THE EFFECT OF A POST OXIDATION IN-SITU NITROGEN ANNEAL ON SI SURFACE PASSIVATION

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ABSTRACT

The thermal stability of Si / SiO_2 stacks and Si / SiO_2 / Si_3N_4 stacks with and without post oxidation in-situ anneal in nitrogen is investigated by Quasi-steady state photoconductivity decay (QSSPCD) and Electronic Paramagnetic Resonance (EPR). With in-situ annealing in nitrogen, the Si-SiO_2 interface shows a reduced density of paramagnetic defects and better thermal stability. Si / SiO_2 / Si_3N_4 stacks have a much slower depassivation rate than Si / SiO_2 stacks due to hydrogen stored in nitride layer.

INTRODUCTION:

Thermally grown oxide layers are well known to provide good surface passivation. While for most commercial cells PECVD SiN is now the material of choice for surface passivation, there are applications where a thermally grown oxide is very useful, such as some novel cell designs, for example SLIVER cells, which utilize an oxide / LPCVD silicon nitride stack as an antireflection coating. [1,2,3] It is therefore important to understand in detail how surface recombination at the Si-SiO_2 interface can be minimised. Also the thermal stability of the interface passivation is of interest, since the interface is subjected to high temperatures both during and possibly after the deposition of the silicon nitride, which is usually carried out at ~775°C.

Post oxidation in-situ anneals in nitrogen or argon at high temperatures are known to be an effective method to improve the quality of the Si-SiO_2 interface following thermal oxidation, as measured by a reduction in surface recombination.

In this paper, the effects of in-situ N_2 anneals on the Si-SiO_2 interface properties are discussed. (100), (111) and textured Si wafers were used for the experiments since they have different sensitivity to thermal treatments. Si/SiO_2 stacks and Si/SiO_2/ LPCVD SiN stacks were investigated. Rapid Thermal Anneals (RTAs) were used to investigate the thermal stability of the passivation of oxidized surfaces. Quasi-Steady State Photoconductivity Decay (QSSPCD) and Electron Paramagnetic Resonance (EPR) measurements were used to gain information on surface recombination and paramagnetic defect densities, respectively.

EXPERIMENTAL DETAILS:

Float Zoned (FZ), (100) oriented, p-type, 100Ω-cm, 500µm thick wafers and FZ, (111) oriented, n-type, 100Ω-cm, 500µm thick wafers were taken as the starting materials for QSSPCD measurement. CZ, p-type, ~10Ω/cm, 500µm thickness (111) wafers were used in the Electron Paramagnetic Resonance (EPR) measurements. To fit into the cavity, EPR samples were cut by a diamond saw into 25mm×2.5mm pieces. All samples are initially etched in 10:1 HNO_3: HF solution until shiny. Some (100) wafers were textured to form inverted pyramids on top.

After a standard RCA clean, all samples were passivated by a thermally grown oxide (~50nm) in dry oxygen at 1000°C. Selected wafers received an in-situ N_2 anneal after oxidation at 1000°C for 30 minutes. All QSSPCD wafers had a forming gas anneal (5%H_2 in 95% argon) at 400°C for 30 min. LPCVD Si_3N_4 deposition was done at 775°C and 0.5torr, with an ammonia to DCS flow ratio of 4:1, to give a 50nm nitride layer on selected QSSPCD samples. Isochronal and isothermal RTAs were performed on some QSSPCD samples to test the thermal stability.

RTA at 800°C in high flow dry nitrogen for 3 min was done on EPR samples to completely dehydrogenate the (111) Si-SiO_2 interface, and thus allow measurement of the total paramagnetic interface defect (P_b centre) density. This treatment is known not to generate significant amounts of additional defects.

QSSPCD measurements were carried out using a white flash with a known light spectrum. The measurements were modeled using PC1D[4], for different values of the surface recombination velocity and the light intensity, and assuming a very high bulk lifetime (30ms). This allowed derivation of an empirical equation relating the measured minority carrier lifetime at a particular injection level to the effective surface recombination velocity, S_{eff}, valid for S_{eff} values of no more than ~7000cm/s. The S_{eff} was estimated for the highest effective lifetime at the injection level range of $1 \times 10^{14}/cm^2$ to $2 \times 10^{14}/cm^2$.

EPR spectra were obtained with a Bruker 300 X-band (9.44GHZ) spectrometer. Measurements were taken using 5G modulation and 20µW microwave power at a temperature of 8K. The low microwave power is carefully chosen to prevent signal

saturation. The paramagnetic P_b centre, known to be by far the dominant defect on (111) surfaces, can be detected from these measurements. The $[P_b]$ concentration was calculated by double integrating the original signal and comparing with a standard solution signal, which is obtained under similar conditions.

RESULTS AND DISCUSSION

Effect of in-situ N_2 anneal

Figure 1 shows the effect of the in-situ N_2 anneal on the lifetime measured directly after oxidation. The line with open circles represents oxidised wafers without in-situ anneal in N_2, while the line with solid circles represents wafers with in-situ N_2 anneal. The effective lifetime for the oxidized sample with in-situ N_2 anneal is higher than the oxidized sample without in-situ N_2 anneal at all injection levels. The bulk lifetime for both samples should be the same, therefore, the difference in the effective lifetime must be due to a difference in surface passivation. Clearly oxidation with an in-situ N_2 anneal results in a better passivated surface.

On (111) silicon surfaces, a P_b defect is an unpaired electron on a trivalently bonded silicon atom generated at the Si-SiO_2 interface as the result of mismatch. P_b centres are initially generated during the oxidation process. The EPR measurements indicate that the in-situ N_2 anneal leads to a significant reduction in the P_b centre density, with $[P_b]$ of $4.6 \times 10^{12}/cm^2$ for a sample with in-situ anneal compared with $1.1 \times 10^{13}/cm^2$ without an anneal.

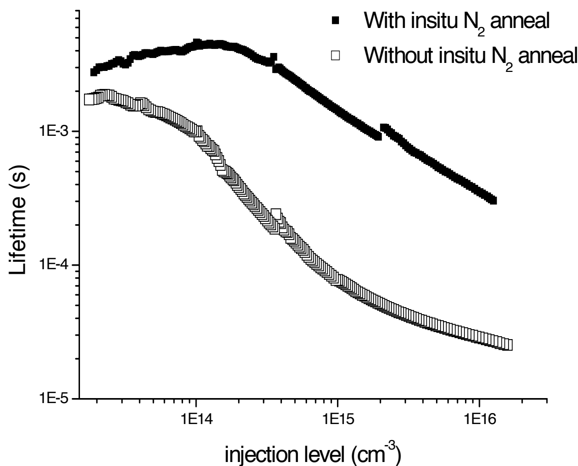

Fig 1. Effective lifetime vs injection level

In-situ N2 Anneal effects on Si-SiO2 thermal stability under RTA

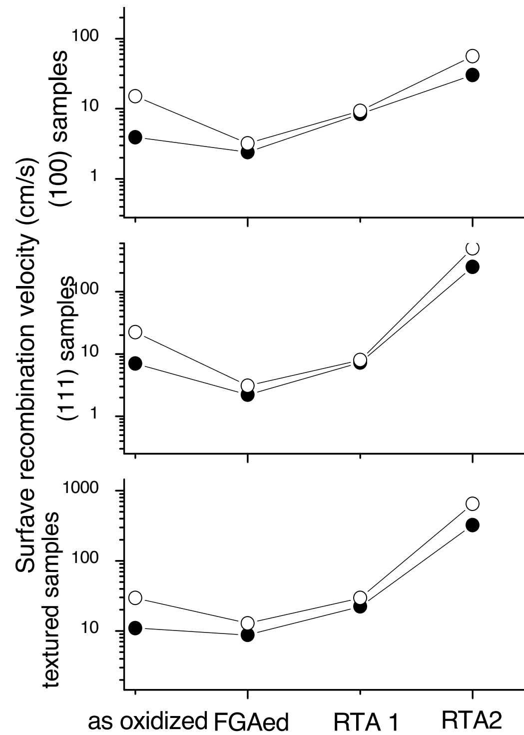

Figure 2. surface recombination velocity vs thermal treatments

Figure 2 shows the effective surface recombination velocities of (100), (111) and textured, oxidized wafers with and without an in-situ N_2 anneal, and the effect of thermal treatments on S_{eff}.

In figure 2, the open datum presents the values from 'without in-situ N_2 anneal' samples. The solid datum presents the values from 'with in-situ N_2 anneal' samples. 'As oxidized' represents values measured just after oxidation. 'FGAed' represents the values following forming gas annealing. 'RTA1' and 'RTA2' were performed at 500°C for 3 minutes and 600°C for 3 minutes in N_2 gas respectively.

All of the (100), (111) and textured orientations display the same trend. After oxidation, samples with in-situ N_2 anneal have lower recombination velocity. The FGA process introduces hydrogen to the Si-SiO_2 interface and lowers S_{eff}. 'RTA1' increases S_{eff}. The difference between samples with and without in-situ N_2 anneal is small at these two steps. As samples were FGAed, the majority of dangling bonds at the interface are passivated with hydrogen. An RTA at 500°C for 3 mins does not lead to a significant release of hydrogen from the interface. However, after RTA2, a significant fraction of hydrogen has been driven away from the Si-SiO_2 interface. A bigger difference in S_{eff} between samples with and without in-situ N_2 anneal is apparent. At this stage, the in-situ annealed samples

have only around half the S_{eff} values of the samples without in-situ anneals.

It can also be concluded from figure 2 that (100), (111) and textured samples display a different depassivation rate. From step ‘RTA1’ to ‘RTA2’, the textured samples have the most rapid and (100) samples the slowest depassivation rate. The behaviour of (111) samples is similar to that of the textured samples. These observations are quite consistent with our other results presented elsewhere [4].

In-situ N_2 Anneal effects on Si/SiO_2/SiN stacks under RTA

Figures 3 and 4 show the effect of an in-situ N_2 anneal on nitride stacks after isochronal and isothermal RTAs.

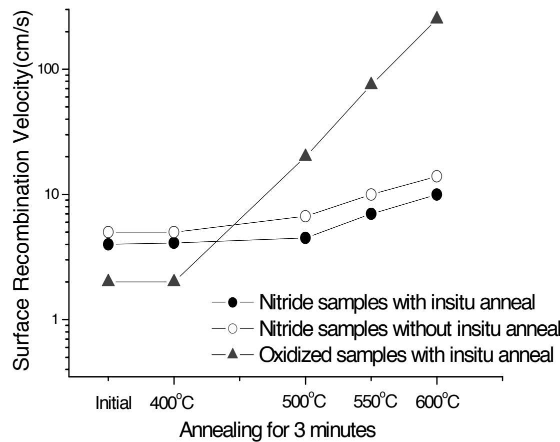

Figure3. isochronal anneal on Si/SiO2/SiN stacks

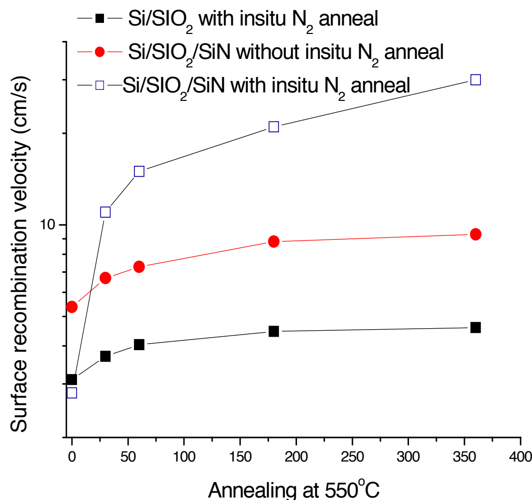

Figure 4. isothermal anneal on Si/SiO2/SiN stacks

In figure 3, (111) Si wafers were used. The ‘initial’ value for oxidized samples was taken after oxidation, an in-situ N_2 anneal and a FGA. The ‘initial’ values for nitride samples were taken after oxidation with / without an in-situ N_2 anneal, an FGA and LPCVD deposition. Since the deposition was carried out at 775°C, the ‘initial’ values for nitride samples are higher than for the as oxidized samples.

As the annealing temperature increases, the nitride samples display a better thermal stability than the oxidized samples. With an in-situ N_2 anneal, the nitride stacks have the lowest S_{eff} values after RTAs from 500°C to 600°C. The reason for the increased stability of the samples with a nitride is likely to be the release of hydrogen from the nitride at elevated temperatures, which provides an additional source of hydrogen for re-passivation of the Si-SiO_2 interface.

CONCLUSION

Post oxidation in-situ annealing in nitrogen reduces the density of interfacial defects generated during the oxidation process. Nitrogen annealed (100), (111) and textured, oxidised samples display lower S_{eff} values and slower depasivation rates than samples without nitrogen anneals. With a nitrogen anneal, Si/SiO_2/SiN stacks show good thermal stability after isochronal and isothermal RTAs.

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