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Dopant Redistribution during Rapid Thermal Annealing in a Self-Aligned Polysilicon Emitter Bipolar Structure Compatible with a Complementary Metal–Oxide–Semiconductor Technology

By

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Arsenic and boron concentration profiles, diffused from polycrystalline silicon (polysilicon) into an underlying single crystalline silicon, are analyzed by secondary ion mass spectrometry. This bilayer is the basic structure of a self-aligned bipolar transistor, compatible with a complementary metal–oxide–semiconductor; arsenic and boron codiffusions are studied in an emitter and extrinsic base configuration of bipolar transistors. Rapid thermal annealings are performed to obtain shallow junctions, with temperature and annealing plateau duration as parameters. Finally, the codiffusion process is investigated using simulations. It indicates that diffusion of the dopant at the lowest fluence is slowed, much more because of the in-depth inhomogeneous grain growth induced by amorphization and annealing, than a built-in electric field. Then, it should be assumed that the dopant at the highest dose saturates the grain boundary traps. This hypothesis concerns essentially arsenic, but also boron, to a less extent.

1. Introduction

In recent years, the complementary metal–oxide–semiconductor (MOS) combined with a compatible bipolar transistor (BiCMOS) has emerged as a new device. The key idea is to merge the high density of MOS circuits with high current-drive bipolar circuits. In addition, bipolar transistor performances are enhanced when doped polysilicon serves as a diffusion source and as the emitter and extrinsic base contact material [1, 2], so when a thin interfacial oxide layer between the polysilicon and the monocrystalline silicon acts as a tunneling barrier to minority carrier injection into the polysilicon [3]. In fact, in the support BiCMOS technology of our study, the NPN transistor structure is similar to the PMOS one, i.e. polysilicon is used as the contact emitter and as the gate [4]. The extrinsic base is formed during source/drain implantation. The emitter and base junctions of the self-aligned bipolar transistor are formed by alternately driving arsenic and boron atoms from the polysilicon layer into the single crystal silicon substrate. Dopant drive-in must be accomplished with a minimum thermal budget in order to form and maintain the shallow emitter and base structure. The aim of our paper is essentially to study the process diffusion of the dopants into and from polysilicon during rapid thermal annealing. Discussion will be aided by use of a process simulation.

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2. Experimental Procedures

The test wafers used throughout this work are phosphorus-doped (100) Czochralski-grown substrates, $0.5 \Omega \text{ cm}$. P-type $8.15 \Omega \text{ cm}$ boron-doped silicon substrates were also studied. However, as no difference in dopant redistribution between the N and P wafers was noticed, no further reference to the substrate type will be made hereafter. Immediately after a standard RCA cleaning which left a less than 2 nm thick oxide layer on top of the single crystal Si, a polysilicon is formed at 620°C from SiH_4 decomposition in a LPCVD reactor with a residual pressure of 80 Pa. This thin oxide interface has been shown to be effective in preventing the early epitaxial realignment of the polysilicon layer onto the monocrystalline substrate for the RTA parameters used in this study [5], while minimizing the possible diffusion barrier effects of the interface. Moreover, this oxide acts as a tunneling barrier to minority carrier injection into the polycrystalline silicon [6]. Afterwards, the polysilicon receives either a single implantation with B or As, or a double implantation starting with As or Ge and followed by B. The RTA is performed in a 30 kW ADDAX R1000 machine under Ar atmosphere. The implanted wafers are cut in $1 \times 1 \text{ cm}^2$ samples and placed on a 4 in. diameter Si sample holder, at the center of which a K-type thermocouple was cemented for temperature control and measurement via a data acquisition system. The SIMS analysis is achieved by a Cameca IMS4F instrument using 10 keV Cs^+ primary ions and a beam current of 80 nA. The vertical axis of the concentration versus depth curves is calibrated using a standard sample for As with a $5 \times 10^{20} \text{ cm}^{-3}$ maximum concentration. At higher As concentration, this calibration is subjected to some errors, to be taken into account only at the concentration maximum of the as-implanted As profiles. The concentration scales of the B and Ge profiles are obtained by normalizing the SIMS signal to the known implant dose assuming no significant outdiffusion of these species. Depth scale on the horizontal axis is obtained by measurement of the crater depths using an "alphastep" profilometer. We assume no significant difference in the erosion rate between polysilicon and monocrystalline silicon.

3. Experimental Results

Fig. 1a and b deal with single diffusion of arsenic and boron, respectively, after a RTA plateau duration of 1, 5, 10, and 20 s, and a 1050°C onset temperature, a typical temperature for BiCMOS process of CNET [4]. The implantation energy and fluence are respectively 100 keV and $10^{16} \text{ atoms cm}^{-2}$ for Ar, and 30 keV and $2 \times 10^{15} \text{ atoms cm}^{-2}$ for B. As soon as at 5 s, the arsenic profile appears flat in polysilicon, while the boron one is roughly uniform only from 10 s. For 1 and 5 s annealing plateau duration, arsenic diffusion is enhanced, if we compare to the boron one. If we take into account also that the boron as-implanted profile is deeper than the arsenic one, it can be straightforwardly concluded that arsenic diffuses faster than boron in polysilicon. It is well known that arsenic dopants move along polysilicon grain boundaries, when annealing is performed, and can present a wide range of diffusivities, from 100 up to 10000 higher than arsenic diffusivity in monocrystalline silicon during classical thermal annealings (CTA), depending especially on the polysilicon deposition process [7]. On the other hand, the boron diffusion coefficient is assumed to be from 50 up to 200 times greater than B diffusivity in monosilicon during CTA [6]. Some authors underline that boron does not diffuse at grain boundaries, according to Hall effect measurements which show a constant carrier concentration versus annealing

temperature [8]. To explain its greater diffusivity into polysilicon, with regard to monocrystalline silicon, it has been proposed that boron diffuses via a cluster process, when the solubility limit is exceeded [9]. Concerning the present temperature, the solubility limit is in the order of $(2 \text{ or } 3) \times 10^{20} \text{ cm}^{-3}$, greater than the boron implantation peak. So, this argument cannot be employed.

On Fig. 2 arsenic and boron co-diffusion are shown for a 1, 5, 10, 20 s annealing plateau duration, which are processed in emitter and extrinsic base configuration of a NPN transistor.

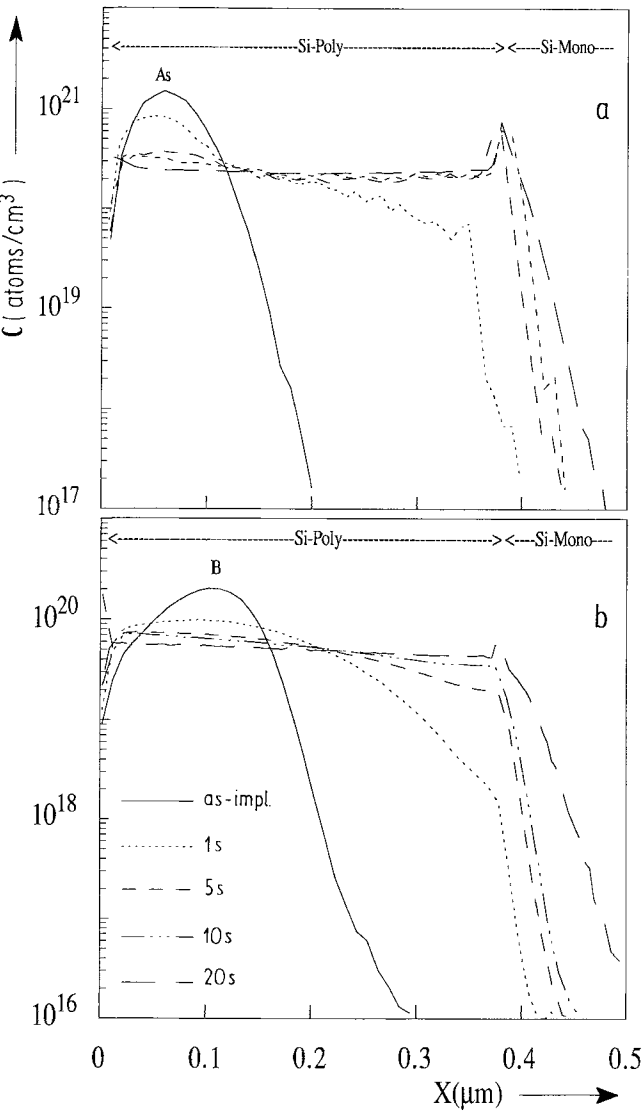


Fig. 1. SIMS profiles of a) arsenic (100 keV , 10^{16} cm^{-2}) and b) boron (30 keV , $2 \times 10^{15} \text{ cm}^{-2}$) implanted alone in a 380 nm thick polysilicon LPCVD layer deposited at 620°C on n-type monocrystalline silicon; RTA at 1050°C for 1, 5, 10, and 20 s

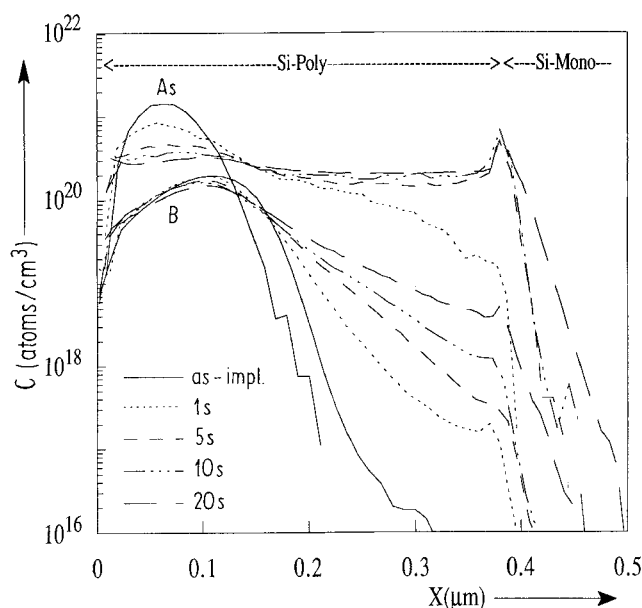


Fig. 2. SIMS profiles of As and B co-implanted, using the parameters mentioned in Fig. 1, in the polysilicon/monocrystalline silicon structure, RTA at 1050 °C for 1, 5, 10, and 20 s

The dopant implantation parameter sets are the same as for the single implantations. Arsenic is first implanted, so that at such a fluence a polysilicon upper layer, at least as large as the arsenic projected range, is amorphized [10]. Firstly, we have to outline that the annealing plateau duration must be more than 5 s to obtain uniform arsenic profile, for the

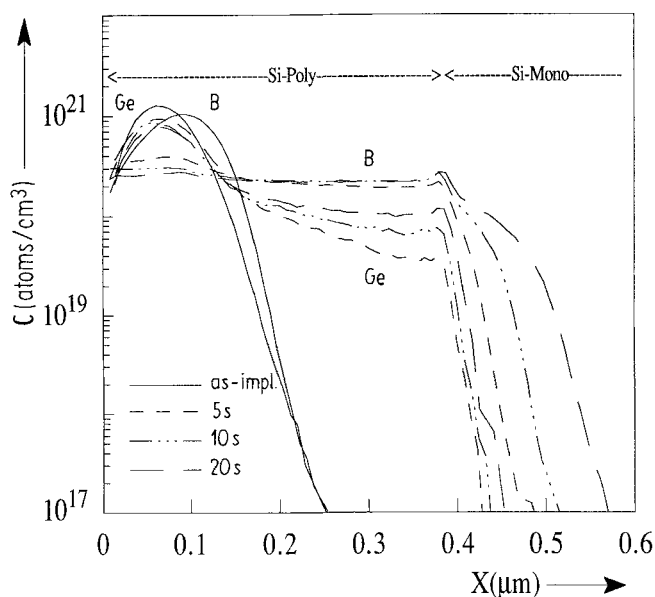


Fig. 3. Germanium (100 keV, 10^{16} cm⁻²) and boron (25 keV, 10^{16} cm⁻²) SIMS profiles after RTA at 1050 °C for 5, 10, and 20 s

1050 °C RTA. In this case, the carrier profile can be also expected flat, even if only roughly 20 or 25% of the total chemical concentration is ionized, because of an important segregation at grain boundaries [6]. In other words, a uniformly high carrier concentration is necessary to obtain good emitter contacts.

Moreover, a strong boron retardation should be observed along the polysilicon depth, when this dopant is in the presence of a high arsenic dose. This phenomenon seems too pronounced to be only attributed to the electric field created by two species of opposite charge. A key idea is to suppose that the polysilicon morphology intervenes in this diffusion process. Grain structure modification during annealing should influence boron diffusion. Grain size can be modified in two ways: an amorphization due to a high dose implantation, followed by a fast recrystallization with an important grain growth during the first ms of annealing [11], or a lower grain growth involved by the annealing itself, assisted by defects in the neighborhood of the grain boundaries, which can be enhanced by donors as reported by Zheng et al. [12].

To perform an amorphized layer similar to the arsenic implantation, but without involving an electrical process, we implant germanium, which is neutral in silicon, with the same fluence and energy parameters as arsenic. Co-diffusion of boron (25 keV and 10^{16} atoms cm^{-2}) and germanium (100 keV and 10^{16} atoms cm^{-2}) is presented on Fig. 3 for 5, 10, 20 s annealing plateau duration. As can be observed, boron diffuses very rapidly into polysilicon, even with such a high dose which could involve cluster formation, because its peak concentration is more than five times the solubility limit. A flat profile is obtained as early as at 5 s along the polysilicon depth; boron profiles are Gaussian-like in monocrystalline silicon, whatever the annealing duration. Boron acts as if it is in single diffusion. We could conclude, at first, that a large grain structure due to the recrystallization of the amorphous upper layer, involved by arsenic (Fig. 2) or germanium (Fig. 3) implantation, does not

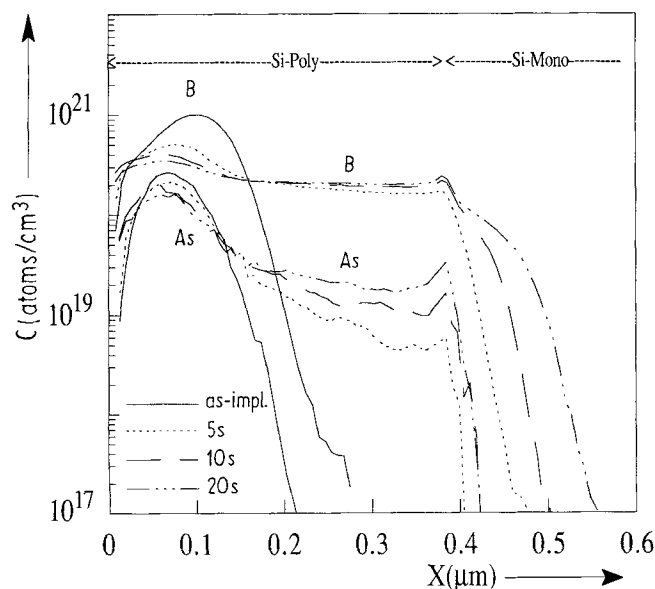


Fig. 4. Co-diffusion of arsenic (100 keV, 2×10^{15} cm^{-2}) and boron (25 keV, 10^{16} cm^{-2}) after RTA at 1050 °C for 5, 10, and 20 s

intervene in the boron diffusion process. On the other hand, the boron implantation peak slightly remains after the annealing, which could explain why the boron profile plateau cannot exceed $2 \times 10^{20} \text{ cm}^{-3}$, the solubility limit in polysilicon [7]. Consequently, it could be proposed that boron clusters of the implantation peak diffuse along the grain boundaries, as long as boron can diffuse from the grain boundary to the grain. Anyhow, cluster assisted boron diffusion is another troublesome point.

Finally, we present on Fig. 4 the co-diffusion of boron (25 keV and $10^{16} \text{ atoms cm}^{-2}$) and As (100 keV and $2 \times 10^{15} \text{ atoms cm}^{-2}$) for 5, 10, and 20 s annealing plateau, at 1050 °C. We realize, in this way, an emitter and an extrinsic base of a PNP bipolar transistor. Boron profiles, in presence of such a low arsenic dose, are similar to boron when it is co-implanted with germanium (Fig. 3). However, in the former case, the remaining implantation bump is more apparent in the upper polysilicon layer. So, besides a flat profile in the deeper polysilicon after 10 s annealing, the Gaussian-like boron profiles in monocrystalline silicon are a little less deep in the presence of arsenic. This spectacular boron diffusion into single-crystal silicon, very different from a classical erfc-like profile, when polysilicon is considered as a simple dopant source, could be awkward to process PNP transistors; it should be hard to control emitter junction depths, and, for instance, to avoid overlapping of the intrinsic base by boron.

4. Simulation and Discussion

With a view to analyse the redistribution of dopants during annealing, we perform simulations using the two-dimensional TITAN V program [13]. Such a process simulator is very fruitful to facilitate developments of new technologies, since decreasing dimensions and increasing complexity lead to geometrical and physical effects which have been considered as second-order effect to have to be accurately taken into account in submicron technology.

In practice, we use an Arrhenius law for arsenic and boron diffusivity, i.e.

$$D = D_0 \exp(E_0/kT).$$

The commonly used defect parameters, for CTA in monocrystalline silicon [13], are for boron $D_0 = 0.5554 \text{ cm}^2/\text{s}$, $E_0 = 3.42 \text{ eV}$; for arsenic $D_0 = 22.83 \text{ cm}^2/\text{s}$, $E_0 = 4.1 \text{ eV}$.

We show on Fig. 5, the fitting of polysilicon diffusivity for 1050 °C, 20 s RTA (As: 100 keV, $10^{16} \text{ atoms cm}^{-3}$, B: 30 keV and $2 \times 10^{15} \text{ atoms cm}^{-3}$). In contrast to arsenic diffusion, which can be taken into account by only a low variation of the diffusivity prefactor along the polysilicon depth, a constant boron diffusion coefficient, typically $D'_{0,B} = 70 \text{ cm}^2/\text{s}$, does not give a good fit of the experimental profile (see figure). Let us note that the built-in electric field intervenes in the equations by assuming that all the dopants are ionized. In fact, taking a lower diffusivity is not the good way to get a better fit for the B profile. With a $D'_{0,B}$ as low as $20 \text{ cm}^2/\text{s}$, the B profile is already flat between surface and the projected range, while boron does not diffuse enough in depth. Consequently, the first idea should be to divide the polysilicon layer in two parts, because of the fast recrystallization of the amorphous surface layer which is roughly 45% of the whole polysilicon thickness [10]. But, to obtain a much better accuracy, especially concerning boron, we need to split the polysilicon depth in approximately four equal layers (95 nm each). As supposed, the diffusion coefficient is actually a function of the polysilicon depth. From the surface to the oxide interface, the prefactor diffusivity $D'_{0,B}$ varies: 2.5, 8, 30, and $70 \text{ cm}^2/\text{s}$. Moreover, a very low

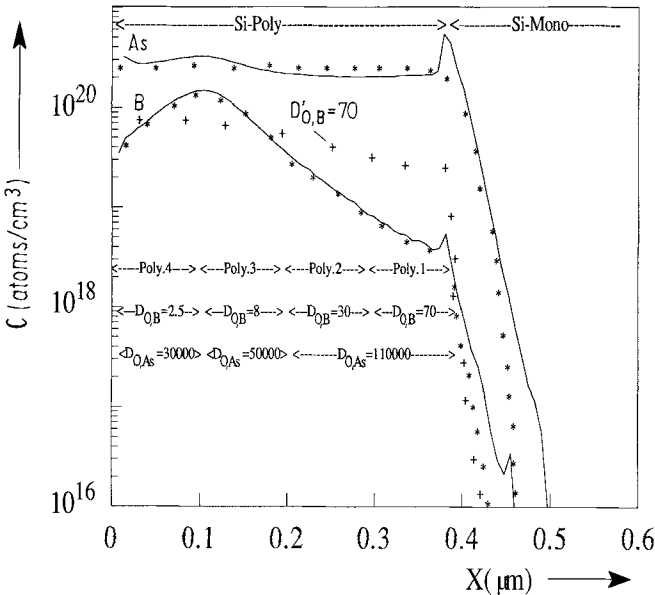


Fig. 5. Co-diffusion of arsenic (100 keV , 10^{16} cm^{-2}) and boron (30 keV , $2 \times 10^{15}\text{ cm}^{-2}$) after an RTA at $1050\text{ }^{\circ}\text{C}$ for 20 s . Comparison between SIMS data (—) and computer simulation considering four polysilicon sublayers (*) or only one (+) (D_0 in cm^2/s)

variation of these prefactors changes drastically the shape of the curve. The uniqueness of these D_0 values for a given deposition process, seems to be a key point. This increasing diffusivity versus polysilicon depth could be attributed to an inhomogeneous grain structure and/or to an active arsenic dopant profile which should be very different from the SIMS profile. The latter assumption, which implicitly proposes that the carrier profile is not as flat as the dopant one, but decreases versus depth, is in contradiction with reported previous measurements [6], as mentioned above. Since arsenic atoms penetrate into grain boundaries at the early stage of annealing (Fig. 2) and then go faster than boron ones into the polysilicon, we think that dopant–dopant electrical interaction, or an anomalous built-in electric field, is not the principal feature to explain this inhomogeneous diffusion into polysilicon. Moreover, it is well known that polysilicon is used efficiently to get excellent emitter contacts, so as to perform electrical activity of emitter doping in monocrystalline silicon. Then, the grain size which appears to be greater in the upper polysilicon layer (measured by TEM [10]), because of the fast recrystallization of the initial amorphous layer, seems to play a leading part in boron diffusion. In the case of single diffusion, if, as expected at $1050\text{ }^{\circ}\text{C}$, a flat arsenic (100 keV , $10^{16}\text{ atoms cm}^{-3}$) profile is obtained all along the polysilicon depth, and if we use a prefactor diffusivity extracted from co-diffusion analysis, i.e. $D'_{0,As} = 110000\text{ cm}^2/\text{s}$, we have a roughly uniform boron (30 keV , $2 \times 10^{15}\text{ atoms cm}^{-3}$) concentration only for $D'_{0,B} = 150\text{ cm}^2/\text{s}$ (see Fig. 6), which is much higher compared to co-diffusion. So it can be assumed that boron fastly diffuses from a region located inside the grain, but very near the grain boundary, a defect-rich region. This is not in contradiction with Hall effect measurements as reported before. Let us still note the difference between arsenic and germanium: the former one is electrically active in silicon, while germanium is neutral. Grain boundaries cannot be considered to act only mechanically as pipelines, but dopants

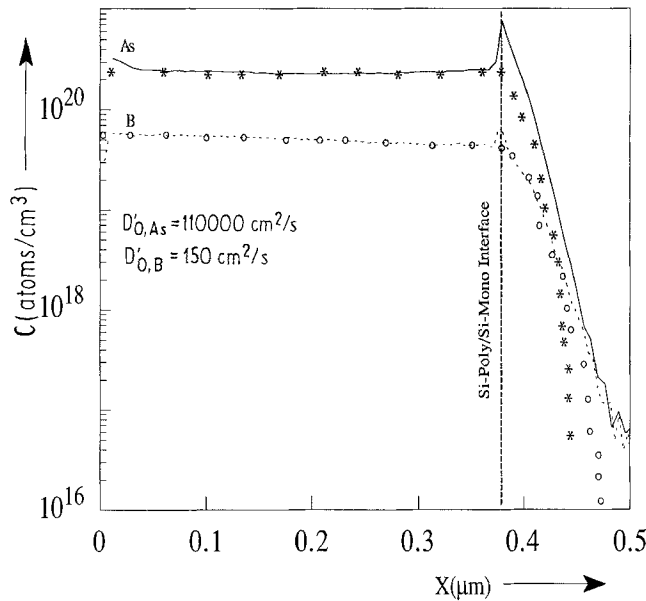


Fig. 6. Diffusion of arsenic (100 keV , 10^{16} cm^{-2}) after RTA at 1050°C for 20 s: experimental SIMS profiles (—), computed curves (*), and boron (30 keV , $2 \times 10^{15} \text{ cm}^{-2}$) after RTA at 1050°C for 20 s experimental SIMS profiles (---), computed curves ($\circ$)

diffuse there assisted by electrical charges (perhaps a part of dangling bonds), which can be saturated by arsenic in As/B co-diffusion and then slow boron diffusion. In conclusion, polysilicon has a structural (i.e. depth-dependent grain boundary density) and an electrical (i.e. grain boundary trap saturation) influence on boron diffusion.

To complete this study, we worked with three other temperatures for As and B co-diffusion, i.e. 1150 , 1100 , and 1000°C , since working at low temperature tends to ultra-large scale integration (ULSI). For a given depth, diffusivity decreases with temperature, since grain size increases versus this parameter. This agrees well with the grain structure influence in boron diffusion. We define a multiplying F_B coefficient as the ratio of polysilicon RTA diffusivity over single crystal CTA one. It is shown versus depth in Fig. 7. Dots are located at the center of each of the four polysilicon sublayers. The behavior is truly exponential.

Fig. 8 deals with co-diffusion of arsenic and boron in a PNP configuration, when the boron concentration is greater than the arsenic one, at 1100°C , for a 20 s annealing duration. The implantation parameters are 100 keV and $2 \times 10^{15} \text{ atoms cm}^{-2}$ for arsenic, and 25 keV and $10^{16} \text{ atoms cm}^{-2}$ for boron. Let us point out that we need diffusivities in a wide range all along the polysilicon depth to fit the arsenic profile. Since boron fastly diffuses in polysilicon, and since boron implantation is deeper than the arsenic one, we cannot expect once again that an electric field plays a dominant part in the arsenic diffusion slow down. So, in such a configuration, arsenic diffusion is also expected to depend on grain size. In other words, it could be an indirect evidence that in this case, a part of boron or more probably complexes of boron, fill the grain boundaries, giving place to slow arsenic diffusion. It can also be due to traps saturated by boron atoms at the border between grain and grain boundary, a defect-rich region. Consequently, due to such a trap saturation, this dopant (As) cannot travel so easily along grain boundaries. As for boron, we define the F_{As} multiplying coefficient

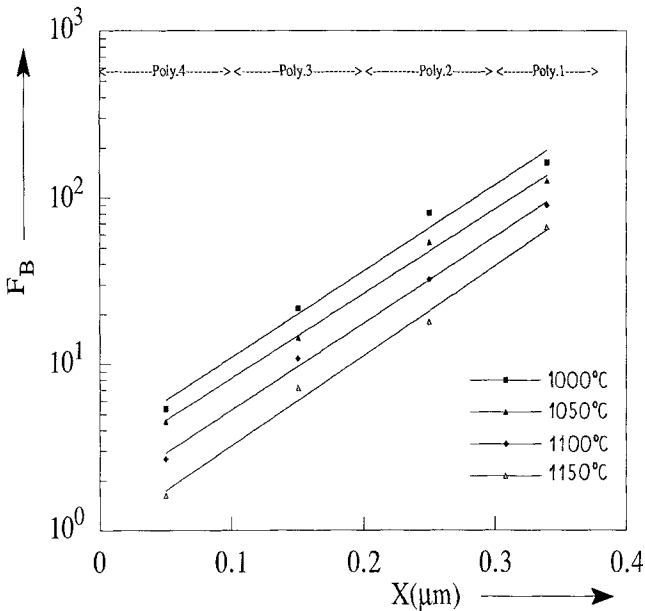


Fig. 7. Boron (30 keV, $2 \times 10^{15} \text{ cm}^{-2}$) diffusivity enhancement prefactor vs. polysilicon depth after RTA for 20 s

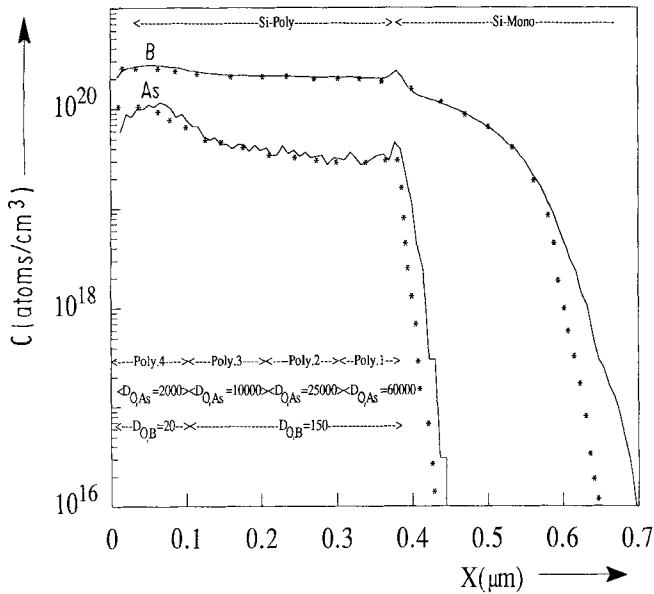


Fig. 8. Co-diffusion of arsenic (100 keV, $2 \times 10^{15} \text{ cm}^{-2}$) and boron (25 keV, 10^{16} cm^{-2}) after an RTA at 1100 °C for 20 s: experimental SIMS profiles (—), computed curves (*)

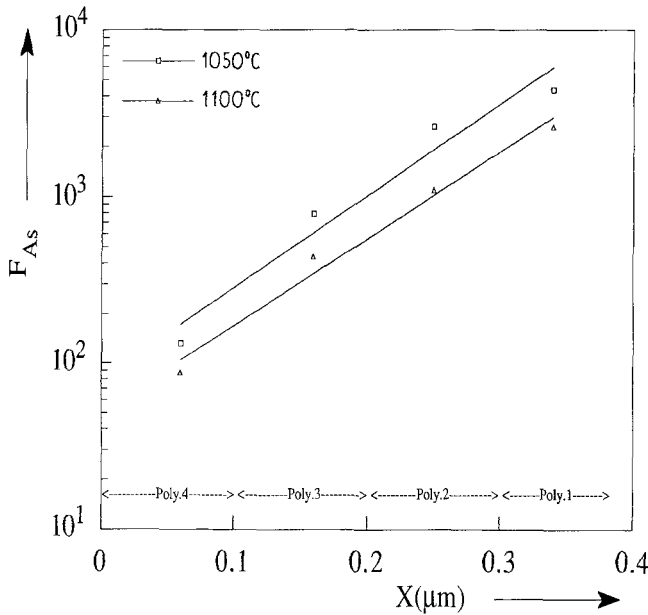
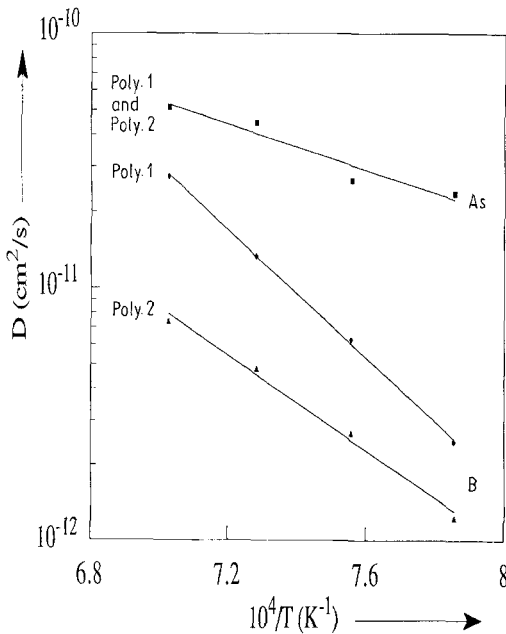


Fig. 9. Arsenic (100 keV, $2 \times 10^{15} \text{ cm}^{-2}$) diffusivity enhancement prefactor in polysilicon after RTA at 1050 and 1100 °C for 20 s

for arsenic diffusivity in polysilicon. It is shown in Fig. 9 versus polysilicon depth for 1050 and 1100 °C. The behavior seems still exponential, as for boron (cf. Fig. 7), especially at 1100 °C.



In the last part of our paper, we should like to focus on the co-diffusion process of arsenic and boron, when implantation energy and fluence are 100 keV and 10^{16} cm^{-2} for Ar and 30 keV and $2 \times 10^{15} \text{ cm}^{-2}$ for B, respectively. On Fig. 10 boron and arsenic diffusivities are presented versus temperature into the non-pre-amorphized polysilicon, i.e. roughly from 200 to 400 nm in depth (corresponding to the second and first polysilicon sublayers of the simulation).

Fig. 10. Boron (30 keV, $2 \times 10^{15} \text{ cm}^{-2}$) and arsenic (100 keV, 10^{16} cm^{-2}) diffusivities vs. temperature in the non-pre-amorphized polysilicon layer after RTA for 20 s

It is an Arrhenius law with a higher slope for boron. We can easily extract the prefactor diffusivity (D_{eff}) and the energy of activation (E_{eff}) both for boron and arsenic. The diffusivity can be written as $D = D_{\text{eff}} \exp(-E_{\text{eff}}/kT)$, for arsenic and boron, in the non-pre-amorphized polysilicon sublayer, around 55% of the whole thickness, taken from the interface. In fact, it seems reasonable to consider different activation energies for the grain and the grain boundary. Since we consider the underneath polysilicon (second and first sublayers), this effective activation energy tends to the grain boundary activation energy. These new average activation energies are roughly 1/4 and 2/3 lower than for CTA in monocrystalline silicon, for arsenic and boron, respectively. This result could be compared to metals whose grain boundary activation energy is about half the bulk one. Since these energies are evaluated in the richest grain boundary polysilicon zone, we get an over-estimation of the grain boundary activation energy for each dopant. By fitting, the arsenic diffusivity is expressed as

$$D_{\text{As}} = 7.85 \times 10^{-8} \exp(-0.9/kT) \text{ cm}^2/\text{s}.$$

For boron, we obtain in the first polysilicon sublayer

$$D_{\text{B1}} = 1.9 \times 10^{-2} \exp(-2.5/kT) \text{ cm}^2/\text{s}$$

and in the second polysilicon sublayer

$$D_{\text{B2}} = 3.2 \times 10^{-5} \exp(-1.86/kT) \text{ cm}^2/\text{s},$$

when arsenic and boron are in co-diffusion in a NPN configuration (As: 100 keV, 10^{16} cm^{-2} ; B: 30 keV, $2 \times 10^{15} \text{ cm}^{-2}$).

The last remark is that we have not treated quantitatively dopant diffusion in the underlying monocrystalline silicon. The first reason is the very shallow junction in monosilicon. We have found a diffusivity enhancement factor in monosilicon (compared with defect CTA values) of 1 to 5 up to 15. Since the first values seem correct, the interfacial oxide can act as a defect sink and then undergoes an enhancement diffusion underneath, the latter, i.e. 15, is too high. It could be an evidence that sputtering rates, both into polysilicon and monocrystalline silicon, concerning SIMS measurements, cannot be taken exactly equal. Then, the depth profiles in monosilicon should be exaggerated. Another artefact is addressed to the arsenic profile. Since we have not modelled the interface arsenic pile-up, it seems difficult to fit its diffusivity in the monocrystalline silicon.

5. Conclusions

Boron and arsenic diffusion, and their co-diffusion into and from polysilicon, used as the emitter of a CMOS compatible bipolar transistor, have been analyzed after rapid thermal annealings. A comprehensive study of the chemical profiles has been undertaken. Simulations of boron diffusion into polysilicon reveal that its diffusivity prefactor varies over a wide range, for instance from 35 (1150 °C) to 90 (1000 °C) cm^2/s in the richest grain boundary density region. Boron diffusivity is then 65 to 160 times larger than the diffusivity of boron in single-crystal silicon during classical thermal annealings, when boron is in co-diffusion with a higher dose of arsenic. In addition, diffusivities associated to polysilicon are also depth dependent, decreasing when polysilicon grain size increases, both for boron and arsenic. Finally we have extracted for these dopants new activation energies in polysilicon, always when the arsenic fluence is greater than the boron one. Their ratio between polysilicon

and single-crystal silicon is apart those of metals (roughly 1/2), i.e. 1/4 for arsenic and 2/3 for boron. Some questions still remain, especially concerning the dependence of activation energy and diffusivity prefactor on polysilicon deposition process conditions.

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