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Characterization and Development of High Dose Implanted Resist Stripping Processes

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Abstract. With the increase of implantation dose in new technologies, implanted photoresist stripping is even more challenged in terms of efficiency and substrate consumption. In this work, the effect of implantation parameters (energy and implanted specie) on the photoresist modifications are studied and several plasma chemistries are evaluated to remove it. A good removal efficiency with a low substrate consumption has been found with H_2-based processes especially N_2H_2.

Introduction

Stripping of photoresist after High Dose Implantation (HDI) is becoming a critical step with the increase of both implantation acceleration energy and dose. During the implantation, the photoresist surface is exposed to energetic ion bombardment and a modified layer (called "crust") is formed. This crust is difficult to remove by conventional dry strip processes.

The main requirements of stripping processes are: to remove completely the photoresist without leaving residues on the surface, to avoid the formation of added defectivity such as blisters, to minimize the consumption and oxidation of underlying materials (Si substrate, epitaxial SiGe) and to avoid dopants loss and redistribution on the implanted areas.

N_2/H_2 and O_2/N_2 plasmas are commonly used in dry strip processes. O_2/N_2 is known to achieve a high ashing rate and consume the non-modified photoresist preferentially [1] while non-oxidizing plasmas are less reactive to strip the photoresist but are very efficient to remove the crust [2].

In this paper, we focused on the stripping efficiency of oxidizing and reductive plasma chemistries. First, several characterization techniques have been used to evaluate the physical and chemical modifications induced in the photoresist by the implantation step. The impact of both dopant energy and chemical nature have been investigated. Based on this understanding, several plasma chemistries are investigated for removing the implanted resist properly with no remaining residues and minimal substrate loss.

Experimental set up

In this work, 200nm-thick 248nm photoresist (PR) coated on 300mm wafers and commonly used for Complementary Metal Oxide Semiconductor applications has been exposed to either As or P implantation processes with an energy of 4 or 9 keV and a dose between 1.5 and 2.10^{15} atoms/cm². Several characterizations techniques (TEM, ToF-SIMS…) have been used to analyze the physical and chemical modifications of the PR exposed to the implantation process. TEM allows to determine the modified layer thickness and the implantation depth respectively. ToF-SIMS is used to get information on chemical profiles in the implanted PR but also to analyze residues composition. These analyses are performed with an Ion-TOF TOF-SIMS[5] instrument with a dual beam acquisition and detection of the negative ions only. A Bi^+ beam at 25 kV is used for both analyses, with a 50 x 50 µm² raster. For the implanted PR characterization, a 50µs cycle time is used with a 128 pixels resolution whereas for the residues analysis, the cycle time is 90µs and the resolution 1024 pixels. The sputtering is performed using a Cs (500 eV) beam, with a 300 x 300µm² raster for the photoresist and a 300eV beam with a 300 x 300 µm² raster for the residues . An electron flood gun with -20 V bias is also used to overcome charging problems.

Oxidizing and non-oxidizing dry strip processes are developed in Gamma GxT tool (Lam Research) on patterned 300mm wafers. Dry stripping processes efficiency is evaluated by CD-SEM observations on a Hitachi 5001 tool.

Experimental results

Implanted Resist characterization. A methodology has been set up to study the influence of implantation parameters (dopant specie and ions energy) on the PR modifications. TEM analyses on resist blanket wafers allow to determine the modified layer thickness for several implantation conditions (Table 1). An example of TEM picture is presented on Figure 1 and allows to discriminate two distinct areas: the underlying non-modified layer (“bulk“) and the crust on the PR surface.

Table 1 TEM analyses: crust thickness depending on implantation parameters

Implanted specie	Energy (keV)	Crust thickness (nm)
P	4	7
P	9	18
As	4	8
As	9	17

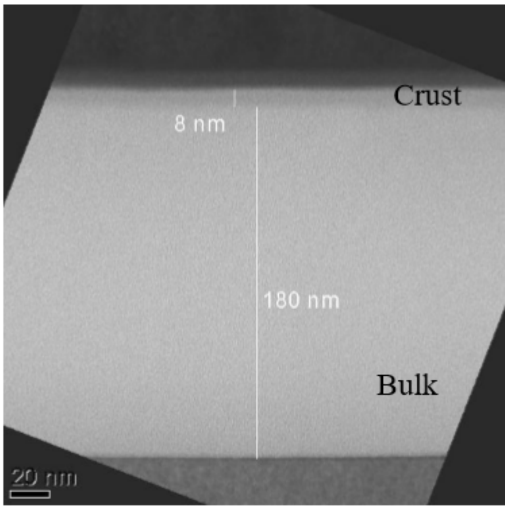

Figure 1 TEM picture of implanted PR (As 4keV)

For both As and P-implanted PR, the crust thickness depends on the implantation energy. At higher energy, the dopants go deeper into the photoresist which is modified on a thicker layer. On the other hand, the dopant specie (As or P) does not influence the crust thickness. However, XRR measurements (not shown here) show a higher density for the As-implanted photoresist.

ToF-SIMS analyses have been performed on As and P-implanted photoresist. Figure 2 presents the depth profiles for an energy of 4 kev.

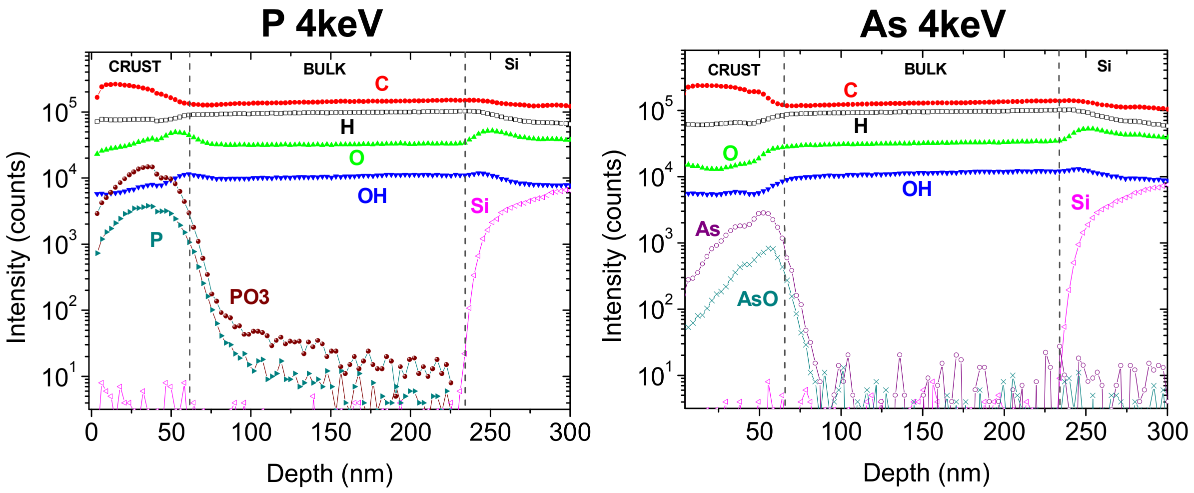

Figure 2 Tof-SIMS analyses of implanted PR : P 4keV 1.5E15 at/cm² (left), As 4keV 2E15 at/cm² (right)

Similar chemical modifications of the PR are observed for both implantations. The first 60nm of the photoresist analyzed by ToF-SIMS correspond to the crust observed in TEM picture and are depleted in O and H and enriched in C and dopants (either As or P). It should be noted that the crust thickness obtained by the ToF-SIMS analyses do not correspond to the thicknesses given by the TEM. Indeed, the depths given in Figure 2 are calibrated considering the sputtering rate of the non-modified resist which is certainly higher than the sputtering rate of the crust layer. Thus, the crust thickness given by the ToF-SIMS is overestimated.

These analyses clearly show that the photoresist is modified on the first 50nm whereas the dopants are located until 100nm. This means that the resist is not modified on the entire implanted depth.

Another interesting point is that dopants are present in their oxidized and metallic forms in the crust. ToF-SIMS experiments performed with As and P-implanted resist at an energy of 9kev show similar chemical depth profiles, except for the modified depth which is thicker.

Dry strip process development. The dry strip efficiency is evaluated for the same 200nm-thick photoresist with As and P implantation at both 4 and 9 keV using CD-SEM top-down observations. The results obtained for N_2/H_2 plasma are presented on Figure 3.

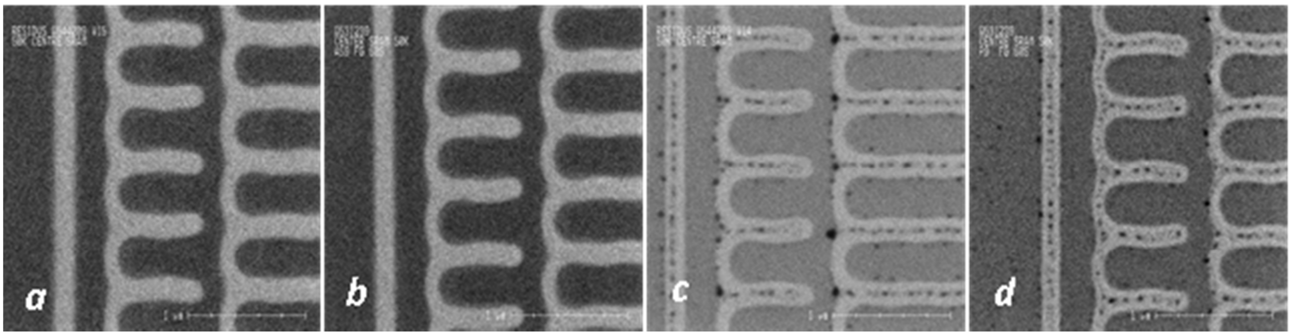

Figure 3 CD-SEM top view observations after N_2/H_2 dry strip process with several implantation energies
a) As 4keV   b) As 9keV   c) P 4keV   d) P 9keV

N_2/H_2 is found to be very efficient to remove As-implanted photoresist for both 4keV and 9keV energies and there is no residues left. On the other hand, little black residues on both implanted and non-implanted areas are observed when the resist is implanted with phosphorus.

These black residues have been identified by ToF-SIMS analyses as phosphorus oxides. They are likely coming from the implanted photoresist because they are not observed on the wafer surface after the same process without photoresist.

These results indicate that N_2/H_2 chemistry is not efficient to remove phosphorus oxides coming from the crust, while we assume that it can eliminate arsenic oxides. However, a SPM-SC1 wet cleaning (SPM 5:1 at 80°C and SC1 1:2:80 at 65°C) following the dry strip process (Figure 4) can remove them completely.

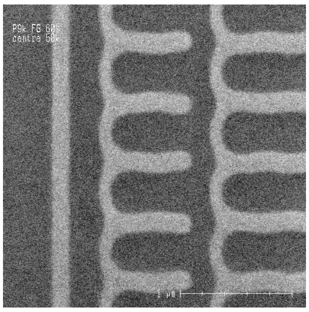

Figure 4 CD-SEM top view observation after N_2/H_2 dry stripping followed by a SPM-SC1 wet cleaning of P-implanted photoresist at 9keV

Concerning the O_2/N_2 dry strip chemistry, two kinds of residues are observed for both As and P implantations (Figure 5).

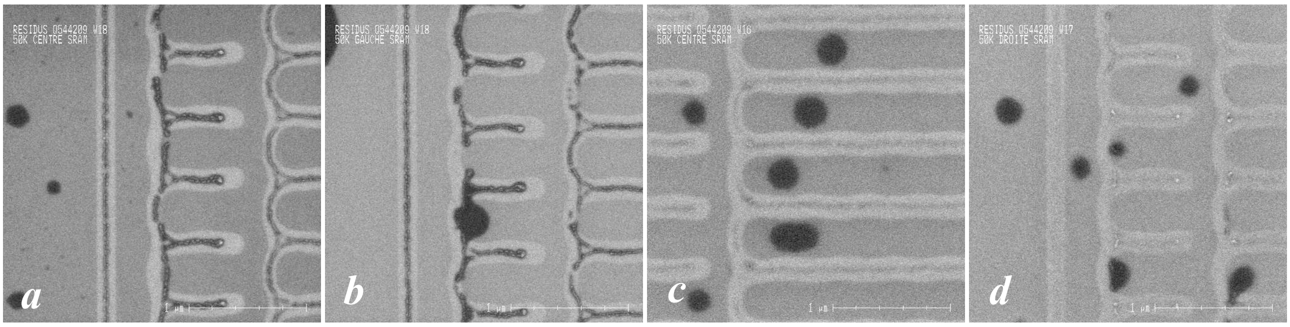

Figure 5 CD-SEM top view observations after O_2/N_2 dry strip process with several implantation energies
a) As 4keV b) As 9keV c) P 4keV d) P 9keV

Black residues larger but similar to those obtained with N_2/H_2 plasma are observed as well as small residues present on the non-implanted area previously protected by the photoresist.

The black residues have also been analyzed by ToF-SIMS (Figure 6) for P 4keV condition and identified as phosphorus oxides. O_2/N_2 plasma is not efficient to remove oxidized dopants present in the implanted resist and certainly contributes to the oxidation of the metallic dopants also present. That could explain why the black residues are larger with O_2/N_2 process.

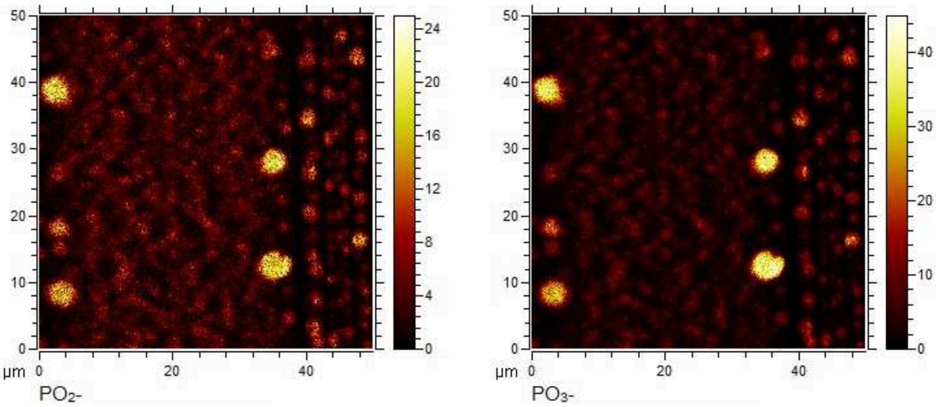

Figure 6 Tof-SIMS 3D view of PO_2^- and PO_3^- residues after O_2/N_2 dry strip

No chemical information could be obtained for the other small residues present on the non-implanted area but they are likely coming from the crust which is known to be hardly removed by O_2-based plasma chemistries.

After a wet cleaning, the black residues identified as oxidized dopants are efficiently removed for both As and P-implanted resist, but the small residues attributed to the crust layer remain on the non-implanted areas (Figure 7).

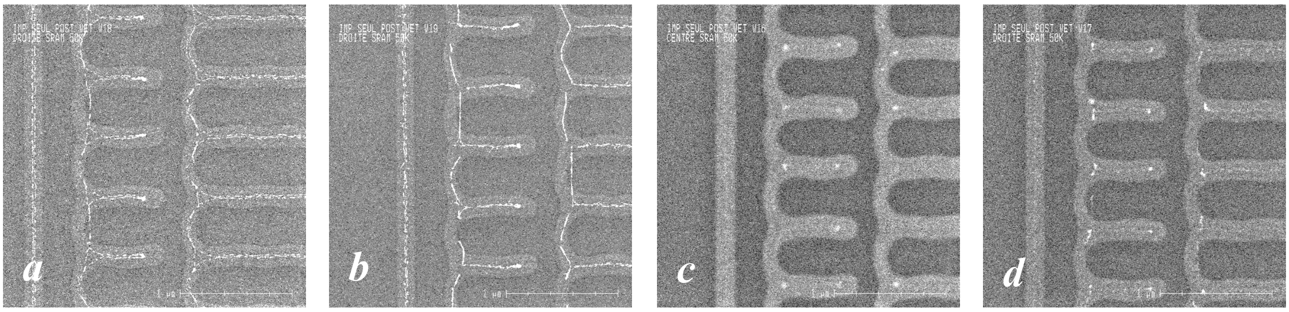

Figure 7 CD-SEM top view observations after O_2/N_2 dry strip followed by a SPM-SC1 wet clean
a) As 4keV b) As 9keV c) P 4keV d) P 9keV

To evaluate stripping chemistries, the effect on substrates (spacer, Si, epitaxial material like Boron-doped SiGe called SiGeB) is also an important parameter which has to be taken into account. Several phenomena are commonly observed: the oxide growth at the surface and the substrate consumption. Table 2 presents the results obtained on Boron-dopped SiGe blanket wafers after N_2/H_2 and O_2/N_2 plasma processes. As expected, the oxide growth is higher with the oxidizing plasma. N_2/H_2 is more promising because of the minimal consumption and oxidation phenomena induced in Boron-dopped SiGe.

Table 2 Ellipsometric thickness measurements of oxide growth and Boron-dopped SiGe consumption with N_2/H_2 and O_2/N_2 processes

	Oxide growth (A)	SiGeB consumption (A)
N_2/H_2	12	2
O_2/N_2	32	7

Finally, the comparison between the two commonly used chemistries N_2/H_2 and O_2/N_2 indicates that N_2/H_2 is the most efficient to remove implanted photoresist without consuming substrate like Boron-dopped SiGe. Even if some phosphorous-oxides residues could remain after dry strip process, they are entirely removed by the wet cleaning. With O_2/N_2 plasma, residues assumed to come from the crust layer are still observed on the non-implanted regions even after a wet cleaning.

However, some added defectivity called blisters can be observed after several N_2/H_2 plasma processes [3].

Other chemistries are thus evaluated to remove implanted photoresist with at least the same efficiency as N_2/H_2 and without blisters formation.

Alternative dry strip chemistries either reductive (He/H_2 or Ar/H_2) or oxidizing (N_2O, O_2/Ar, O_2/He) have been investigated with phosphorus implanted at 4keV (Figure 8).

H_2-based chemistries show interesting results with no remaining black residues after dry strip process (Figure 8a and 8b) even if some residues remains on the non-implanted area (light area on Figure 8). These residues are likely coming from the crust which was not stripped efficiently even after a wet cleaning. However, He/H_2 is clearly more efficient than Ar/H_2 and the stripping efficiency could be improved for instance by increasing H_2 ratio.

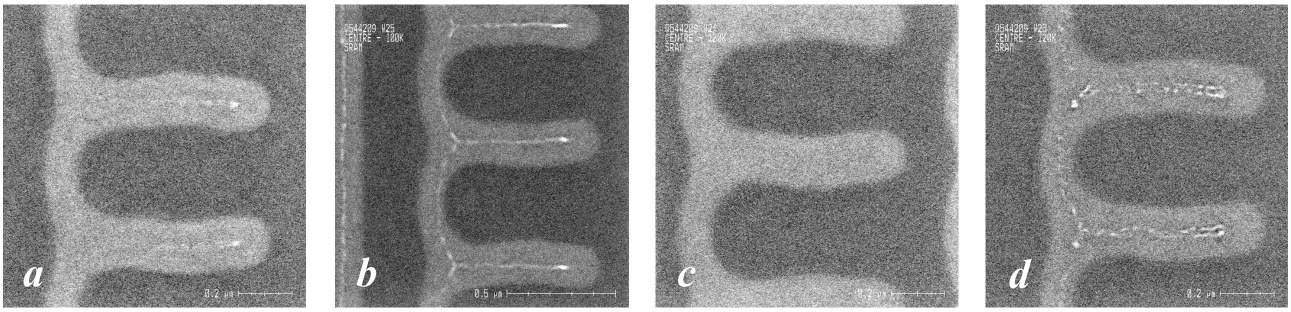

Figure 8 CD-SEM top view observations after a) He/H_2 b) Ar/H_2 c) N_2O d) O_2/He dry strip process of a P-implanted PR (4keV)

Remaining crust is also observed for O_2/He as well as for O_2/Ar and $N_2/H_2/O_2$ (data not shown). Only N_2O allows to remove the crust properly. Furthermore, for all these O_2-based chemistries, black residues of phosphorus oxide are seen at the edge of wafer after dry strip. So far, N_2/H_2 plasma followed by a wet cleaning remains the most efficient dry strip process

Conclusions

The photoresist mask is highly modified by the implantation step. A cross-linked carbon layer depleted with H and O but enriched with As or P dopants is formed on the resist surface. The dopants are present both in their elemental and oxidized forms. Several plasma chemistries have been tested to remove the implanted resist. After dry strip process, two kinds of residues can be observed according to the plasma chemistry used: black residues identified as oxidized dopants which are easily removed by a wet clean and smaller residues attributed to the crust. So far the most efficient dry strip process is N_2/H_2 plasma but such process can introduce some blister defects. Some alternative chemistries show interesting preliminary results especially N_2O and He/H_2 and further investigations are ongoing on these chemistries especially to evaluate the sensitivity to blisters.

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