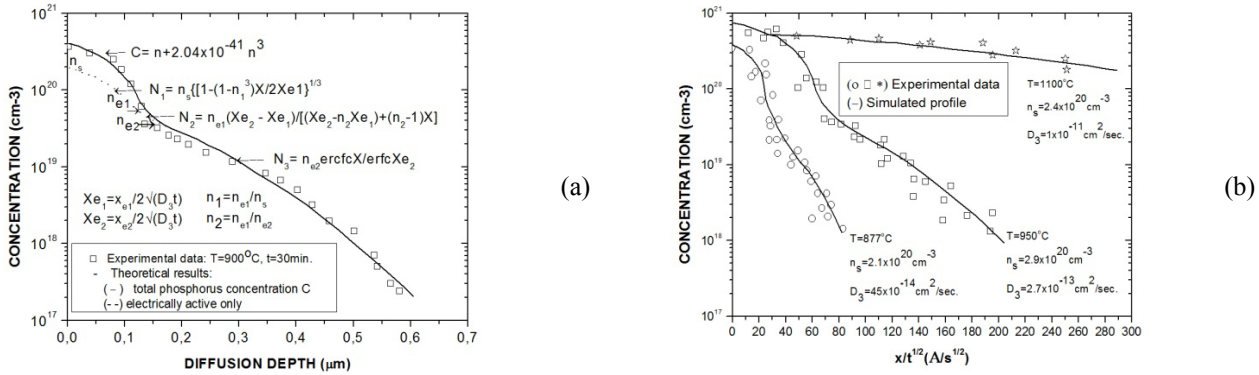


Fig. 6 – a) Simulated phosphorus profile on the three regions (our results [22]), defined by the corresponding depths x_{e1} and x_{e2}, $n_s = N_1(x=0)$, $n_{e1}=N_1(x_{e1})$, $n_{e2}=N_2(x_{e2})$, N being the active phosphorus concentration, compared with experimental data [21]; b) simulated phosphorus profiles for various temperatures, compared with experimental data [21].

3. CRITICAL CONDITIONS FOR THE GENERATION OF MISFIT DISLOCATIONS

Due to the mismatch between the impurity and the host lattice atom radius, a dens misfit array of boron induced dislocations at high concentration is generated near the plane of maximum gradient [28], and based on this assumption, we calculated the critical conditions of the generation of misfit dislocations by means of rel. (3) and we expressed these conditions in terms of variation C_0 vs. diffusion depth (Fig. 7a), C_0 vs. the critical diffusion time (Fig.7b) and critical time vs. temperature (Fig. 7c), with further applications on the control of the boron induced stress in thin silicon membranes obtained by bulk micromachining technology [29].

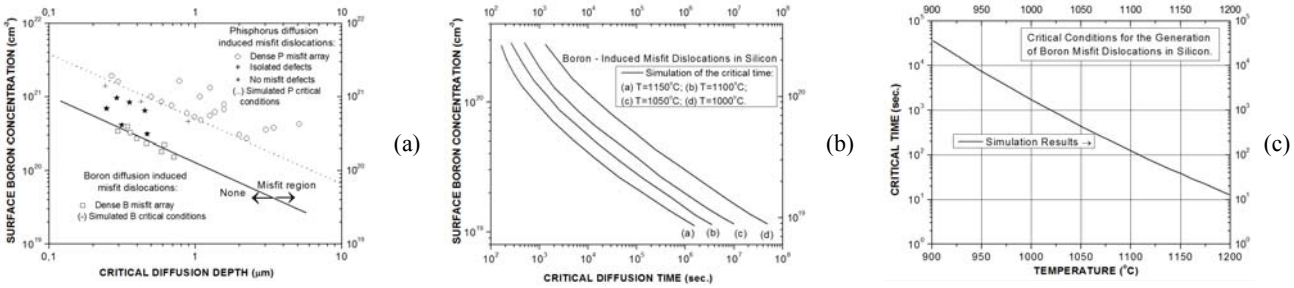


Fig. 7 – a) Simulated critical conditions for the boron-induced misfit dislocations, in terms of: a) C_o vs. critical diffusion depth, compared with P misfit critical depth in silicon; b) C_o vs. critical diffusion time; c) critical time vs. diffusion temperature.

4. SIMULATION OF GOLD DIFFUSION IN SILICON AND GETTERING PHENOMENA

Gold is an impurity acting as a recombination centre in both p and n-type silicon and is intentionally introduced in silicon wafers by a diffusion process for the fabrication of the fast switching transistors with computer applications. Gold diffusion in silicon can be described by a relation $D \sim C^2$ and by a corresponding diffusion profile shown in Fig 8a, so that this non uniform profile modifies the ideal forward current density Ji through a p-n junction, converting it in a current density J dependent on the junction depth x_j and on the gold diffusion conditions (time and temperature) [30], as it is illustrated in Fig. 8b and c. The correction factor J/J_i is expressed as a ratio between two Bessel's functions, K_o (of zero order) and K_1 (of the first order): $J / J_i = K_o[(2 / L(0)m)\sqrt{(mw+1)}] / \sqrt{(mw+1)}K_1[(2 / L(0)m)\sqrt{(mw+1)}]$, where $L(0)$ is the minority carrier length corresponding to the junction depth and w the thickness of the depleted region.

In opposition to the previously described situation, the objective of the gettering process is to trap the metallic impurities in the highly doped layers, in order to increase the minority carrier life time in the electrically active silicon bulk regions and to improve consequently the efficiency of the photovoltaic cells or other sensitive devices. By a careful analysis of the diffusion profiles of P, B, Sb and As doping impurities

with respect to that of Au in silicon and of the corresponding Si self-interstitial currents injected by the diffusion, it was shown [31] (Fig. 8a) that the self-interstitial current generated by *P* and *B* diffusion is favourable to enhance the transport and gettering of Au and Pt near the silicon surface, while As and Sb diffusion in silicon do not induce a similar transport and gettering process because their corresponding dominant diffusion mechanism is done by means of vacancies.

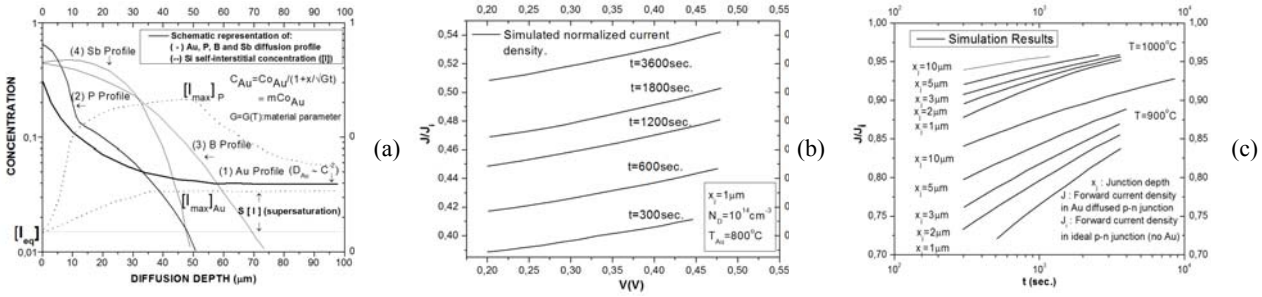


Fig. 8 – a) Au, P, B and Sb schematic representation profile and corresponding Si self-interstitial concentration; b) variation of J/J_i (V) with Au diffusion time; c) variation of J/J_i with x_j and T_{au}.

The interstitial current induces a drift of 3d metallic elements (cobalt group) near the surface, because the substitution component has a significant concentration only in the highly P doped layer. In highly B doped silicon, the 3d elements exhibit an increased solubility of their interstitial component and therefore the interaction with the Si self-interstitials is not an operative transport mechanism in that case.

5. SIMULATION AND MODELLING OF SPECIFIC PROCESSES IN SILICON AND POLYSILICON LAYERS FOR MEMBRANE ACHIEVEMENT

Our researches devoted to the silicon membrane achievement for the capacitive pressure sensors for biomedical applications within the frame of CASE European project [32], started from the observation that the specific boron profile redistributed after the implantation [33] or after thermo-chemical diffusion [34] in the bulk micromachining technology will determine a variation of the chemical etching rate *R* with respect to the rate R_i in weakly doped silicon in 10% KOH (LiOH, NaOH) or EDP (ethylene-diamine-pyrocatechol) solution at the etching temperature $T_e = 60^oC$ for which $a = 4$ and in 24% alkaline type solutions for which $a = 2$ in the relation $R/R_i = 1/[1+C/C_o)^a]^{4/a}$ [35]. The results of our simulated chemical etching rate and of the corresponding etching time Δt, allowing a correct control of the etching process, are shown in Fig. 9.

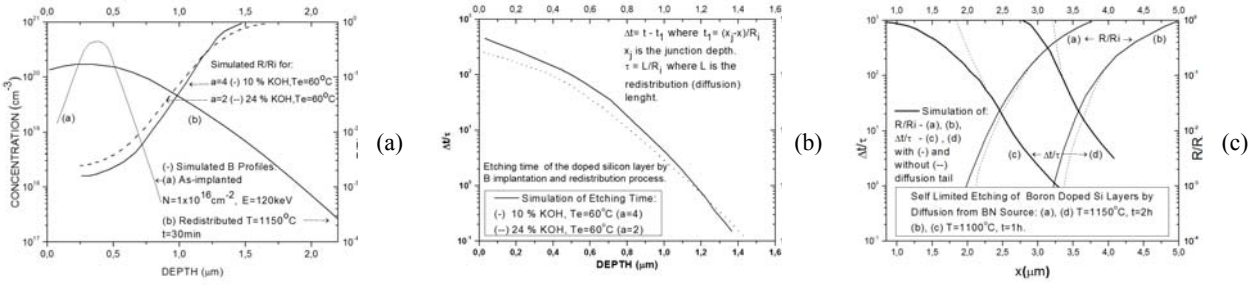


Fig. 9 – a) Variation with the depth of R/R_i in silicon layers doped by implantation; b) $\Delta t/\tau$ vs. depth during the etching of the implanted layer; c) R/R_i and $\Delta t/\tau$ vs. depth during the etching of the BN diffused layers.

The main objective of the researches to obtain membranes by surface (polysilicon based) micromachining technology was to reduce or eliminate the internal stress or stress gradient induced by the atomic mismatch in the polysilicon layers doped by phosphorus diffusion and for this purpose we used the secondary ion mass spectroscopy (SIMS) and spreading resistance profiling (SRP), correlated with cross-section electron transmission spectroscopy (XTEM) to analyse the structure of LP-CVD polysilicon after the deposition (Fig.10) and after the diffusion steps [36]. We proposed a doping-restructuring model [37] of the

polysilicon layers to explain the mechanism of the restructuring processes as follows: the P diffusion in polysilicon and the oxidation during the P thermo-chemical process ($POCl_3$) inject Si self-interstitials which determine an enhancement of the grain growth. During the growth, the surface of grain boundary decreases correspondingly and thereby the inactive P amount segregated there. The enhancement of grain growth determines an enhancement of P atom incorporation in the grains, so that their diffusion in Si bulk furthermore generates self-interstitial atoms which additionally contribute to the growth enhancement, in a continuously self-promoted doping-restructuring process. This mechanism well explains the restructuration of the initial columnar type structure (Fig. 10b) to a large grain one (Fig. 10c) and the reduction/ elimination of the internal stress by applying the optimal conditions of drive-in diffusion process for the fabrication of the silicon membrane for the capacitive pressure sensors with biomedical applications [38].

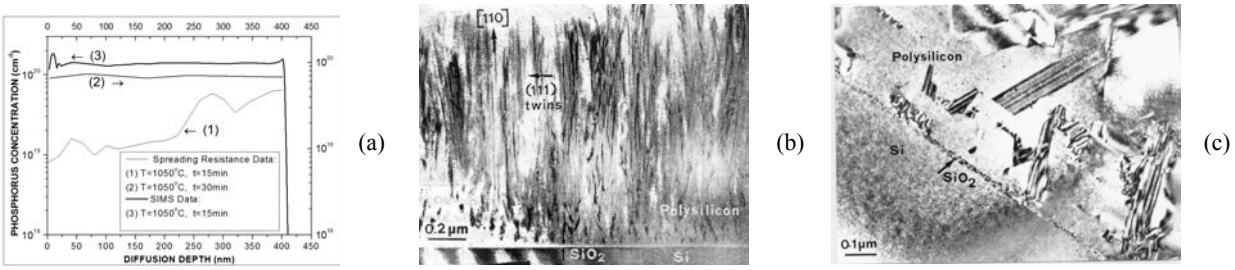


Fig. 10 – a) SIMS and SRP phosphorus diffusion profiles showing the electrical activation of P atoms after diffusion; b) the columnar structure of the initial LP-CVD polysilicon layer; c) the large grain structure after the drive-in thermal process (T = 1030°C, 20 min).

6. CONCLUSIONS

A careful analysis of the spread experimental data on B diffusion in silicon shows that the B diffusion coefficient $D \sim C^{1/2}$ during the diffusion from BBr_3 source, suggesting that the Si self-interstitial atoms contribute to the diffusion mechanism, while during the diffusion from a BN source not ($D \sim C$). A complete set of analytical relations where deduced to adequately describe the boron diffusion profile in both cases, on the extrinsic and intrinsic concentration range and the interest material parameters. B, P, Sb and As diffusion in silicon were adequately simulated under various conditions after the diffusion by using conventional (thermo-chemical) and non conventional techniques (implantation and laser-assisted annealing, polysilicon sources, doped oxide). The conditions of the generation of misfit dislocations were explicitly deduced in terms of technological control parameters (time and temperature). The influence on the forward characteristic of a p-n junction after Au diffusion was analytically expressed and the gettering contributing mechanism by self-interstitial injection was proposed to explain the behaviour of Au, Pt and other metallic impurities in silicon. These results permitted innovative solutions included in fabrication patents and process simulators. The optimisation of the polysilicon drive-in processing by a doping-restructuring model and the simulation of etching process of the boron doped layer were successfully applied for the membrane achievement for the capacitive pressure sensors fabricated by surface and bulk micromachining technology.

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