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Effect of oxygen in low temperature boron and phosphorus diffusion gettering of iron in Czochralski-grown silicon

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Abstract. Low temperature boron and phosphorous diffusion gettering (BDG and PDG) of iron in Czochralski-grown silicon were experimentally studied. Differences and similarities between the gettering techniques were clarified by using intentionally iron contaminated wafers emphasizing especially the effect of oxygen. Experiments showed that the surprisingly high gettering effects of BDG could be explained by B-Si precipitates. Oxygen precipitation was seen to decrease minority carrier diffusion length after long gettering at low temperatures in both BDG and PDG. In the case of BDG oxygen precipitation affected more as a higher thermal budget was needed to obtain similar sheet resistance to that of PDG. According to experiments the efficiency of BDG can not be concluded from the sheet resistance, whereas the efficiency of PDG can. This has practical influences in a process control environment.

Introduction

One of the very detrimental contaminants in silicon, unavoidable in a semiconductor processing environment, is iron. Plenty of research on iron gettering in silicon has already been done, and it is widely acknowledged that both boron diffusion gettering (BDG) and phosphorus diffusion gettering (PDG) are effective techniques to remove pernicious iron contamination. By conveniently adding a low temperature anneal after the formation of the junction or the back surface field in photovoltaic devices by phosphorus or boron diffusion, the gettering efficiency of iron can be even further increased [1,2,3,4].

The mechanisms behind BDG, including segregation of iron to the gettering layer and iron precipitation to the surface of the wafer, are believed to be largely understood due to thorough investigations [5]. In the case of PDG of iron, despite the enormous experimental and theoretical studies on iron in silicon, the gettering mechanisms have been ambiguous [5]. However, recently modeling of PDG based on experimental segregation coefficient has given promising results [6]. In this paper we study experimentally both BDG and PDG using intentionally iron contaminated silicon wafers in order to clarify differences and similarities between the gettering techniques. Emphasis is especially on the effect of oxygen in low temperature boron and phosphorus diffusion getterings of iron in Czochralski-grown silicon.

Experimental

Silicon wafers used in the experiments were boron doped p-type, <100>-oriented Czochralski-grown wafers with a diameter of 100 mm. The wafers were divided into two groups according to their initial oxygen concentration; wafers with high initial oxygen level (14 – 16 ppma) and wafers with low initial oxygen level (7 – 9 ppma MCz). The thicknesses of the wafers with high initial oxygen level and low initial oxygen level were 525 μm and 400 μm respectively and their resistivities were 4 – 40 Ωcm and 2.7 – 3.0 Ωcm respectively.

As a first process step intentional iron contamination was introduced on all the wafers. This was done by immersing the wafers in an iron spiked $NH_4OH:H_2O_2:H_2O$ solution and subsequently diffusing iron at 850˚C for 55 min and finally removing the surface contamination by etching the wafers in a $H_2O:HF:H_2O_2$ (24:1:1) solution and by RCA cleaning. As a result of the contamination, an iron level of 2×10^{13} cm^{-3} was achieved. After contamination the wafers were dry oxidized to a thickness of 27 nm (measured by ellipsometer) for surface passivation. Prior to boron and phosphorous diffusion gettering treatments the oxide was removed from the front side of the wafers by etching in BHF. Boron and phosphorus spin-on-dopants were applied on selected wafers and different BDG and PDG treatments consisting of high temperature diffusion and low temperature tail were done. Boron and phosphorus in-diffusion times and temperatures were chosen so that the sheet resistances were comparable: about 40 Ω/□ in BDG, about 45 Ω/□ and 30 Ω/□ in 30 or 60 minutes PDG, respectively. The BDG and PDG treatments used in the experiments are presented in Table 1 and Table 2. After the diffusion gettering treatments the remaining spin-on-dopants were etched away in BHF and the wafers were RCA 1 cleaned. Finally the minority carrier diffusion lengths and the remaining interstitial iron concentrations were measured by surface photovoltage (SPV) method [7] to determine the efficiency of gettering after diffusion gettering anneals.

Table 1. The BDG treatments used in the experiments.

Oxygen level [ppma]	Gettering profile	Tail temperature [˚C]
14 – 16	60 min at 930˚C + 2 h at 800˚C	800˚C
14 – 16	60 min at 930˚C + 3.5 h at 750˚C	750˚C
14 – 16	60 min at 930˚C + 5.5 h at 700˚C	700˚C
14 – 16	60 min at 930˚C + 8 h at 650˚C	650˚C
7 – 9	60 min at 930˚C + 2 h at 800˚C	800˚C
7 – 9	60 min at 930˚C + 3.5 h at 750˚C	750˚C
7 – 9	60 min at 930˚C + 5.5 h at 700˚C	700˚C
7 – 9	60 min at 930˚C + 8 h at 650˚C	650˚C
7 – 9	60 min at 930˚C + 15 h at 650˚C	600˚C

Table 2. The PDG treatments used in the experiments.

Oxygen level [ppma]	Gettering profile	Tail temperature [˚C]
14 – 16	30 min at 870˚C + 2 h at 800˚C	800˚C
14 – 16	30 min at 870˚C + 3.5 h at 750˚C	750˚C
14 – 16	30 min at 870˚C + 5.5 h at 700˚C	700˚C
14 – 16	30 min at 870˚C + 8 h at 650˚C	650˚C
7 – 9	60 min at 870˚C + 2 h at 800˚C	800˚C
7 – 9	60 min at 870˚C + 3.5 h at 750˚C	750˚C
7 – 9	60 min at 870˚C + 5.5 h at 700˚C	700˚C
7 – 9	60 min at 870˚C + 8 h at 650˚C	650˚C

Results and discussion

Effect of oxygen in low temperature boron diffusion gettering. The Arrhenius plots of gettering results and activation energies, obtained from the results of SPV measurements from centre (radius < 20 mm) and from edge (radius > 30 mm) of low oxygen level boron diffusion gettered wafers with different low temperature anneals, are presented in Fig. 1. The gettering efficiencies of iron in the wafers are much higher than predicted by segregation coefficients calculated using electrically active boron concentration [8] with ideal in-diffusion profile and 0.25 µm junction depth [9] for boron. The electrical model presented in [8] can not alone explain the results as there is a rather large difference in the gettering efficiencies between the wafer centre and edge although the measured sheet resistances do not show such a large change. The results are not in agreement with the BDG model presented by the authors [10] either, in which electrical segregation coefficient and surface precipitation is combined, which seems to work in the case of relatively high sheet resistance, as then the gettering should show step like response as in [11]. The activation energies of gettering are about 2.5 eV and 2.2 eV (Fig. 1) at the edge and centre of wafers, respectively. These

values fit quite well to the activation energies of 2.1 eV [12] and 2.27 eV [13] obtained for iron gettering by B-Si precipitates. Thus we propose that the surprisingly high gettering effect of BDG is due to B-Si precipitates and the difference between wafer edge and centre is due to the difference in the amount of precipitated boron.

Similar differences between the gettering efficiencies at the wafer centre and edges were also noticed in the wafers with high initial oxygen concentrations. We speculated that a possible explanation for the difference could be that the segregation gettering induced by the boron diffusion layer is insufficient to prevent internal gettering, i.e., iron precipitation to oxide precipitates in the bulk of the wafer during cooling down of wafers. Thus the difference could arise from the difference in cooling rate and density of oxide precipitates between wafer centre and edge. However, a more probable reason could be the difference in the amount of precipitated boron as suggested by the results obtained from low oxygen samples.

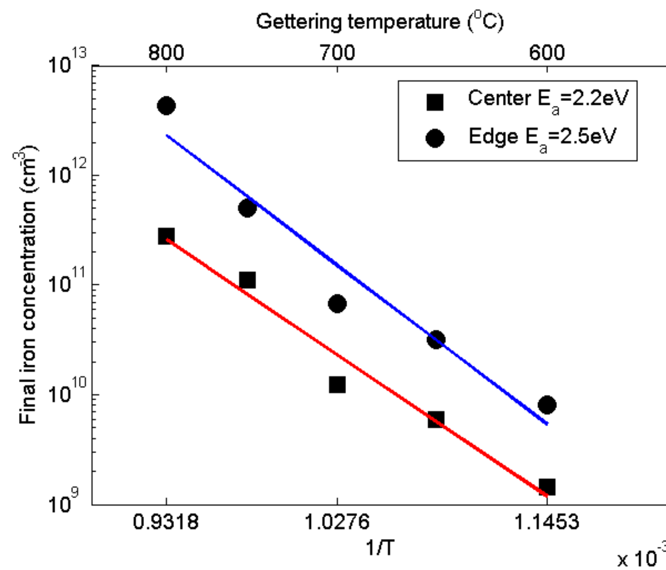

Fig. 1. The Arrhenius plots of gettering results and activation energies obtained from the results of SPV measurements from centre (radius < 20 mm) and from edge (radius > 30 mm) of low oxygen level boron diffusion gettered wafers with different low temperature anneals.

The final iron concentrations at the centre of BDG wafers with low and high initial oxygen concentrations are compared in Fig. 2. From Fig. 2 it can be seen, that the gettering efficiency in wafers with high oxygen concentration is noticeably lower. The differences in wafer thicknesses between the series explain at least part of the lower gettering efficiency. However, the annealing times were chosen so, that based on simulation of PDG [6], the gettering time is long enough at low temperature for a 525 µm wafer to reach a steady state iron concentration. Thus, if the iron diffusion in the boron layer (B-Si precipitate layer) is much slower than the in phosphorus layer, the time might be insufficiently short, but this is at least partly compensated by the slightly higher segregation coefficient in the case of PDG. At the moment we are unable to separate the effect of wafer thickness from the possible effect of oxygen to the formation of B-Si precipitates and to iron gettering.

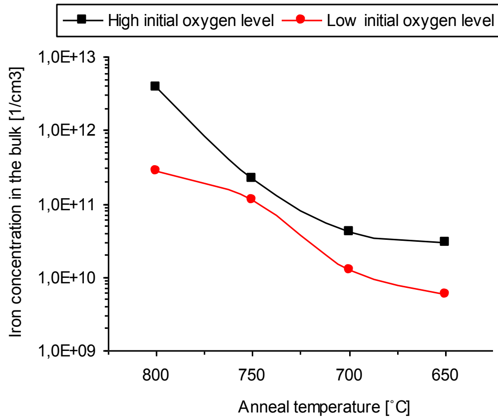

Fig. 2. Iron concentrations in the bulk obtained from the SPV measurements of boron diffusion gettered wafers with different low temperature anneals.

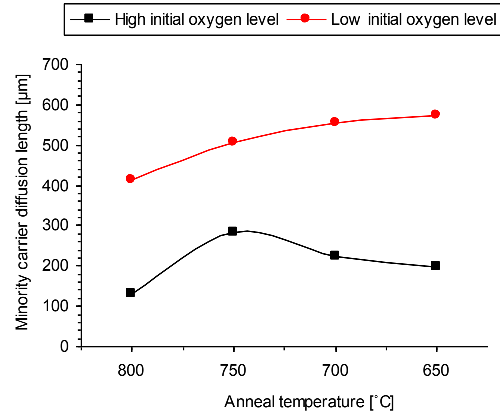

Fig. 3. Minority carrier diffusion lengths obtained from the SPV measurements of boron diffusion gettered wafers with different low temperature anneals.

Minority carrier diffusion lengths obtained from the SPV measurements of boron diffusion gettered wafers with different low temperature anneals are presented in Fig. 3. As can be seen, there is a tremendous difference in the minority carrier diffusion lengths of boron diffusion gettered wafers with low and high initial oxygen levels; the diffusion lengths in the low oxygen level wafers are 2 to 4 times longer. The explanation for this is the higher gettering efficiency obtained in the case of low oxygen wafers at 800 ºC. The trend of the minority carrier diffusion lengths as a function of anneal temperature is also different between the wafer series. In wafers with low oxygen content, the diffusion lengths get longer when the anneal temperature drops and the gettering efficiency increases, but in wafers with high oxygen content, the diffusion lengths start to decrease in anneal temperatures lower than 750˚C. This difference in the trends of the diffusion lengths at low temperatures between wafers with high and low initial oxygen concentrations can be explained by oxygen precipitation which naturally is stronger in high oxygen level wafers. As the anneal temperature is lowered, more and more oxygen precipitates are formed. These oxygen precipitates act as effective recombination centers and thus the minority carrier diffusion length decreases in spite of the more efficient gettering of iron.

Effect of oxygen in low temperature phosphorus diffusion gettering. Minority carrier diffusion lengths obtained from the SPV measurements of phosphorus diffusion gettered wafers with different low temperature anneals are presented in Fig. 4. As can be noticed, in the wafers with high initial oxygen levels, the diffusion lengths seem to decrease at low temperatures, whereas in the wafers with low initial oxygen levels, the diffusion lengths do not seem to decrease but instead continue increasing at low temperatures due to more efficient gettering of iron. As in the case of BDG, this difference in the trends of the diffusion lengths at low temperatures between wafers with high and low initial oxygen concentrations can be explained by oxygen precipitation.

The gettering efficiency of iron is independent of the initial oxygen level in PDG wafers. The difference in the iron concentrations between the wafer series can be quantitatively explained by differences in phosphorus diffusion time and wafer thickness with model taken from [6]. The activation energy of gettering is in both cases about 2.6 eV, which agrees with the value of 2.4 eV obtained by Nadahara et al. [14]. The difference in gettering efficiency between wafer centre and edge is small. This means that the measured sheet resistances, which varied only slightly between centre and edge, can be used as a figure of merit of gettering efficiency which has great practical influence.

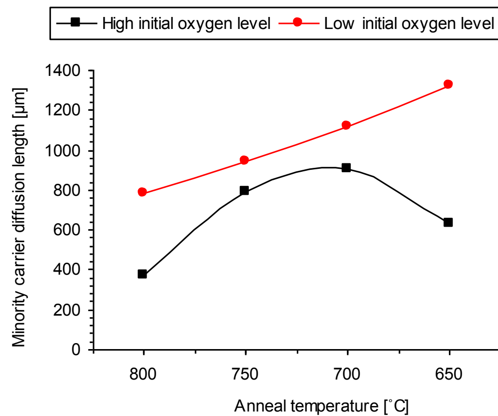

Fig. 4. Minority carrier diffusion lengths obtained from the SPV measurements of phosphorus diffusion gettered wafers with different low temperature anneals.

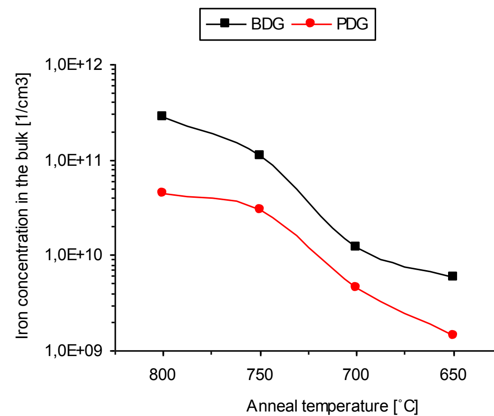

Fig. 5. Iron concentrations in the bulk obtained from the SPV measurements of low oxygen boron and phosphorus diffusion gettered wafers with different low temperature anneals.

BDG vs. PDG. The activation energies of BDG and PDG for iron gettering are quite close to each other and PDG is clearly more efficient (Fig. 5). However, we could speculate that in both cases the gettering is actually related to the formation of an electrically inactive layer; in the case of boron the gettering component is B-Si precipitates and in the case of phosphorus the clusters and P-Si precipitates are responsible for the gettering effect. The difference is that the formation of a gettering layer is faster in the case of PDG than in BDG, which can be attributed to the slower diffusion of boron. Oxygen precipitation in the bulk has a much stronger effect in the case of BDG due to the higher thermal budget needed to obtain a sheet resistance similar to that of PDG.

Conclusions

Oxygen precipitation decreases minority carrier diffusion length after long gettering at low temperatures in both BDG and PDG. In the case of BDG oxygen precipitation affects more as a higher thermal budget is needed to obtain similar sheet resistance to that of PDG. High gettering efficiency at least in the case of BDG seems to be related to an electrically inactive part of doping and the efficiency of BDG can not be concluded from measured sheet resistance. However, the gettering efficiency of PDG can be concluded from the sheet resistance, even though we speculated that the exact gettering mechanism is related to electrically inactive part of doping. This has practical influences in a process control environment.

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