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Blister formation mechanism during high dose implanted photoresist stripping

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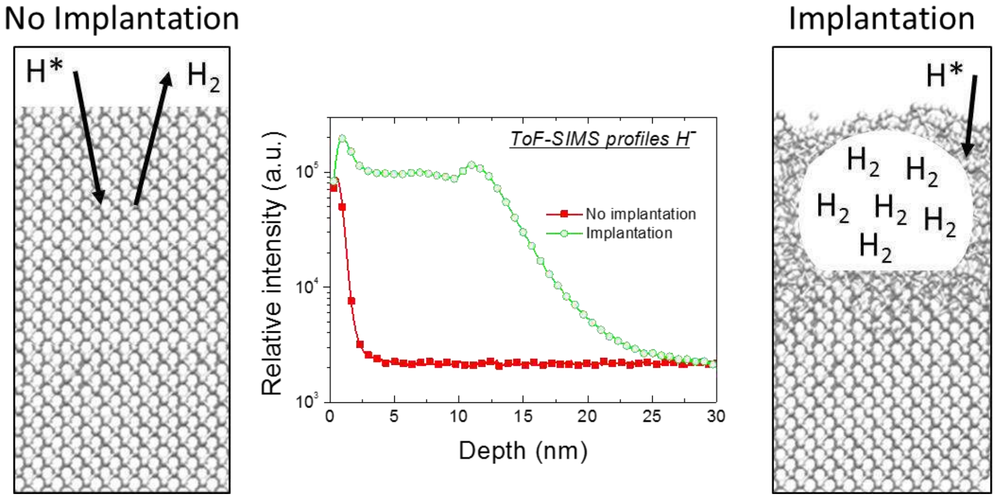
Graphical Abstract



Highlights

- The mechanism of blister formation in implanted silicon during H_2-based plasma dry strip processes is understood in correlation with SRIM simulation
- Influence of implantation parameters (dopant species, energy and dose) is investigated and compared to SRIM simulations
- Solution is proposed to delay blister formation

Abstract

Dry strip processes performed after implantation steps have to remove efficiently the photoresist mask protecting the non-implanted area without leaving any defects on the substrate. In this study bubble-like defects called blisters are observed on implanted areas after several N_2H_2 dry strip processes. Analyses have been performed to study the blistering phenomenon. The formation of these defects is due to hydrogen diffusion and accumulation in the amorphized silicon layer formed by the implantation step. The effects of implantation parameters (dopant species, dose and energy) on blister formation have been demonstrated. The experimental results have been compared to simulations (using SRIM software) highlighting the main influence of amorphization rate against amorphized layer thickness. Optimization of the stripping process and integration modification are then proposed to delay the appearance of the blisters.

Keywords : blister, hydrogen plasma, stripping, defectivity, implanted substrate, High Dose Implant Stripping

1. Introduction

Integrated circuit manufacturing requires many dry strip operations to remove photoresist (PR) either after implantation steps or for lithographic rework. Indeed, junction fabrication needs several implantations using a PR mask to define the area to be implanted. Then, the PR has to be efficiently removed usually by a dry strip process. For advanced technologies, the increase of implantation dose makes the stripping of implanted PR more and more challenging due to the formation of a hard modified layer ("crust layer") during the implantation step [1]. One of the main requirements of the stripping process is to remove the implanted photoresist efficiently without leaving residues on the surface. The consumption and oxidation of underlying materials should also be minimized as well as defect formation on the implanted substrate. To fulfill all these criteria, several plasma chemistries have been evaluated in our previous study [2]. The results showed that N_2H_2 plasma is the most suitable chemistry to remove the resist without leaving residues and with minimal substrate consumption. However, an issue has been identified with the use of hydrogen-based plasma while not with O_2-based-plasma processes. After several dry strip processes, bubbles also called "blisters" are formed on the implanted areas as shown in Figure 1. These blisters are not observed after the implantation step. The time at which blisters appear depends on both the implantation parameters and the dry strip conditions. Jenny et al.

suggested that these bubbles come from nucleation initiated on defects formed in the substrate during the implantation step [3].

In this paper, the blister formation has been studied thanks to in-depth characterization techniques. The impact of implantation parameters on these defects has been studied and compared with ion implantation simulations to understand the results obtained and propose a mechanism for blistering phenomena. Finally, some solutions to delay the blisters appearance have been proposed.

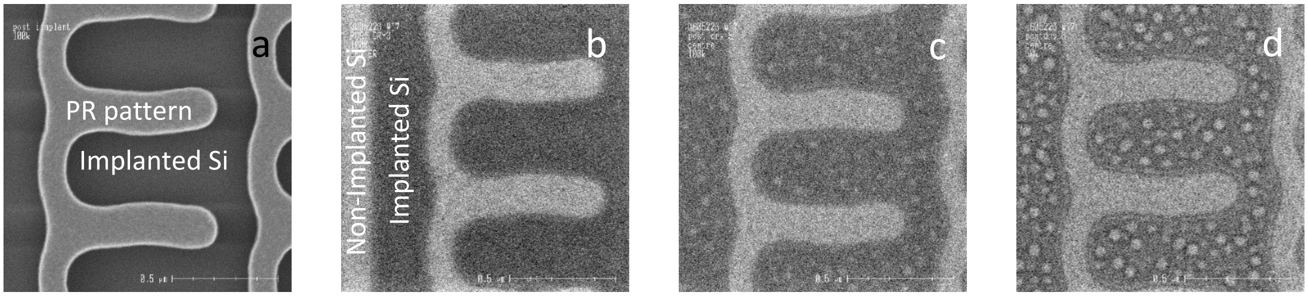


Figure 1 Top-view observations of patterns after a) P implantation at an energy of 4keV and after b) 4 c) 5 and d) 6 N_2H_2 dry strip processes. The blister phenomenon appears in the present case after 5 strip processes on the implanted area and get worse afterwards

2. Experimental

In this work, 300mm silicon wafers are patterned with a 215nm-thick 248nm-Deep-Ultra-Violet (DUV) photoresist. They are then exposed to As or P implantation with various ion implantation conditions in an Applied Materials VIISta ion implanter. N_2H_2 dry strip processes are performed on a LamResearch GAMMA stripper at high temperature (285°C) with a downstream plasma containing 3% hydrogen.

After the stripping process, the defects were observed on a top-view Critical Dimension-Scanning Electron Microscope (CD-SEM) (CG5000 tool from Hitachi). Some additional off-line techniques have also been performed to characterize the defects. Cross-section view of the defects were performed using an Osiris Transmission Electron Microscope (TEM) instrument in scanning mode. Time of Flight-Second Ion Mass Spectroscopy (ToF-SIMS) analyses were carried out with an Ion-TOF TOF-SIMS5 instrument using a dual beam acquisition and detection of the negative ions only. A Bi^+ beam at 25 kV is used for the analysis with a 100 x 100 µm² raster, a 10.2ns cycle time and a 128 pixel resolution. The sputtering is performed using a Cs^+

(500 eV) beam, with a 400 x 400 µm² raster and an electron flood gun with -20 V bias was also used to overcome charging problems.

SRIM (Stopping and Range of Ions in Matter) simulations [4] of ion implantation in silicon substrate have been performed using quick damage calculations (Kinchin-Pease model) to determine Si recoil profiles created by the implantation. Si recoil profiles give information on the damage created by the implantation on the substrate and are an indicator of amorphization rate. Amorphized layer thickness has also been determined on Si recoil profiles by fixing a limit above which the silicon is considered amorphous. In this study, the value is fixed at 3.6 10^{21} recoils/cm^3.

3. Results and discussion

3.1. Blister characterization

In this section, the impact of the implantation conditions on blister appearance is investigated, and a correlation is made between experimental results and simulated data of the damage generated by the implantation step in the silicon substrate.

3.1.1. Impact of implanted species

The blister appearance after N_2H_2 dry strip processes is compared in the case of P and As implanted substrates (Table 1). For the same implantation energy and dose (4keV 2E15 atoms/cm²), blisters appeared after two strip processes for P-implanted samples and after five for As. This clearly indicates that the dopant species has an impact on blister formation. Moreover, blister top-view observations (Figure 2) show that the defects are larger with phosphorus (70-100nm) compared to arsenic (50-60nm).

Table 1 Blister observations depending on the number of N_2H_2 processes and implanted species for the same implantation dose and energy (x indicates the observation of blisters)

Implantation conditions	Number of N_2H_2 processes							
	1	2	3	4	5	6	7	8
P		x	x	x	x	x	x	x
As					x	x	x	x

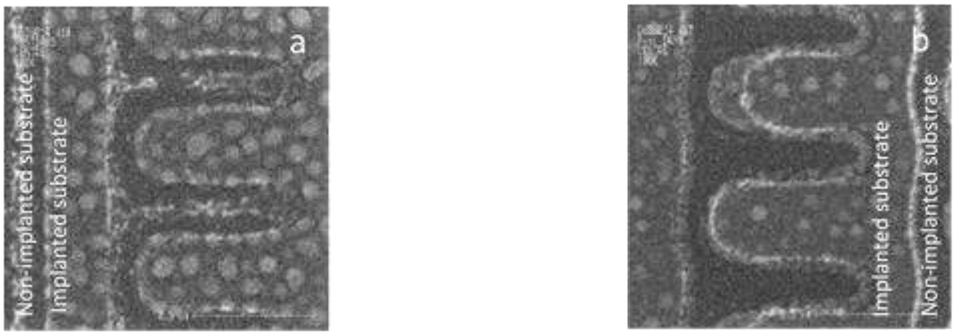


Figure 2 CD-SEM top view observations of blisters obtained after a) P implant and 3 N_2H_2 processes b) As implantation and 8 N_2H_2 processes

STEM cross-section observations are carried out on silicon areas presenting blisters after implantation and dry strip processes (Figure 3). Two areas are observed for both P and As-implanted samples: a 15nm-thick amorphized silicon layer (a-Si) caused by the implantation step; and the crystalline silicon substrate (c-Si). The blisters are clearly observed in the a-Si layer. This result is consistent with other studies which clearly observed blisters in the higher defect density area.[5] [6] [7]

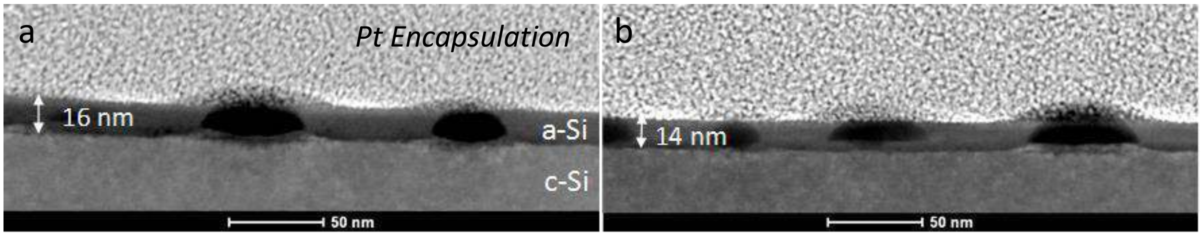


Figure 3 STEM cross-section view of Si surface after a) P implantation and 2 N_2H_2 processes b) As implantation and 6 N_2H_2 processes

SRIM simulations have been performed to explain the differences observed between arsenic and phosphorus implantation. The silicon recoil profiles calculated for As and P implantation are compared in Figure 4. These simulations indicate the number of defects generated in the Si lattice and thus the amorphization rate. Furthermore, the thickness of the amorphized layer for each implantation condition can be estimated by considering that the silicon is amorphous above $3.6\text{x}10^{21}$ Si recoils/cm^3. The concentration of Si recoils is an indicator of the amorphization level and the maximum is used to compare the amorphization rate of the samples. Thus, it is observed that for similar implantation conditions the amorphization rate is 30% higher for As than for P dopant while the amorphized silicon thickness is slightly thinner (14nm vs 18nm). These thicknesses values are also confirmed by TEM observations in Figure 3.

These results suggest that the delayed formation of blisters for As implantation could be due to either a higher amorphization rate or a thinner amorphized layer. Thus to determine which parameter has the more important impact on blisters formation, the influence of ion energy and dose during the implantation is investigated in the following sections.

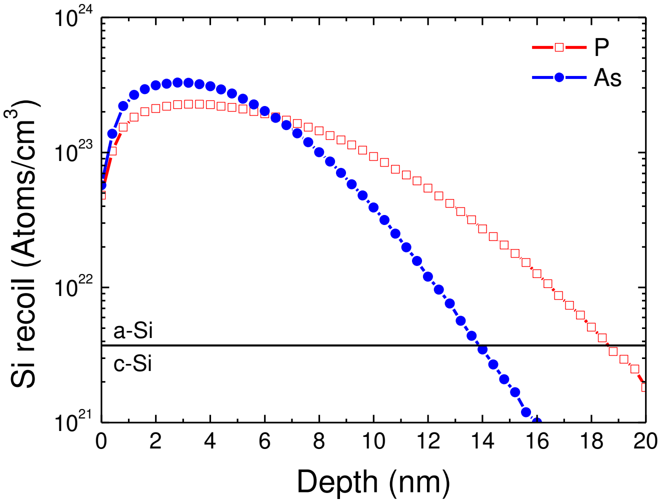


Figure 4 SRIM simulation of silicon recoils profiles after As and P implantation at an energy of 4keV and a dose of 2E15 atoms/cm²

3.1.2. Impact of implantation dose

The impact of As implantation dose on blister formation is shown in Table 2. This implantation parameter seems to play a major role in blisters appearance. Indeed, with a dose of 1 10^{15} As atoms/cm², the blisters are observed after the first stripping process whereas when the dose is doubled, they appear after 6 N_2H_2 processes (Table 2). Si recoil profiles have also been simulated for these As-implantation conditions (Figure 5) and the extracted amorphized silicon thicknesses are reported in Table 3. These simulated results show that the amorphized layer thicknesses for both dose values are very close. However, the amorphization rate is twice higher for higher implantation dose.

These results suggest that the formation of blisters is mainly driven by the amorphization rate rather than the amorphized layer thickness. The more the silicon is amorphized; the later the blisters appear. This will be discussed in section 3.2.

Table 2 Blister observations depending on the number of N_2H_2 processes and As implantation dose (x indicates the observation of blisters)

Implantation conditions	Number of N_2H_2 processes							
	1	2	3	4	5	6	7	8
As 3keV 2E15 at/cm²						x	x	x
As 3keV 1E15 at/cm²	x	x	x	x	x	x	x	x

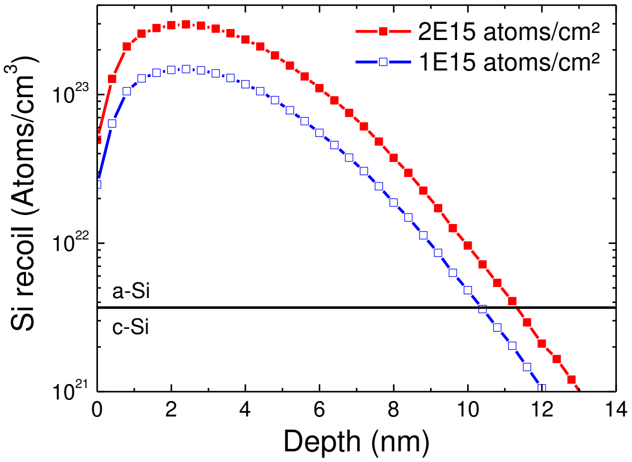


Figure 5 SRIM simulations of Si recoil profile in Si substrates depending on implantation dose

Table 3 Amorphized layer thicknesses determined from SRIM simulations depending on implantation dose

Implantation conditions	Amorphized layer thickness (nm)
	Simulated
As 3keV 2E15 at/cm²	11.4
As 3keV 1E15 at/cm²	10.4

3.1.3. Impact of implantation energy

Finally, the impact of implantation energy (3keV, 4keV and 5keV) on blister appearance after N_2H_2 dry strip processes is shown in Table 4 in the case of As implantation. Blister defects appeared a little earlier with low implantation energies, but the trend is not very clear and the effect is limited in the range of energies studied.

Table 4 Blister observations depending on the number of N_2H_2 processes and the implantation energy used (x indicates the observation of blisters) for As implantation

Implantation conditions	Number of N_2H_2 processes							
	1	2	3	4	5	6	7	8
As 5keV 2E15 at/cm²							x	x
As 4keV 2E15 at/cm²					x	x	x	x
As 3keV 2E15 at/cm²						x	x	x

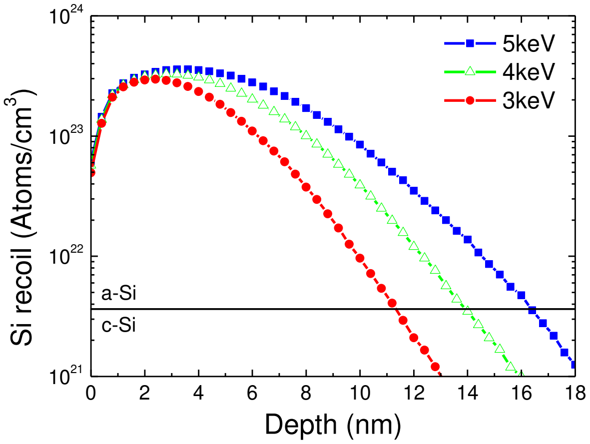


Figure 6 SRIM simulations of Si recoil profile in Si substrate depending on implantation energy for As implantation.

Table 5 Amorphized layer thicknesses determined from SRIM simulations depending on implantation energy

Implantation conditions	Amorphized layer thickness (nm)
	Simulated
As 5keV 2E15 at/cm²	16.4
As 4keV 2E15 at/cm²	14
As 3keV 2E15 at/cm²	11.4

The Si recoil profiles simulated for 3, 4 and 5keV implantation energies are shown in Figure 6 and the extracted amorphized silicon thicknesses are reported in Table 5. These simulated results show that the amorphized layer increases with the implantation energy and that the effect on amorphization rate is not significant. In this set of experiments, no correlation between the amorphized layer thickness and blister appearance is observed meaning that a-Si thickness is not the main parameter which influences blister formation in the range of energies investigated in this study.

3.2. Discussion on blisters formation mechanism

Experimental and simulated data in the last section show that blisters appearance is delayed when the implantation conditions lead to higher silicon amorphization. This observation seems at first sight paradoxical because the blisters are not observed on a bulk crystalline silicon substrate exposed to N_2H_2 dry strip processes. Thus, the blisters only appear if the silicon substrate is amorphized, but their appearance is delayed for high amorphization levels.

To understand the mechanisms involved, ToF-SIMS analyses have been performed on three samples: a P-implanted substrate with no subsequent N_2H_2 dry strip process (no blisters), a non-implanted substrate exposed to two dry strip processes (no blisters) and a P-implanted substrate subsequently exposed to two N_2H_2 dry strip processes. The aim is to evaluate and compare the diffusion of the species present in the N_2H_2 plasma through implanted and non-implanted Si substrates.

The ToF-SIMS signals of SiN^-, SiH^- and H^- are monitored during the Si sputtering by Cs^+ ions to reconstruct the depth concentration profiles (Figure 7). The concentration profiles of the P-implanted substrate are used as a reference since this sample has not been exposed to N_2H_2 plasma processes.

The diffusion mechanism of nitrogen in silicon has already been studied in literature. [8] [9] [10] Nitrogen diffusion occurs by breaking and reforming the bonds between the nitrogen atoms and the surrounding silicon atoms. Thus, the monitoring of SiN^- profiles can be used as an indicator of nitrogen diffusion in the samples. Unfortunately, the use of a Bi^+ beam for ToF-SIMS analyses does not allow the observation of a N^- profile which would have been an indicator of the presence of N_2 molecules in the sample.

Figure 7.a shows that the SiN^- signal is higher for substrates exposed to N_2H_2 plasma process indicating that the diffusion of nitrogen through silicon during the stripping process is enhanced. Moreover it is noticed that the concentration profiles in the non-implanted and implanted substrates are very similar suggesting that nitrogen diffusion is not influenced by the amorphization of silicon generated by the implantation step. So far, there is no data on the

accumulation of N_2 and its impact on blister formation even if it is known that N_2 tends to aggregate in strained area like amorphized silicon and out-diffuse if few defects are present in the Si lattice. [8]

A similar mechanism has been proposed in the literature for H_2 diffusion with the creation of intermediate Si-H bonds with the Si atoms. [11] SiH^- and H^- profiles are then monitored (Figure 7.b) and allow to follow the diffusion of hydrogen and the accumulation of H_2 molecules. In the reference sample, some SiH^- are detected probably due to the incorporation of H during the implantation process, but no H^- is detected meaning that H_2 molecules are not present and that they have probably out-diffused. [7] [12] For the non-implanted sample exposed to N_2H_2 stripping processes, neither SiH^- nor H^- are detected by ToF-SIMS. Since Figure 7.a) suggests that nitrogen species diffuse in crystalline Si, it is likely that hydrogen species also penetrate into crystalline silicon lattice. Moreover, several studies have already reported on the ability of hydrogen to diffuse in both c-Si and a-Si. [13] [14] The main explanation for not detecting hydrogen species is that H atoms that diffuse though the Si substrate recombine into H_2 molecules and out-diffuse from the substrate.

On the other hand, the implanted sample exposed to N_2H_2 plasma clearly shows a significant accumulation of H_2 and Si-H bonds in the first 20nm corresponding to the amorphized area formed during the implantation step. T. Höchbauer and al observed that defects in silicon substrate act like traps for hydrogen and prevent long-range diffusion. [7] Moreover, it is known that hydrogen is easily trapped by defects like dandling bonds, vacancies, dislocation, impurities or precipitates. [5] [6] [13] [15] Based on the reported literature, a mechanism for the blistering phenomenon can be proposed: H atoms diffuse into the amorphized silicon and react with dangling bonds. As the diffusion proceeds and all the defect sites have reacted with H atoms, H recombine to form H_2 molecules which are then trapped in the voids formed in the amorphized Si layer by the agglomeration of vacancy defects. This accumulation results in an increase of internal pressure and plastic deformation. [16] Consequently, the blisters are formed, and the top silicon layer swells.

This is consistent with the study of Reboh and al who demonstrated that blisters are composed of H_2 and the inner surface of the cavity is made of Si-H bonds. [17]

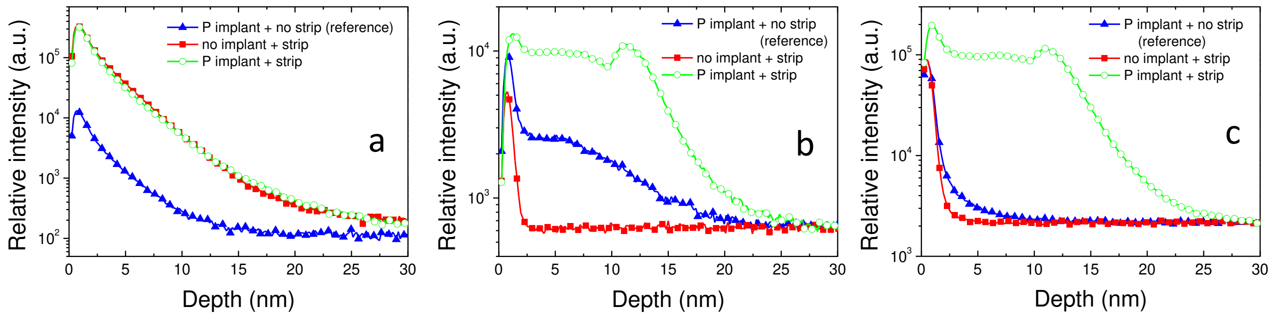


Figure 7 Comparison of ToF-SIMS profiles of a) SiN^- b)SiH^- and c) H^- for three investigated samples: a P-implanted substrate with no subsequent N_2H_2 strip processes (no blisters), a non-implanted substrate exposed to two N_2H_2 processes (no blisters) and a P-implanted substrate also exposed to two N_2H_2 processes (blisters)

ToF-SIMS results presented in this section highlight the diffusion of hydrogen during the dry strip processes and thus help to explain the formation of blisters in amorphized silicon, but the link between blisters appearance and the amorphization rate remains unexplained. In fact, blister appearance depends on the H_2 molecules accumulation in the substrate, the hydrogen diffusion rate which can be influenced by the N_2H_2 stripping conditions (chamber pressure and wafer temperature), and also by the amorphization rate. Indeed, if the silicon substrate is highly amorphized, hydrogen diffusion is slowed and consequently, blister formation is delayed explaining the results observed in Table 1 and Table 2.

3.3. Solution to delay blisters formation

Based on the blister formation mechanism suggested above, two strategies are proposed to limit the blistering effect: an optimization of the stripping process; and an integration modification. For a typical CMOS device, at least 3 N_2H_2 dry strip processes are required.

3.3.1. Dry stripping recipe optimization

The first solution to decrease hydrogen diffusion in the substrate is to optimize the stripping process. Consistent with Morral's work [14] which showed that lowering the process pressure decreases the number of hydrogen radicals in the plasma, the process temperature and pressure were lowered to reduce the amount of hydrogen reaching the silicon surface. For stripping efficiency concerns, the process time has been increased to balance the decrease in process temperature. The results presented in Table 6 show that this first optimized recipe gains one stripping process compared to the reference recipe. However, some residues remained on the non-implanted area after the low pressure and low temperature dry strip process and the following SPM-SC1 wet cleaning (Figure 8). To overcome this efficiency issue, another recipe has been tested with only lowering the pressure. The blisters were formed after the same time of exposure to N_2H_2 chemistry, but no remaining residues were observed after the stripping.

Table 6 Blister observations depending on number of N_2H_2 processes and stripping recipe (x indicates the observation of blisters)

Dry strip recipe	Number of N_2H_2 processes				
	1	2	3	4	5
POR recipe		x	x	x	x
Low T low P			x	x	x
Low P			x	x	x

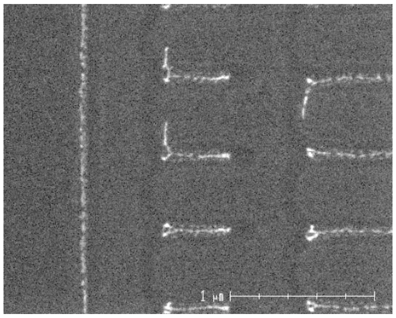


Figure 8 Top-view SEM-CD observations after a SPM-SC1 wet cleaning following the optimized dry strip process (low P and low T)

3.3.2. Integration modification

Another solution is to limit hydrogen diffusion through the substrate by introducing a “screen oxide” on the top of the silicon. Because of integration considerations, the growth of this oxide layer has to be made before the lithographic and implantation steps. Consequently, the implantation step is made through the oxide layer and has to be adapted to have the same dopant profile on the Si substrate. SRIM simulations have been used to find adapted implantation conditions which could correspond to phosphorus implanted at 4keV. Considering dopant profiles and Si recoil profiles (Figure 9), phosphorus implanted at 6keV through the oxide has been found to match with an implantation made at 4keV directly on the Si substrate.

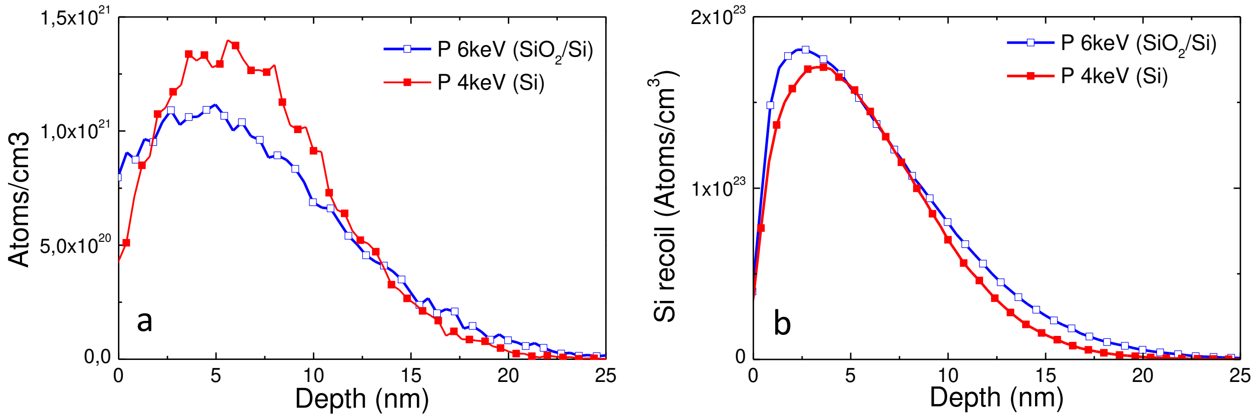


Figure 9 SRIM simulation of a) dopants profile and b) silicon recoils profile after P implantation (P 6keV in SiO_2/Si and P 4keV in Si)

The effect of the screen oxide on blister formation is shown in Table 7. The results clearly indicate that the presence of an oxide layer during the stripping process delays the appearance of defects (line 1 and 2 of Table 7). The oxide is assumed to play the role of a barrier to hydrogen diffusion. To verify this assumption, another test has been made on which the oxide is removed before the N_2H_2 process with a HF-based clean. Table 7 (line 3) shows that the formation of blisters appears nearly at the same time as without the use of the oxide layer. This confirms that the presence of the oxide layer limits hydrogen diffusion and delays blister formation. This is consistent with hydrogen diffusity values given in literature: 10^{-10} cm²/s in c-Si and 1.2 10^{-13} cm²/s in SiO_2. [15]

Table 7 Blister observations depending on the number of N_2H_2 processes and the presence of thermal oxide before implantation step (P 4keV) (x indicates the observation of blisters). P implantation conditions are equivalent to 4keV implantation on Si substrate.

Substrate	Number of N_2H_2 processes				
	1	2	3	4	5
Si		x	x	x	x
Thermal oxide (55A)/Si					x
Si (Oxide removed before stripping process)			x	x	x

4. Conclusions and perspectives

After the implantation step, the implanted PR mask can be efficiently removed by N_2H_2 chemistry, but blisters can appear on the implanted substrate. Characterization of the defects have shown that the blisters are formed near the Si surface in the amorphized layer and that they are due to hydrogen diffusion in the implanted substrate. A mechanism is proposed: H atoms diffuse through the silicon substrate and are trapped by the defects found in the amorphized silicon layer then H atoms recombine to form H_2 molecules which accumulate in the substrate. Nitrogen diffusion has also be highlighted, but its involvement in the blistering phenomenon is not demonstrated. To minimize the blister formation phenomenon, solutions have been investigated to limit the diffusion of hydrogen into the silicon substrate. Dry strip parameters have been optimized and especially the chamber pressure which allows to delay the blister formation without impacting the stripping efficiency. Furthermore, the growth of an oxide layer before implantation is a suitable approach to delay blister formation by limiting H diffusion into the Si substrate. The study of implantation parameters influence on the appearance of blisters has also shown that the silicon amorphization rate is the key factor. Indeed, blister formation is delayed with higher amorphization level meaning that increasing silicon amorphization could be also a promising way to avoid the blistering issue.

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