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Effect of transition metals on oxygen precipitation in silicon

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Effect of transition metals on oxygen precipitation in silicon

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Abstract. Effects of iron and copper impurities on the amount of precipitated oxygen and the oxide precipitate and stacking fault densities in Czochralski-grown silicon have been studied under varying thermal anneals. Silicon wafers were intentionally contaminated with iron or copper and subsequently subjected to different two-step heat treatments to induce oxygen precipitation. The iron contamination level was 2×10^{13} cm^{-3} and copper contamination level 6×10^{13} cm^{-3}. Experiments did not show that iron contamination would have any effect on the amount of precipitated oxygen or the defect densities. Copper contamination tests showed some indication of enhanced oxygen precipitation.

1. Introduction

Metal contamination is very harmful in the IC technology since it decreases device performance and thus lowers the device yield. In MEMS technology metal contamination is not considered that detrimental. However, oxide precipitates and oxygen precipitation induced secondary defects affect the quality of anisotropically etched cavity surfaces in silicon. [1] If metal contamination has an effect on the precipitation behaviour of oxygen, metallic contamination becomes an issue in MEMS technology as well. Iron contamination has indeed been found to increase both the amount of precipitated oxygen and the density of oxide precipitates. [2, 3, 4] It is expected that iron could promote the nucleation of oxide precipitates. Copper precipitates have been shown to enhance oxygen precipitation, too. [5] The copper precipitates and copper precipitation induced defects are thought to serve as nucleation sites for oxide precipitates. In these previous studies metallic contamination levels have usually been rather high. In this paper we investigate the effect of iron and copper on the amount of precipitated oxygen and oxygen precipitation induced defects concentrating on more realistic contamination levels.

2. Experimental

The studied wafers were boron doped p-type, <100>-oriented Czochralski-grown silicon wafers. The wafer diameter was 100 mm, thickness 550 μm and resistivity 7 – 15 Ωcm. The initial oxygen concentrations varied between 11.5 ppma and 12.9 ppma.

As a first process step the wafers were subjected to a homogenization treatment, 15 min at 1050 °C, to dissolve the as-grown oxide precipitates. Iron contamination was performed in iron spiked ammonium hydroxide - hydrogen peroxide - water standard cleaning solution and iron diffusion treatment was 55 min at 850 °C. After the diffusion the surface contamination was removed. Exactly the same thermal treatment was done for equal number of uncontaminated reference wafers. Different two-step thermal treatments were carried out for iron contaminated and uncontaminated wafers to induce oxygen precipitation. The duration of the first step, the nucleation treatment, at 550 °C or 650

°C was varied. After the nucleation treatment the temperature was raised at a rate of 1 °C/min to 1050 °C, where the second step, the growth treatment, lasted for 10 h. Then the temperature was ramped down 4 °C/min to 800 °C and the wafers were unloaded. Also an experiment without the nucleation treatment was performed. In that case wafers were loaded into the furnace at 800 °C and the ramp up rate to growth temperature was 10 °C/min. Some wafers were also unloaded after the nucleation treatment and loaded again for the growth treatment at 800 °C so that the wafers experienced a fast ramp between the nucleation and growth temperatures.

Copper contamination was done by spinning 0.5 % HNO_3 solution with 1.6 ppm Cu on the wafer surface. Copper diffusion treatment was 20 min at 800 °C and again, the same treatment was done for uncontaminated wafers, too. Copper contaminated wafers were subjected to illumination for 1 h to create copper precipitates. [6] Then two-step thermal treatments were carried out for copper contaminated and uncontaminated wafers to induce oxygen precipitation. The nucleation treatment duration at 650 °C was varied and the growth treatment after 1 °C/min ramp was 10 h at 1050 °C.

Metal concentrations were measured by μPCD method using Semilab WT-85X 400 lifetime scanner. In iron contaminated wafers the iron concentration was about 2×10^{13} cm^{-3}. In the case of copper contaminated wafers the amount of copper was calculated with formulas [6]

$$\tau_{Cu}^{-1} = (4.0 \pm 0.5) \times 10^{-24} C_{Cu}^{2} \quad (1)$$

$$\tau_{Cu}^{-1} = \tau_{final}^{-1} - \tau_{init}^{-1} \quad (2)$$

where C_{Cu} is copper concentration in cm^{-3}, τ_{init} is the carrier lifetime before the illumination in seconds and τ_{final} is the carrier lifetime after the illumination in seconds. The copper concentrations were measured to be about 6×10^{13} cm^{-3}.

The oxygen concentration was determined by Fourier Transform Infrared Spectroscopy (FTIR) measurements before and after processing. The amounts of precipitated oxygen were calculated as the difference between those values. The measurement was performed using a Bruker IFS 28 FTIR spectrometer and New ASTM (ASTM F 121-83) calibration factor 2.45×10^{17} atoms/cm^2 was employed.

Wafers that showed the highest amount of precipitated oxygen were selected for defect etching. Cross sectional samples were prepared and etched with Wright etch. Total defect densities and stacking fault densities were counted from optical micrographs taken from the cross sectional samples.

3. Results and discussion

3.1. Effect on the amount of precipitated oxygen

Wafers that had experienced oxygen precipitation treatment without the nucleation treatment or with nucleation treatment of 2 h at 650 °C showed very small amount of precipitated oxygen, about 1 ppma. In these wafers there was no difference in the amount of precipitated oxygen between iron contaminated and uncontaminated wafers. Oxygen precipitation was higher in samples which had been subjected to the nucleation treatment of 6 h at 650 °C and even higher in samples which had been subjected to the nucleation treatment of 10 h at 650 °C but there was not such a difference in the amount of precipitated oxygen between iron contaminated and uncontaminated wafers that it could be attributed to iron contamination. The differences in the amount of precipitated oxygen are expected to be due to different initial oxygen concentrations in the examined wafers.

Iron contaminated and uncontaminated wafers were treated for oxide precipitate nucleation also at 550 °C, where the supersaturation of iron is higher and the effect of iron was thought to be greater. In those wafers oxygen precipitation clearly occurred, but again iron contaminated wafers did not show higher amount of precipitated oxygen compared to uncontaminated wafers, see figure 1. Oxygen precipitation was low in wafers, which had been out of furnace between the nucleation and growth treatments.

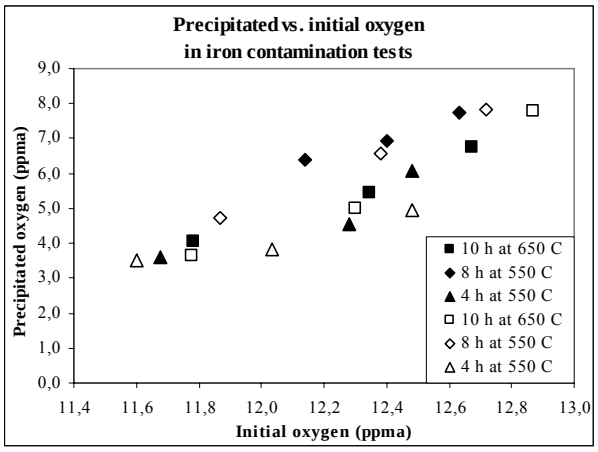

Figure 1. Oxygen precipitation in iron contaminated (filled symbols) and uncontaminated (open symbols) wafers. Time and temperature of the nucleation treatment are shown in the legend. The growth treatment was 10 h at 1050 °C.

Earlier studies [2, 3, 4], usually carried out at higher iron concentrations, have shown that iron contamination in Czochralski-grown silicon increases the amount of precipitated oxygen and precipitate density. The ramp up rate between the nucleation and growth treatments in our studies was chosen to be low to grow as many oxide precipitate nuclei as possible. If the iron atoms decorating the oxide precipitate nuclei stabilize them as proposed in literature [4], this effect may be hidden behind the low ramp up rate, which grows all nuclei, not only those stabilized by iron. On the other hand, oxygen precipitation was very low in contaminated wafers also when the wafers were unloaded after the nucleation treatment and loaded directly at 800 °C, i.e. in the case of fast ramping.

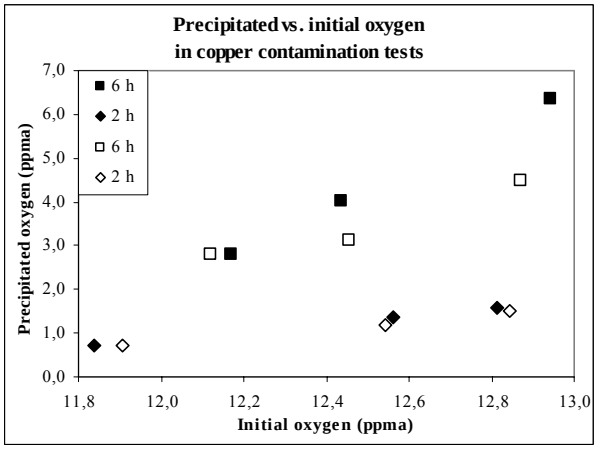

Figure 2. Oxygen precipitation in copper contaminated (filled symbols) and uncontaminated (open symbols) wafers. The nucleation treatment was done at 650 °C, time shown in the legend. The growth treatment was 10 h at 1050 °C.

Copper contaminated and uncontaminated wafers, which had undergone nucleation treatment of 2 h at 650 °C showed equally low amount of precipitated oxygen. When the nucleation duration was raised to 6 h, some copper contaminated wafers showed higher amount of precipitated oxygen compared to uncontaminated wafers of the same initial oxygen concentration, see figure 2.

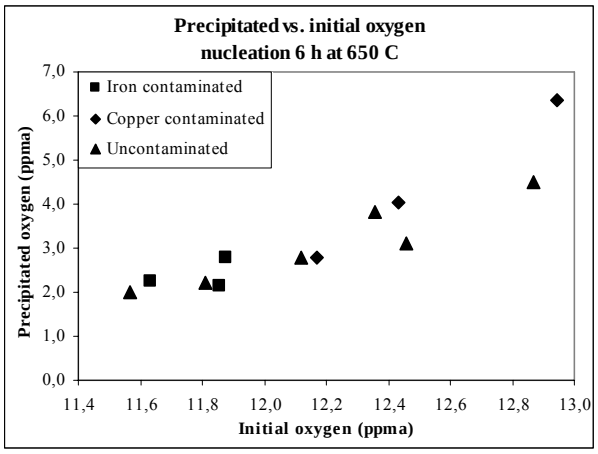

Figure 3. Comparison between iron contaminated, copper contaminated and uncontaminated wafers when the nucleation treatment was 6 h at 650 °C and the growth treatment 1050 °C.

3.2. Effect on the density of oxide precipitates and stacking faults

Defect etching was done for iron contaminated wafers treated for oxide precipitate nucleation 10 h at 650 °C, 8 h at 550 °C or 4 h at 550 °C and for equally treated uncontaminated wafers of the same initial oxygen concentration. In both iron contaminated and uncontaminated wafers the total defect densities were about the same, about 6×10^5 cm^{-2}. Iron contamination did not increase the stacking fault density either. In copper contaminated wafers, which had higher amount of precipitated oxygen compared to the uncontaminated wafer of the same initial oxygen concentration, the total defect density was also higher.

4. Conclusions

Our investigations about the effect of iron on oxygen precipitation in silicon at iron contamination level of 2×10^{13} cm^{-3} showed that iron has not any effect on oxygen precipitation. In our copper experiments at copper contamination level of 6×10^{13} cm^{-3} only part of the copper contaminated wafers showed indication of enhanced oxygen precipitation. Copper precipitates have previously been found to increase both the total amount of precipitated oxygen and the density of oxide precipitates. [5] As copper precipitates easier in n-type silicon, experiments with n-type wafers might reveal clearly the effect of copper. More information is needed about the effect of iron at different contamination levels, in n-type wafers and in different oxygen precipitation treatments, e.g. in wet oxidation treatment, which is known to induce more stacking faults than dry oxidation treatment.

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