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Atomic redistribution of implanted Fe and associated defects around moving SiO₂/Si interfaces

Anthony De Luca¹, Nelly Burle^{1*}, Alain Portavoce¹, Catherine Grosjean², Stéphane Morata³, Michaël Texier¹

¹ Aix Marseille Université, CNRS, IM2NP UMR 7334, bd Escadrille Normandie Niémen F-13397 Marseille, France

² ST Microelectronics, ZI Peynier Rousset F-13790 Peynier, France

³ Ion Beam Services, ZI Peynier Rousset F-13790 Peynier, France

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The behaviour of Fe atoms at the Si/SiO₂ interface, as a modelisation of an involuntary Fe contamination before or during the oxidation process has been studied in Fe-implanted wafers. As-implanted and oxidized wafers were characterized by SIMS, APT, HR-TEM and STEM-HAADF. Successive steps of Fe segregation, iron-silicides precipitation and dissolution were identified. As expected for such a temperature range, the iron-silicide precipitates adopt the FeSi₂ structure. Fe enriched phases

were also identified in an advanced step of precipitation. Dynamic mechanisms are proposed, taking into account the competitive oxidizing of precipitates and silicon matrix, to understand the different steps and precipitation phases observed in the samples during the non-equilibrium conditions due to the oxide layer growth. The correlation between the formation of characteristic pyramidal defects at the SiO₂/Si interface and the presence of the Fe-rich precipitates is explained.

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1 Introduction Silicon oxide remains the main gate oxide used in C-MOS technology. It still plays a key role in the advanced MOSFET technology as constituting a thin transition layer between the Si substrate and the high-k gate oxide layer [1]. However, metallic impurities in silicon, even for low contamination levels, may affect hugely the reliability of the component by creating electric defects in the active region as well as by disturbing the quality of the interface SiO₂/Si.

Iron is one of the most deleterious metallic contaminants in silicon; various steps of the process can lead to Fe contamination *via* different sources (polishing slurries, impurities in quartz tubes material, SiC boats, furnaces liners) [2], and because its high diffusivity [3] and capacity to act as donor [4] it is known to strongly degrade the device performances.

Fe contamination may affect the SiO₂/Si interface integrity as it has been shown in various studies. For example, Honda *et al.*, showed that α -FeSi₂ precipitates can nucleate at the SiO₂-Si interface, which is responsible for the increase of leakage currents and leads to dielectric breakdown in MOS capacitors [5]. SIMS measurements performed on Fe-contaminated, dry-oxidized Si wafers also evidenced iron atoms accumulation at the SiO₂/Si interface while a part of the iron atoms is trapped in the oxide layer [6]. Sadamitsu *et al.* identified the precipitation of the cu-

bic phase FeSi at the Si/SiO₂ interface and identified inclusions in the oxide as probably being Fe₃O₄ and γ -Fe₂SiO₄ precipitates [7]. Pyramidal defects and β -FeSi₂ precipitates have been observed, with the same density, at the SiO₂/Si interface in surface Fe-contaminated Si wafers [8]. These authors suggested that the injection of excess self-interstitial Si atoms by FeSi₂ precipitation would enhanced the formation of such pyramids. Anyway, the alteration of electrical characteristics of devices would be due not only to the Fe-induced levels in the gap, but also to the reduction of the grid oxide thickness [6]. It must be noticed that the size of the observed precipitates does not change with the contamination level and remains close to 10 nm in diameter. Similar pyramidal defects and precipitates were not observed in bulk-contaminated samples.

The aim of this work is to evidence the links between the two main defects in iron-contaminated wafers: precipitates and pyramidal defects, and to justify this correlation.

2 Materials and methods Fe implantation has been performed in P doped (2-20 Ω -cm) (001) Si wafers (extraction voltage of 65 kV, fluence of 1.0×10^{15} atoms·cm⁻²). The incidence angle of 7° from the Si(001) surface allowed reducing the channelling effect [9, 10].

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SIMS measurements were performed in as-implanted and oxidised samples until 500nm in depth. Fe-implantation profiles were also simulated by Stopping and Range of Ions in Matter (SRIM) calculations [11], taking into account the possible mixing artefact [12], and by Atomic Probe Tomography (APT). These various techniques gave well correlated results; the concentration profiles follow a gaussian distribution centred on a 55 nm-average implantation depth.

Oxidation of the implanted wafers was carried out by thermal annealing in oxygen atmosphere at 900 °C or 1100 °C for various durations. For this, the wafers were first introduced in a furnace at 800 °C under N₂ flux. Afterward, the wafers were maintained under (N₂)_{90%} +(O₂)_{10%} flux to avoid undesired nitriding of the surface while the temperature was increased using a ramp of 5 °C·min⁻¹ until the annealing temperature (900 °C or 1100 °C) was reached. After being annealed under O₂ flux, the oxidized wafers were then cooled down to the room temperature under N₂ atmosphere at 5 °C·min⁻¹. Oxide layer thicknesses were determined using ellipsometry measurements.

Samples for transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) analyses were prepared by focused ion beam (FIB) micromachining using a FEI Helios 600 Nanolab microscope equipped with a Ga⁺ ion source.

TEM and STEM analyses were performed using a FEI Titan 80-300 C_s-corrected microscope operating at 300 kV and equipped with annular HAADF-STEM detector. For both optimizing spatial resolution and reducing spatial delocalisation, spherical aberration C_s was adjusted to -7 μm for TEM imaging.

3 Results and discussion

2.1 Fe implantation and precipitation SIMS

measurements and APT analyses revealed that the initial Fe distribution follows a gaussian profile with a maximum concentration at the depth of 55 nm. In as-implanted samples, the presence of a superficial amorphous layer (thickness: 92±5 nm) was evidenced by TEM imaging.

However, the recrystallisation of this layer was ever complete in the sample annealed at 900 °C during 5 min, which is not surprising since the recrystallisation rate is estimated to at least 1800 nm·mn⁻¹ at 800°C [14] so the whole 92 nm would be cured in less than 30 s. This fast recrystallisation leads to the formation of numerous end-of-range (EOR) defects [15] in the area corresponding to the initial interface between amorphous and crystalline silicon. However, no Fe segregation is evidenced on these defects, in contrast with the observation of Fe-decorated extended defects already reported in various studies [16--19]. In spite of the very short duration of the thermal annealing performed on this sample, *post mortem* TEM analysis also reveals the presence of precipitates at the SiO₂/Si interface.

A rough estimation of 3×10⁸ precipitates per surface square centimetre is found. The observed precipitates exhibit faceted shapes, with facets parallel to the {114} and {111} atomic planes of the Si substrate. These precipitates reach in few cases a few tens of nanometres in diameter. It must be noticed that they are systematically totally included in the silicon substrate.

On the contrary, the precipitates observed in samples annealed for a longer time (*i.e.* 3h and 10h) usually straddle the interface between the substrate and the oxide layer. In that case, although the precipitates' density and size (between 20 nm and 50 nm) remain similar to the ones of the precipitates observed in the sample annealed during 5 min, their shape is slightly different. In particular, the part of the precipitates embedded in the oxide layer is rounded, that is in sharp contrast with the other part, faceted, contained in the silicon substrate (figure 1). This morphological change suggests that the precipitates were partially oxidized during the oxidation process of the silicon, leading to a vanishing of the faceting imposed by the symmetry of the surrounding crystalline matrix when included in the silicon substrate, to the benefits of a more energetically favourable spherical shape in the amorphous oxide layer. The analysis of the Fourier transform of the HRTEM images systematically confirms that the structure of these precipitates coincides with the β-FeSi₂ silicide.

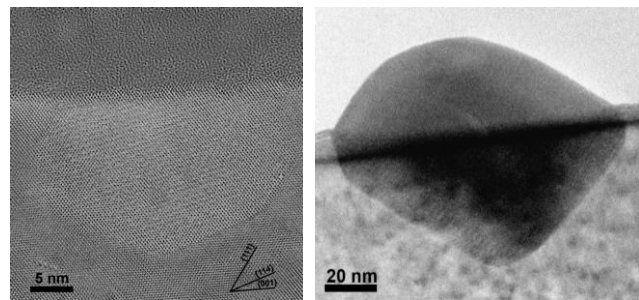


Figure 1 Precipitates observed in Fe-implanted silicon substrate (fluence: 1.0×10¹⁵ cm⁻²) and dry-oxidized at 900 °C during a) 5 min (left) and b) 10 hours (right).

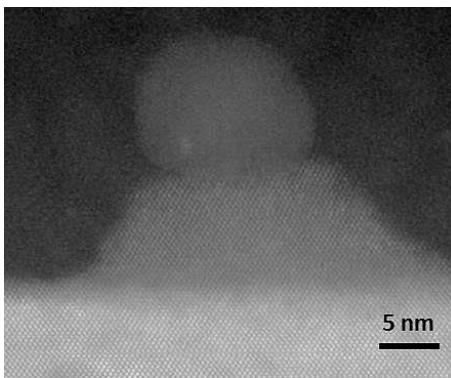
2.2 Pyramidal defects at SiO₂/Si interfaces and correlation with precipitates

Numerous pyramidal defects, identified from HRTEM imaging as crystalline silicon, were systematically observed at the SiO₂/Si interface in all samples. Their density and size are roughly about 2×10⁸ cm⁻², 10 nm × 30 nm in 900 °C samples, about 3×10⁷ cm⁻², 10-30 nm × 60 nm in 1100 °C samples (estimated from TEM observations).

Moreover, spherical β-FeSi₂ precipitates were frequently observed at the top of pyramids (figure 2), that is supporting the hypothesis of a correlation between the presence of the precipitates and the formation of the pyramids. In the case of softer pyramids, smaller FeSi precipitates have also been identified, whereas their small size can

1 avoid them to be systematically detected. Finally, STEM-
 2 HAADF imaging revealed the presence of small Fe-rich
 3 clusters at the vicinity of pyramids in the oxide layer.

4 Considering the respective oxidation rates of silicon
 5 and iron-silicide precipitates, a faster oxidation rate of the
 6 β -FeSi₂ precipitates in comparison with silicon would sys-
 7 tematically lead to the observation of precipitates totally
 8 embedded in the silicon layer. On the contrary, the obser-
 9 vation of some of them partially or totally included in the
 10 oxide layer necessarily implies that bulk silicon is faster to
 11 oxidise than FeSi₂ precipitates. Thus, natural explanation
 12 of figure 2 is that the precipitate hinders the oxydation of
 13 silicon.

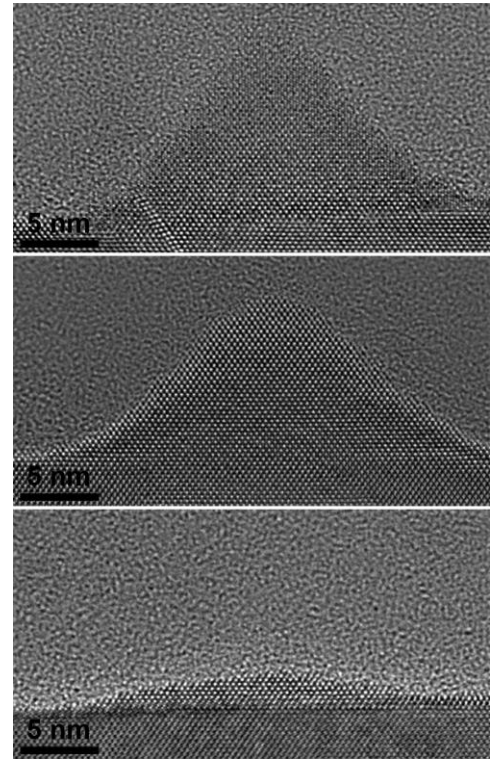


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Figure 2 Example of pyramidal defect observed at the
 SiO₂/Si interface in oxidized silicon substrates previously im-
 planted with Fe atoms, observed by HAADF-STEM imaging.
 Annealing conditions are 1100 °C, 12 min but similar configura-
 tions are observed in the others annealing conditions (except
 900 °C, 5 min). The precipitate composition is FeSi₂.

36 The advance of the SiO₂/Si interface being locally
 37 masked by the presence of a precipitate, a pyramid
 38 is formed below. Nevertheless, the lateral sides of pyramids
 39 are also oxidised, which progressively leads to the inclu-
 40 sion of the precipitate in the growing oxide layer. As far as
 41 the precipitate is totally included in the oxide, the pyramid
 42 is progressively consumed in the same time the interface is
 43 moving forwards. The shape evolution of pyramids would
 44 probably follow the sketch illustrated in figure 3.

45 Some pyramidal defects are also observed whereas no
 46 precipitate is visible (figure 3). It could be attributed to
 47 natural roughness of the layer, but the most probable ex-
 48 planation is that the thinning of the sample can be located
 49 out of the medium plane of the pyramid so that the sample
 50 surface would be crossing the basis of the pyramid without
 51 intersecting the precipitate.

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**2.3 Diffusion of chemical species inside the
 precipitates** Two main observations give evidence of
 competition between the moving of interface and some dif-
 fusion mechanisms:



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Figure 3 Various pyramidal defects observed at the SiO₂/Si
 interface in oxidized silicon substrates previously implanted with
 Fe atoms; Si pyramids are clearly coherent with the Si substrate.
 A stacking fault is visible within the pyramidal defect on the up-
 per image.

a) SIMS measurements reveal that the maximum con-
 centration of iron is always located at the interface, in good
 agreement with TEM observations in which big precipi-
 tates are consistently located in the vicinity of the SiO₂/Si
 interface whatever the oxidising time. So we can conclude
 that whereas the oxidation of Si is quicker than the oxida-
 tion of FeSi₂, the precipitates move with the interface. It
 implies both dissolution of the part of the precipitates in-
 cluded in the growing silicon oxide layer and the contin-
 uous growing of the FeSi₂ phase at its interface with the sili-
 con substrate; this is possible only if Fe atoms diffuse to-
 wards the substrate, whereas Si in FeSi₂ is oxidized on the
 top part;

b) In some cases, some other phases with higher Fe
 contents have also been observed, corresponding to ad-
 vanced oxydation phases (figure 4): a detailed analysis of
 these precipitates will be found elsewhere [20].

It is thus likely that diffusion of chemical species: Si
 and Fe, occurs inside the precipitates, and it can be as-
 sumed that several (Fe, Si) phases simultaneously co-exist,
 forming and vanishing in the same time in non-equilibrium
 conditions.

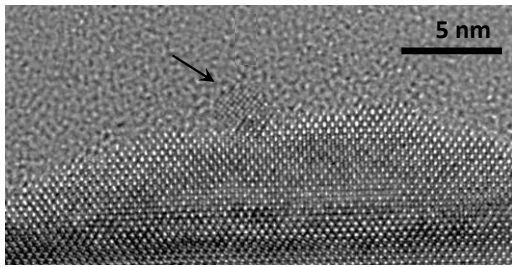


Figure 4 Nanometric FeSi precipitate at the top of a pyramid (oxidation conditions 1100°C, 12 min).

2.4 Diffusion, precipitation and dissolution of Fe at the moving SiO₂/Si interface The behaviour of implanted iron during the oxidation annealing may then be described as follows:

- a) Diffusion towards the surface occurs in 10⁻² s, when the sample is introduced in the furnace at 800°C ;
- b) in less than 5 min at 900 °C, the main part of iron is precipitated as faceted FeSi₂ precipitates;
- c) as the oxidation-front is moving forwards, precipitates follow the interface by Si oxidation-induced dissolution on one side, and simultaneous β-FeSi₂ growth on the other side;
- d) β-FeSi₂ precipitates enrich in Fe because of preferential oxidation of Si atoms leading to the formation of Fe-rich phases for the longer times of oxidation;
- e) nanometric Fe-rich clusters gettered in the SiO₂ oxide layer remains observable in the vicinity of interfacial pyramids which would be the track of a dissolved precipitate overpassed by the oxidation front.

This easy-to-read storyline is hiding more complex behaviour: the dissolution/recrystallisation is an unavoidable mechanism to explain that precipitates are always located at the SiO₂/Si interface whatever the annealing time; nevertheless no change in precipitate compositions would be observed if it was not counterbalanced by the fast growth of the SiO₂ layer and the probable fast diffusion of iron within the β-FeSi₂ precipitates (and perhaps simultaneously in SiO₂).

As several of the steps described above are observed in single samples whatever the annealing time and temperature, we can reasonably conclude that competitive kinetics are involved resulting in the formation of the observed pyramidal defects: Fe segregation and precipitation, advance of the SiO₂/Si interface, Fe-silicide dissolution. The global SIMS measurements show that Fe is mainly located close to the interface; the local (TEM,APT) analyses reveal that the local increase of iron concentration results from unstable, dynamic mechanisms.

4 Conclusion Immediate segregation of Fe close to the surface, and fast re-crystallisation of the amorphous layer during the temperature increase from the room temperature up to 900 °C of the performed thermal annealing. No segregation of Fe is observed on extended defects like

EOR; β-FeSi₂ precipitates were very frequently observed at the SiO₂/Si interface. The characteristic pyramidal defects reported in [10] were also observed by TEM.

The detailed analysis of the various oxidised samples strongly suggests that the formation of these defects at the SiO₂/Si interface is correlated with the presence of the precipitates. Moreover, a mechanism allowing understanding the formation of the pyramidal defects is proposed.

Competition between several kinetics (growth of silicon oxide, Fe-diffusion inside the precipitates, Fe-segregation at the moving interface, Fe-enrichment of precipitates, progressive dissolution of precipitates) is supposed to play a key role, leading to the observed complex microstructure : iron-silicides precipitates and associated pyramidal defects located at the moving SiO₂/Si interface.

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