

Diffusion and segregation of arsenic and boron in polysilicon/silicon systems during rapid thermal annealing

A. Merabet*

Laboratoire Physique et Mécanique des Matériaux Métalliques, Faculté des Sciences de l'Ingénieur, Université de Sétif, Sétif 19000, Algeria

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Abstract

Comparative studies of arsenic and boron diffusion as well as segregation in polysilicon on single-crystal silicon systems have been performed by secondary ion mass spectroscopy. Arsenic (10^{16} atoms/cm²; 100 keV) or boron (2×10^{15} atoms/cm²; 30 keV), (and both of them with As and followed by B), have been implanted in 380 nm polysilicon laid by low-pressure chemical vapor deposition have been diffused into the underlying silicon substrate in effect of rapid thermal annealing for 20 s at temperatures ranging from 1000 to 1150 °C. Before the deposition of polysilicon, the oxide film has been removed. Up to about 11 and 10% of implanted arsenic atoms are segregated at the interface in the case of diffusion and co-diffusion, respectively, while up to 2.6% (diffusion) and 4.45% (co-diffusion) of the implanted boron atoms are segregated at the interface. The As and B doses distributed in the substrate are smaller than the doses segregated at the interface. The continuity of arsenic and boron profiles extrapolated at the interface, shows on absence of the diffusion barrier. Diffused arsenic dose to the single crystalline Si shows a reduction of about 50% in the case of co-diffusion if compared to diffusion. As boron is concerned, the difference is even higher which confirms the stopping of the diffusion of the boron in the presence of the arsenic.

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1. Introduction

Bipolar transistor is used for applications requiring very high speeds, for telecommunications, as well as for power modules. However, complementary metal-oxide-semiconductor (CMOS) technology has become the leader in logic for very large scale integration (VLSI) because of its low static power consumption and possibility of component miniaturization leading to a greater integration. Circuit designers have therefore used the potentials of these two families to create functions requiring high speed, low power consumption and high integration. This leads to a compatible bipolar technology CMOS (BiCMOS).

Recently, several advantages of polysilicon diffusion sources for the formation of shallow junctions in single-crystal silicon have become evident. Highly doped polysilicon can be used as a source of dopants for the single crystalline underlying silicon where the emitter of bipolar transistor created. The dopants are implanted into the

polysilicon layer before undergoing a heat treatment allowing for electrical activation of ions and their rapid redistribution in the polycrystalline layer towards the monocrystalline layer, sometimes through a very thin oxide layer.

The interface between polycrystalline silicon and single crystal silicon is of great importance. The most widely used are two types of surface treatment: the standard RCA cleaning, which produces a surface oxide layer 1.5 nm, and the HF one leaving only about a 0.5 nm thick oxide. The influence in the gain in current between these two treatments is estimated to be in the ratio of 5, favorable to RCA cleaning [1,2].

The standard RCA cleaning [3,4] leaves behind a 1.5 nm oxide layer on the surface of single crystal silicon. This cleaning procedure makes it possible to avoid the epitaxial realignment of the polysilicon layer starting from the polycrystalline silicon/single crystal silicon interface [3,5–7]. This realignment can modify the diffusion process in the polysilicon and makes its control more complicated. The junctions created in the underneath silicon can also present non ideal electrical characteristics [8]. Moreover the RCA cleaning minimizes diffusion barrier effects at the interface

* Tel.: +213-36912681; fax: +213-36925134.

E-mail address: merabet.abdelali@yahoo.fr (A. Merabet).

[5]. According to Batra et al. [9], the thickness of the oxide layer is estimated to be 1.4 and 0.8 nm for RCA cleaning and that one in HF, respectively. This latter treatment was observed by other authors [6,10,11] to lead to epitaxial realignment of the polycrystalline silicon during heat treatment.

The study conducted by Bohm et al. [7] in order to see the effect of RCA cleaning and of the HF one on the diffusion of boron and arsenic shows that, for RCA cleaning, the concentration of dopant in the polysilicon layer is constant whereas the HF cleaning produces a concentration gradient (less rapid diffusion) and induces a fall in the concentration of dopant at the interface due to epitaxial realignment thus leading to a reduction in diffusion in the silicon.

The thin oxide layer often present between the single-crystal silicon substrate and the polysilicon film can greatly alter the diffusion of dopant. Arsenic, and possibly other dopant species, tend to accumulate at the polysilicon-single-crystal silicon interface; the amount of dopant segregated near this interface depends on the thickness of the interface oxide [12].

The rapid thermal annealing (RTA) is considered to be as an alternative to the standard furnace treatments for implantation damage removal in silicon. The short process time involved (<100 s) minimizes dopant diffusion and a high electrical activity is reached because annealing temperatures above 1000 °C may be used [13].

The purpose of this work is to investigate the RTA induced redistribution of implanted arsenic and boron in polysilicon/monocrystalline silicon structures used for BiCMOS circuits. Secondary ion mass spectrometry is used for dopant profiling. In this paper we report the dose of arsenic and boron segregated at the polysilicon on single-crystalline silicon interface and the dose diffused to the substrate.

2. Experimental procedure

The substrates used are B-doped (1 0 0) Czochralski-grown silicon wafers with resistivity of 8–15 Ω cm. Before the deposition of the polysilicon film, the layer of the native oxide was chemically removed using HF followed by RCA cleaning. This type of cleaning [3,4] leaves 1.5 nm thick oxide layer on the surface of the single crystal silicon [8]. This treatment was chosen in order to prevent epitaxial realignment and to minimize possible diffusion barrier effects of the interface. Immediately after the standard cleaning, a 380 nm thick layer of polysilicon was deposited at 620 °C by thermal decomposition of silane (25% SiH₄ and 75% N₂) under a residual pressure of 600 mTorr inside a low pressure chemical vapor deposition (LPCVD) reactor; an example of a horizontal LPCVD system has been presented in ref. [14]. Next, the ion implantation was carried out, either with arsenic or boron or co-implantation with arsenic followed by boron. The doses and energies of implantation were 10^{16} atoms/cm² and 100 keV for arsenic,

and 2×10^{15} atoms/cm² and 30 keV for boron. The heat treatments were carried out, under an argon atmosphere, inside an ADDAX R1000 lamp type furnace designed and made by the Company A.E.T. of Meylan, installed in the laboratory P.M. of INSA Lyon's (France). The specimens were analysed by a CAMECA IMS3F type secondary ions mass spectrometer (SIMS) after having eroded the surfaces to be analysed with a beam of 15 keV oxygen ions.

3. Experimental results and discussion

3.1. Diffusion of arsenic

Fig. 1 shows the SIMS profiles of arsenic after implantation and after rapid thermal annealing for 20 s at different temperatures (1000–1150 °C). The implantation profile is not really Gaussian. The superposition of the diffusion profiles for different annealing temperatures shows a remarkable diffusion of the dopant in polysilicon producing a highly doped N⁺ region. At temperatures above 1050 °C the plateaus with a mean arsenic concentration of 2×10^{20} atoms/cm³ are clearly observed. Knowing that the dose/thickness ratio is 2.5×10^{20} atoms/cm³, the nearly total conservation of the implanted dose within the polysilicon is easily explainable. This fast diffusion of arsenic in the polysilicon layer, creating a flat concentration profile up to the interface, characterizes the absence of epitaxial realignment [5]. The latter would induce, starting from the interface on the polysilicon side, the appearance of monocrystalline silicon, thus stopping diffusion. The penetration of arsenic increases with annealing temperature to reach 508 nm at 1150 °C for a concentration of 10^{18} atoms/cm³. The resulting doping profile in the substrate is very abrupt, as it is

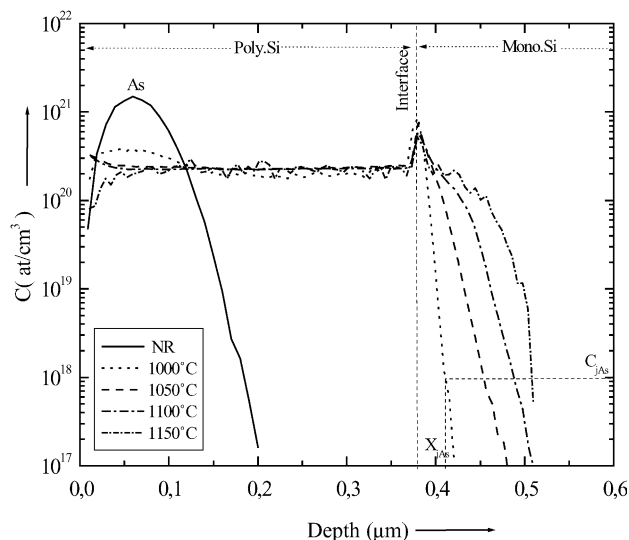


Fig. 1. Diffusion profiles of As before (NR) and after annealing for 20 s at different temperatures (X_{jAs} : diffusion depth corresponding to $C_{jAs} = 10^{18}$ atoms/cm³).

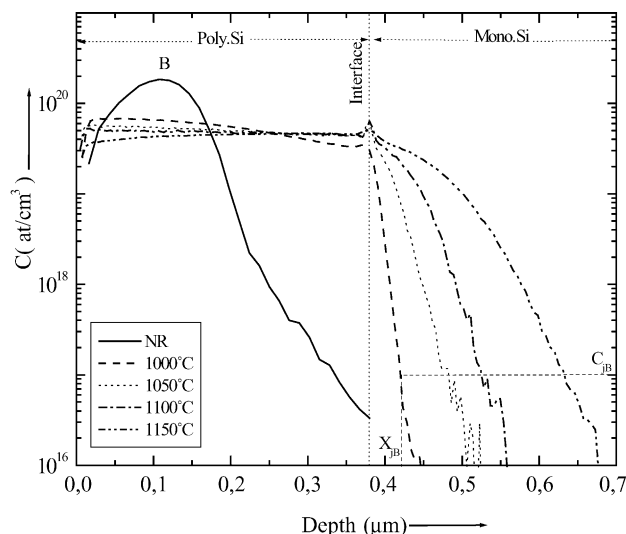


Fig. 2. Diffusion profiles of B before (NR) and after annealing for 20 s at different temperatures (X_{jB} : diffusion depth corresponding to $C_{jB} = 10^{17}$ atoms/cm³).

desired for the creation of a very thin and highly doped N⁺ emitter zone.

3.2. Diffusion of boron

Fig. 2 shows the variation of the B concentration as a function of depth for an anneal at temperatures in the range 1000–1150 °C for a fixed duration of 20 s. The implantation profile, often apprehended by a distribution of type Pearson IV, presents an implantation tail characteristic of channeling. This description [15] uses the four-moment: project range, standard deviation, skewness and kurtosis to describe the tail character of the distribution. The details of this distribution have been well described in ref. [16]. A concentration gradient on the profile corresponding to 1000 °C is observed in polysilicon. This gradient disappears starting from 1100 °C, where a plateau of the B concentration equals to 4.6×10^{19} atoms/cm³ is observed at the right of the implantation peak. The mean concentration given by the B dose to polysilicon thickness ratio is 5×10^{19} atoms/cm³. A small quantity of B dopant diffuses in monosilicon at 1000 °C. The penetration of boron increases with annealing temperature to reach 632 nm at 1150 °C, for a concentration of 10^{17} atoms/cm³. For the same temperature, the penetration of boron in the monocrystalline substrate is more pronounced than that of arsenic. This is due to the differences in diffusion coefficients in monocrystalline silicon.

3.3. Co-diffusion of arsenic and boron

The superposition of the diffusion profiles of arsenic after anneals for 20 s at different temperatures (1000, 1050, 1100 and 1150 °C) shows a plateau with the 2×10^{20} atoms/cm³ mean As concentration between the 180 nm depth and the

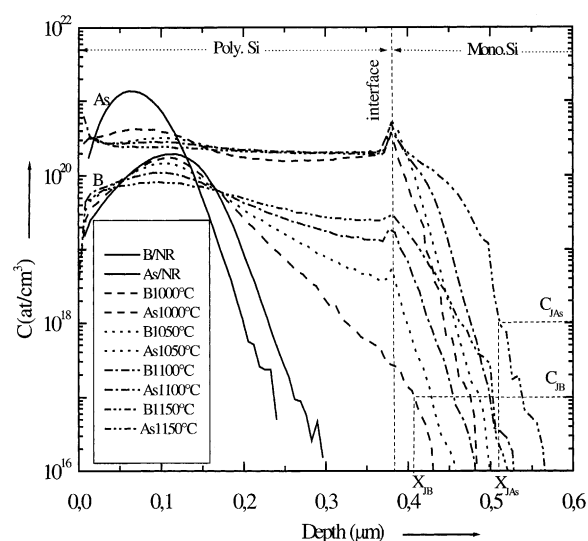


Fig. 3. Diffusion profiles of As and B before (NR) and after annealing for 20 s at different temperatures (X_{jAs} , X_{jB} : diffusion depth corresponding to $C_{jAs} = 10^{18}$ atoms/cm³ and $C_{jB} = 10^{17}$ atoms/cm³).

interface for anneals at $T \geq 1050$ °C (Fig. 3). The arsenic profiles present a segregation of about 5×10^{20} atoms/cm³ at the interface. At a concentration of 10^{18} atoms/cm³, the diffusion depth of arsenic reaches 512 nm at 1150 °C and 7.4% of it has diffused into the substrate, giving an emitter–base junction depth of 132 nm. At the same temperature, boron presents a concentration gradient on all the profiles with a decrease from 6×10^{19} atoms/cm³ at the right of the implanted peak to 2.5×10^{19} atoms/cm³ near the interface. The diffusion of boron reaches a depth of 502 nm at 1150 °C for a concentration of 10^{17} atoms/cm³ and 1.7% of it has diffused into the substrate, giving a collector–base junction depth of 122 nm. An inflexion point, of coordinates (170 nm; 6×10^{19} atoms/cm³), common to all the profiles of boron is observed. This abscissa, situated at 45% of the polysilicon thickness (380 nm) in relation to the surface, corresponds quite well to the limit of the Si zone amorphized by arsenic implantation which has been confirmed by transmission electron microscopy (TEM) [17]. Boron seems to be held at the summit of the profile and to reveal significant curve tails right of the peak. Stopping boron in the presence of arsenic, seems to be a phenomenon too pronounced to be attributed essentially to the electric field created by the two opposite charged species. As a matter of fact, the profile of arsenic becomes flat in a very fast way, thus electric field of its gradient becomes very weak. A first idea is to suppose that the modification of the grain structure during the anneal influences the diffusion of boron. The grain size can be modified by two ways: an amorphization due to a high-dose implantation followed by recrystallisation with important grain growth, or small grain growth activated by the anneal and assisted by defects near the grain boundaries and also accelerated by the donors as reported by Zeng et al. [18]. It is worth to mention the work of Tsai and

Streetman [19], which showed that preamorphization of the Si surface prior to boron implantation caused reduction of the channeling tail, thereby allowing for a creation of shallower, more sharp junctions. The variation of the junction depth X_j with temperature (Fig. 4) in the interval (1000–1150 °C), determined at a concentration of 10^{18} atoms/cm³ for arsenic and 10^{17} atoms/cm³ for boron, shows the alignment of the points according to the straight lines given by the following expressions in case of co-diffusion:

$$X_{jAs} = 4.5 \times 10^{-4} T - 0.01 \mu\text{m} \quad (1)$$

and

$$X_{jB} = 7 \times 10^{-4} T - 0.33 \mu\text{m} \quad (2)$$

The comparison of the junction depths (Fig. 4) in case of diffusion determined for arsenic, boron and co-diffusion from Figs. 1–3, respectively, does not show any significant difference as arsenic diffusion is concerned. The global behavior of arsenic in the double layer (namely the form of the profile in silicon) has not been affected by the presence of boron. However, we can observe that arsenic redistribution has been slowed down in the form of a hump, remainder of the implantation peak in the diffused profile, whereas the diffusion of boron in the presence of arsenic is notably slowed down. The junction depth [X_{jB} (B only implanted) – X_{jB} (implanted B and As)] decreased from 27 nm at 1000 °C, and from 130 nm at 1150 °C. Jain et al. [20] made a comparison between the profiles of boron implanted in the silicon, and in the preamorphized by GeF₂, and showed a significant reduction of the channeling tail. After annealing (1100 °C/1 s) the preamorphization resulted in decreased junction depth to a value estimated as 35 nm.

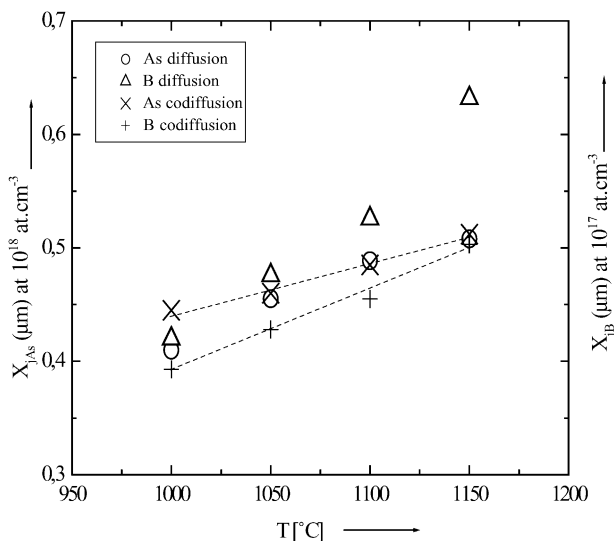


Fig. 4. Comparison between junction depths in diffusion and co-diffusion as a function of annealing temperature (X_{jAs} and X_{jB} : diffusion depth corresponding to $C_{jAs} = 10^{18}$ atoms/cm³ and $C_{jB} = 10^{17}$ atoms/cm³).

3.4. Segregation of arsenic and boron at the interface

The dose of arsenic and boron segregated at the interface is defined by the area between the concentration profile and the thickness in the interval of the two limits of the layer of the interface peak stated from the plateau in polysilicon. Table 1 gives the percentage of the dose segregated at the interface $D_1\%$ (segregated dose/total dose) and the dose diffused in monocrystalline silicon $D_2\%$ (diffused dose/total dose) as a function of temperature in the range (1000–1150 °C) with a 50 °C increment for a constant annealing duration of 20 s. These values are numerically determined from the diffusion profiles of arsenic (Fig. 1) and boron (Fig. 2) in the case of diffusion. Of B and As in the co-diffusion case, they are determined from the profiles in Fig. 3.

From the values in Table 1, it is easy to notice that the percentage of the dose diffused in silicon is smaller than that segregated at the interface. The boron profile shows a peak at the poly/mono interface in the case of diffusion which contains up to 2.6% of the implanted dose (up to 4.45% in the case of co-diffusion), and it appears that up to 11 and 10% of the implanted arsenic atoms segregated at the interface in the cases of diffusion and co-diffusion, respectively. It is important to compare the results obtained in this work and those obtained by Josquin et al. [6]. These authors have noticed that 6% of the implanted dose have been segregated to the interface in polysilicon layers implanted with arsenic, after an anneal for 95 min at 1000 °C. Schaber et al. [5] mention that 4% of arsenic atoms and 1% of boron atoms segregate to the interface (the doses used: 2×10^{16} and 5×10^{15} atoms/cm³ for arsenic and boron, respectively). The comparison between diffusion and co-diffusion of arsenic diffused in silicon shows a decrease of about 50% of the arsenic dose in the case of co-diffusion with respect to diffusion. For boron, the difference is much bigger, thus confirming the slowing down of boron diffusion in the presence of arsenic. Josquin et al. [6] have also determined the percentages of arsenic and boron atoms from the polysilicon to

Table 1

The percentage of the dose segregated at the interface ($D_1\%$) and that diffused in monosilicon ($D_2\%$)

	<i>T</i> (°C)			
	1000	1050	1100	1150
Diffusion				
D_{As1} (%)	12.64	11.58	11.05	11.38
D_{As2} (%)	1.3	3.24	6.4	11.37
D_{B1} (%)	1.78	2.24	2.46	2.62
D_{B2} (%)	1.54	5.5	10.2	16.2
Co-diffusion				
D_{As1} (%)	7.99	10.43	11.07	10.13
D_{As2} (%)	2.06	2.66	4.52	7.4
D_{B1} (%)	0.04	0.49	2.48	4.45
D_{B2} (%)	0.01	0.07	0.57	1.7

the silicon. They found the values equal to 13.4% for arsenic and 6.7% for boron. It is interesting to point out the work of Ranade et al. [21] on the co-diffusion of Ge with dopants (boron or arsenic) in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ structures. These authors observe a pileup of Ge at the interface which has been seen to persist at high temperature with increased time indicating a possible Ge segregation. Moreover, they observed that the co-diffusion of Ge with dopants also leads to enhanced intermixing between Si and Ge.

4. Conclusion

In the case As and B co-diffusion in the polysilicon/silicon systems at 1150 °C/20 s, it has been stated that 7.4% of the arsenic atoms have diffused into the Si substrate, resulting in an emitter–base junction depth of 132 nm (defined as the depth where the dopant concentration has dropped to 10^{18} atoms/cm³) in the substrate, and that 1.7% of the boron atoms have diffused into the substrate, giving a collector–base junction depth of 122 nm (defined as the depth where the dopant concentration has dropped to 10^{17} atoms/cm³). The comparison between junction depths in the case of diffusion and co-diffusion does not show any significant difference in the case of diffusion of arsenic, whereas diffusion of boron in the presence of arsenic is notably slowed down, due to the amorphization of the polysilicon top layer by the high-dose arsenic implantation. The variation of the junction depth X_j with temperature in the interval (1000–1150 °C), shows a linear relationship between diffusion temperature and diffusion depth in the case of co-diffusion.

The percentage of the B and As doses diffused to silicon is smaller than that segregated at the interface. The arsenic and boron diffusion profiles in polycrystalline Si and in single crystal Si, reveal a continuity at the interface, upon extrapolation to the polycrystalline Si–single crystal Si interface. This shows the absence of a diffusion barrier. It appears that nearly 11 and 10% of the implanted arsenic atoms are segregated at the interface in the cases of diffusion and co-diffusion, respectively. For boron, the percentage of the implanted atoms segregated at the interface equals to about 2.6% (diffusion) and 4.45% (co-diffusion).

The comparison between diffusion and co-diffusion of arsenic diffused in to single crystal silicon shows a decrease to about 50% of the arsenic dose, in the case of co-diffusion with respect to diffusion. Regarding boron, the difference is

much bigger. Thus confirms the slowing of boron diffusion in the presence of arsenic.

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