Dynamic segregation of metallic impurities at SiO$_2$/Si interfaces

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Abstract. The behaviour of two metallic impurities, iron and tungsten, during oxidation of silicon wafers has been investigated using transmission electron microscopy and atom probe tomography. Metallic contamination has been introduced by implantation of $^{56}$Fe at 65 keV and $^{186}$W at 150 keV, with a dose of $10^{15}$ at/cm$^2$. Oxidation of Fe-contaminated Si wafer results in the precipitation of iron as $\beta$-FeSi$_2$ at the SiO$_2$/Si interface. The presence of these precipitates hinders the oxidation front which forms silicon pyramidal defects. Further oxidation of the precipitates leads to iron-rich cluster formation in the SiO$_2$ layer, surrounding the pyramids.

Dry oxidation of a tungsten-contaminated Si wafer is characterised by the formation of nanometric spherical precipitates in the Si layer. The size and density of these precipitates versus depth follow the as-implanted W concentration profile.

1. Introduction

With the increasing complexity of the design of the newest generation of transistors, unintentional contamination by metallic impurities, even at low concentration levels, has become one of the major problems in the manufacturing of modern microelectronic devices. In particular, the presence of very small amounts of contaminants in the active area of transistors is enough to have deleterious impact on their electrical properties making them defective. It is thus essential to improve our understanding of metallic contaminant behaviour during the processing of microelectronic devices and, more specifically, at the interfaces of CMOS structures.

In this context, this work aims at a study of the mechanisms of diffusion and precipitation or segregation of two metallic elements at the SiO$_2$/Si interface: iron and tungsten. The parallel study of these two impurities aims to compare and to model the diffusion/precipitation mechanisms of species exhibiting different diffusion behaviours. Indeed, whereas iron diffusion uses an interstitial mechanism and is a fast diffusing species [1], tungsten shows low diffusion rates [1,2] and an unknown diffusion mechanism.

Depending on both the contaminating element and oxidising conditions, various situations have been distinguished. Based on the experimental observations, a qualitative model for the dynamic segregation of metallic impurities in silicon is proposed.
2. Experimental details

In this study, 525 µm-thick P-doped (001) Si wafers (resistivity 2-20 Ω.cm) were contaminated with $^{56}$Fe and $^{16}$W ions, at a dose of $10^{15}$ at/cm$^2$ and with implantation energies respectively of 65keV and 150keV.

In order to study the effect of oxidation temperature and duration, the samples were dry oxidised under O$_2$ flux for various conditions (900°C for 5, 189, 592 min or 1100°C for 12 and 44 min). The oxidation times were set to grow SiO$_2$ layers with comparable thicknesses for both temperatures.

Post mortem analyses of the oxidised specimens were done using several characterisation tools, such as Cs-corrected HRTEM (High Resolution Transmission Electron Microscopy), Z-contrast STEM (Scanning Transmission Electron Microscopy) and LP-APT (Laser-Pulsed Atom Probe Tomography). TEM thin foils and APT tips were prepared by focused ion beam (DBFIB) micromachining using an FEI Helios microscope. TEM lamellae were cleaned using the Fischione Nanomill device. In order to facilitate the evaporation of the oxide layer during APT analysis, the tips were prepared by the lift-out preparation method [3] using a specific sample orientation: the wedge was attached to a microtip with its surface tilted by 10°. APT analyses were carried out with a LEAP 3000xHR at a temperature of 80 K, with a laser pulse frequency of 100 kHz, using a laser power of 1.2nJ, corresponding to a $I_{Si}^{2+}/I_{Si}^{1+}$ ratio of 16.5 and a $I_{W}^{2+}/I_{W}^{1+}$ ratio of 5.6.

3. Results and discussion

3.1. Fe behaviour during dry oxidation

Dry oxidation of iron-implanted Si wafers led to the formation of iron precipitates at the SiO$_2$/Si interface. Their diameters ranged from 20 to 50 nm. For the shortest oxidation times, faceted precipitates were located at the SiO$_2$/Si interface, inside the Si layer. For longer oxidation time, the precipitates got partly incorporated in the SiO$_2$ layer and became round in shape (figure 1).

The precipitate structure was deduced from the Fourier transform (FT) analysis of HRTEM images. All the precipitates have been identified as being the low-temperature stable silicide phase $\beta$-FeSi$_2$ [4, 5]. Except for the shorter oxidation time, analysis of the SiO$_2$/Si interface also revealed the presence of pyramidal-shaped defects (figure 2), already observed in the literature [4]. These defects consist of silicon huts whose origin was unclear. HAADF-STEM imaging revealed the presence of small iron-rich clusters incorporated in the SiO$_2$ layer around these pyramids (figure 2).

![Figure 1. HRTEM image of a precipitate of $\beta$-FeSi$_2$ formed at the SiO$_2$/Si interface.](image1)

![Figure 2. HAADF-STEM image showing iron clusters incorporated in the SiO$_2$ layer around a silicon pyramidal-shaped defect.](image2)

Figure 3 shows a pyramidal-shaped defect surmounted by a precipitate. The observed configuration suggests that the formation of those defects is correlated with the presence of a precipitate which locally hinders the propagation of the oxidation front.
We thus propose the following model for the formation of these iron-induced defects (figure 4):

i) Iron accumulates at the growing SiO₂/Si interface forming facetted β-FeSi₂ precipitates. Oxidation of the precipitate smooths its surface, leading to a spherical shape.

ii) Assuming that the oxidation rate of iron silicide is significantly lower than the one of silicon, the presence of the precipitate modifies the oxidation front and is responsible for the observed defects at the SiO₂/Si interface.

iii) The complete consumption of the precipitate leaves behind pyramidal-shaped silicon huts at the SiO₂/Si interface that are surrounded by Fe clusters.

Dry oxidation of tungsten-implanted Si wafers is characterised by the formation of nanometric spherical precipitates in the Si layer (figure 5). The size and density of these precipitates versus depth follow the as-implanted W concentration profile. APT analysis of the sample oxidised at 900°C for 5 min revealed an asymmetric widening of the W profile toward the growing oxide (figure 5). It thus shows that tungsten atoms can diffuse without forming precipitates at a concentration of ~10²⁰ at/cm³.
Structural analysis of precipitates revealed the coexistence of two phases: tetragonal $W_5Si_3$ and hexagonal WSi$_2$. These precipitates exhibit topotactic relationships with the silicon matrix (topotaxy: the phenomenon of mutual orientation of two or more crystals of different species resulting from a solid-state transformation [6]). However, various precipitates’ orientations have been observed, and no predominant orientation of the precipitates has been evidenced. HAADF imaging also revealed that sub-nanometric W clusters are formed in the SiO$_2$ layer (figure 6).

![Figure 6. HAADF comparison between samples oxidised at 900°C for 592 min (left) and at 1100 °C for 44min (right).](image)

Size evolution of precipitates in Si and clusters in SiO$_2$ has been studied as a function of time and temperature. At 900°C, precipitates’ size increases with time whereas it doesn’t evolve notably at 1100°C, indicating that they probably reach an equilibrium state faster at higher temperature. In addition, it can be noticed that the density of clusters in the SiO$_2$ layer seems to increase with oxidation temperature.

4. Conclusion

As expected, iron and tungsten exhibit very different behaviours during dry oxidation: iron diffuses fast and forms large $\beta$-FeSi$_2$ precipitates at the SiO$_2$/Si interface whereas tungsten diffusion is limited in length and brings about the formation of nanometric $W_5Si_3$ and WSi$_2$ precipitates, with a distribution centred close to the implantation projection range. The Fe-induced pyramidal-shaped defects result from the differences in oxidation rates for iron precipitates and silicon. In both cases, iron and tungsten, oxidation of these precipitates results in the incorporation of metal into the SiO$_2$ layer as metallic clusters.

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