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Enhanced oxidation of thermally grown SiO₂ due to P precipitates

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Abstract

Previous studies of thermal oxidation on a doped structure showed that growth of thermal SiO₂ depends on the charge carrier concentration. Here we show that growth behavior of a thermal SiO₂ layer also depends strongly on the emitter's electrically non-active P concentration. Experimental data show that an increase in P precipitate concentration has a significant influence on the growth kinetics of thermally grown SiO₂ layers. Despite constant charge carrier concentration in the emitter, an increase in growth rate up to a factor of 2 was measured in samples with increased inactive P concentration. Quantitative elemental analysis of the thermally grown SiO₂ layers further shows that the SiO₂ composition can be strongly influenced by the Si substrate's inactive P concentration.

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1. Introduction

Thermal oxidation of Si substrates has been a research field of semiconductor physics for several decades [1]. Today, a variety of different analytical models exists that are able to describe the growth behavior of thermally grown SiO₂ layers. Extended models additionally enable us to take into account the influence of charge carrier concentration on thermal oxidation. Hereby an increase of charge carrier concentration, linked to an increase of electrically active dopant concentration, leads to an enhanced oxidation rate. Beyond this, however, in the current models [2-5] the influence of electrically non-active P concentration on thermal oxidation is not taken into account. As our current study will show, the presence of electrically non-active P at the Si emitter surface and in the Si emitter bulk can cause an increased thermal oxidation rate. This change primarily plays an important role in dielectric passivation of highly doped structures and gettering mechanism in crystalline Si. [6, 7].

2. Experimental details

2.1. Oxidation screening

The present work is divided into three main sections. In the first experiment, a screening was carried out to realize a systematic variation of process parameters during thermal oxidation (design of experiment, DoE). In order to demonstrate the influence of the electrically non-active P concentration on the growth behavior of thermal oxide, two emitter structures were selected as emitter substrates, along with an additional reference group without emitter. For all three studies, we used polished FZ-Si wafers with a base resistivity of 2 and 200 Ωcm , respectively, and a thickness of 200 μm . After wet chemical cleaning, the samples were divided into three groups, whereby these groups differed in concentration of electrically non-active P. Electrically active P concentration was determined by ECV (electrochemical capacitance voltage profiling) while total P concentration was measured by SIMS (secondary ion mass spectrometry). The concentration of electrically non-active P is calculated from the difference between SIMS and ECV data. Emitter formation took place in a conventional POCl_3 diffusion tube, whereby reduction of electrically non-active P was achieved through adaptation of process gases during pre-deposition (Table 1 and [6]). After wet chemical removal of the phosphosilicate glass layer, the samples were oxidized in an ultra-clean oxidation furnace. Oxidation temperature and oxidation duration were varied in the range of 800°C to 900°C and 10 min to 100 min. Selection of oxidation parameters was based on a fractional factorial experimental design. After thermal oxidation, the SiO_2 layers were characterized in terms of thickness and layer composition.

2.2. Variation of electrically non-active P by $\text{POCl}_3\text{-N}_2$ gas flow

In the second experiment, a number of emitter structures was selected in which the electrically non-active P concentration was successively lowered by reducing the $\text{POCl}_3\text{-N}_2$ gas flow during the deposition phase. After processing of the emitter structures, all samples were thermally oxidized at 900°C for 45 min and characterized by ellipsometry, ICP-OES (inductively coupled plasma – optical emission spectroscopy) and GD (glow discharge)-OES. The focus of characterization is to determine the SiO_2 layer thickness and the analysis of the P concentration in the SiO_2 layer as a function of the investigated emitter substrates.

2.3. Variation of electrically non-active P by emitter etch-back

The third experiment was used for final verification of the observed effect that the properties of the thermal oxide are significantly affected by the concentration of the electrically non-active P. In order to reduce the concentration of the electrically non-active P, the emitter etch-back (EEB) process was used [8, 9]. The reference emitter is highly P doped with a pronounced plateau depth of >100 nm. After POCl_3 diffusion, the emitter was etched back stepwise using a wet chemical procedure. Using an acidic etching solution, a homogeneous porous Si layer was formed and removed, and the P concentration of the emitter was reduced.

3. Results

3.1. Oxidation screening

The first part of the experiment is intended to show correlations between characteristics of highly doped emitters and the thermal SiO_2 layer. The here employed two emitter structures differ strongly in concentration of electrically non-active P on the emitter surface and in the surface-near emitter volume. The change of electrically non-active P was realized by variation of the $\text{POCl}_3\text{-N}_2$ gas flow during the POCl_3 diffusion process as already investigated in previous work [6]. The maximum concentration of electrically active and total P was measured by ECV and SIMS and is shown in Table 1.

Table 1: Comparison of max. electrically active and total P concentration of investigated emitters in the oxidation screening experiment.

Emitter structure	Max. electrically active P-concentration [10^{20} cm^{-3}] ECV	Max. total P-concentration [10^{20} cm^{-3}] SIMS
Weakly P-precipitated emitter	3.3	6.8
Strongly P-precipitated emitter	3.3	12.1

Fig. 1 (left) shows SiO_2 layer thicknesses after carrying out thermal oxidation, measured using ellipsometry. Here we clearly see that independently of the set oxidation parameters, SiO_2 layers are significantly thicker for the emitter with higher concentration of electrically inactive P (red) compared to the emitter with lower amount of electrically inactive P (blue). The gain factor of the SiO_2 layer thickness (defined as red bar divided by blue bar) is always >1 with all thermal oxidations carried out, and in the maximal case reaches a factor >2 .

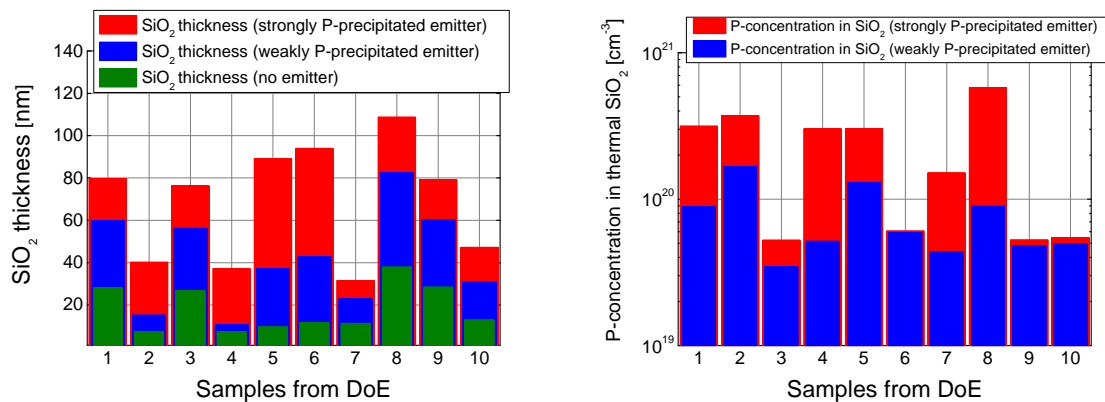


Fig. 1. Left: SiO_2 layer thicknesses on different emitters and on a reference without emitter. Right: P concentration in the thermal SiO_2 layers determined by ICP-OES.

In order to show whether the P precipitate-containing emitter influences the composition of the SiO_2 layer, the layer was wet-chemically removed after the oxidation process and the liquid was analyzed using ICP-OES (Fig. 1 (right)). As is clearly apparent, with all samples, independently of the oxidation parameters, a large quantity of P was found in the SiO_2 layer. This indicates that the existence of the electrically non-active P on the emitter surface leads to a change in the SiO_2 layer composition.

3.2. Variation of electrically non-active P by $\text{POCl}_3\text{-N}_2$ gas flow

The correlation between growth behavior of the thermal SiO_2 layer and concentration of the electrically non-active P was investigated independently in the following two experiments. First, the reduction of the electrically non-active P was achieved by reducing the $\text{POCl}_3\text{-N}_2$ gas flow during diffusion. After processing the homogeneous emitter structures, the samples were thermally oxidized and the SiO_2 layers were analyzed. In parallel, the variation of the P concentrations after the oxidation process is also studied. Fig 2 (left) shows that the activation of the electrically non-active P by the oxidation process occurred at emitter structures, which were processed with $\text{POCl}_3\text{-N}_2$ gas flows above 350 sccm. Thereby we can assume that for higher flows, the maximal electrically active P concentration before oxidation is constant, whereas the concentration of the electrically non-active P steadily increases with increasing $\text{POCl}_3\text{-N}_2$ gas flow.

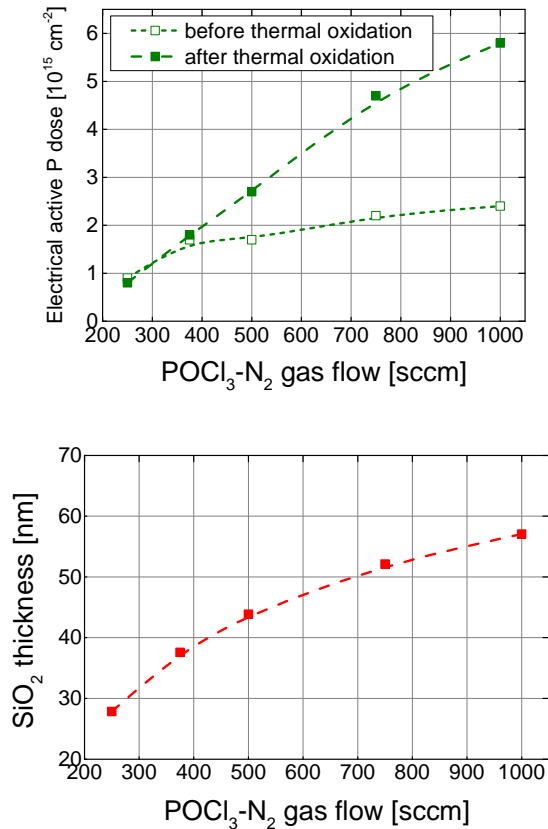


Fig. 2. Green: influence of the thermal oxidation on electrically active P concentration (measured by ECV) of selected emitter structures. Red: SiO₂ thickness measured by ellipsometry as a function of the POCl₃-N₂ gas flow. The variation of the electrical non-active P was realized by variation of the POCl₃-N₂ gas flow during pre-deposition as already presented in [6].

Fig 2 shows a significant increase of the SiO₂ thickness as a function of POCl₃-N₂ gas flow. As shown in previous investigations, a variation of the POCl₃-N₂ gas flow during pre-deposition primarily influences the concentration of the electrically non-active P of an emitter [6]. Here we can conclude that the growth rate of the thermal SiO₂ layer is also a function of the electrically non-active P of the as-diffused emitter. In order to investigate the influence of the electrically non-active P on the SiO₂ layer, in the next step GD-OES measurements are presented.

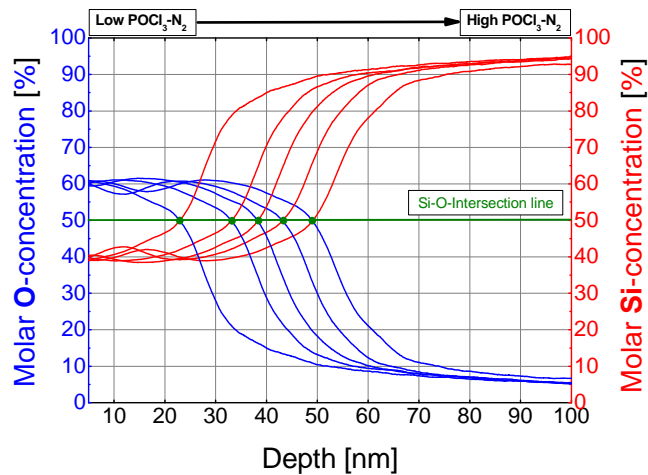


Fig. 3. Molar O and Si concentration profiles of SiO₂ layers measured by GD-OES. The variation of electrically non-active P was realized by variation of the POCl₃-N₂ gas flow during pre-deposition. Thermal oxidation was carried out on all samples at 900°C for 45min.

Molar concentrations of O and Si in the SiO₂ layer by means of GD-OES can be seen in Fig. 3. We see very clearly that the existence of the electrically non-active P in the as-diffused emitter immediately influences the course of the O and Si concentration in the SiO₂ layer. If we compare the SiO₂ layer thickness measured using ellipsometry in Fig. 2 (right) with the Si-O intersection points of the GD-OES measurement, there appears to be shifted in a range of 5 nm to 8 nm. The intersection points characterize a molar distribution of Si and O in a relationship of 1:1, which supports the assumption of the existence of a thin oxide layer containing P close to the Si interface. We assume that the shift between Si-O intersection points and the ellipsometry data is caused by the mentioned thin oxide layer. Fig. 4 shows the course of the P and O concentration in the thermally grown SiO₂ layer.

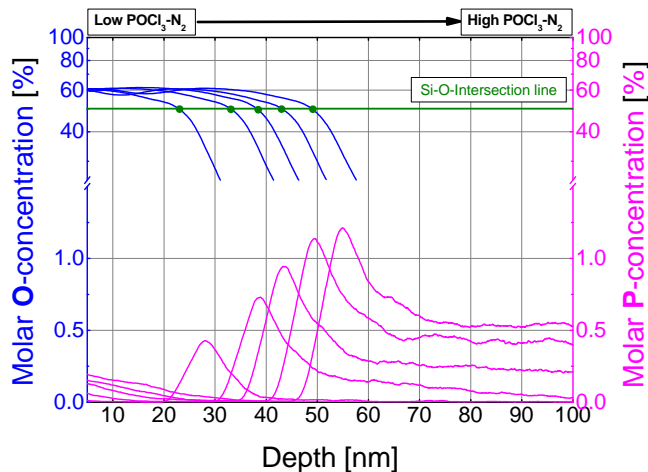


Fig. 4. Molar O and P concentration profiles of SiO₂ layers measured by GD-OES. The variation of electrically non-active P was realized by variation of the POCl₃-N₂ gas flow during pre-deposition.

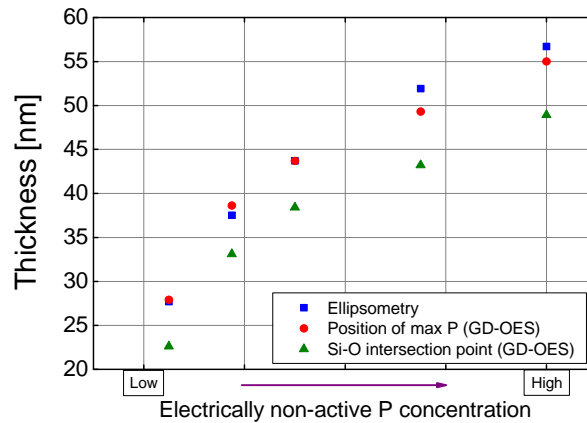


Fig. 5. Thermal oxide layer thicknesses measured with ellipsometry and extracted from GD-OES analysis.

In Fig 5 thicknesses of thermal oxide layers are illustrated. First of all the increase of the electrically non-active P leads to an increase of the thermal oxide layer as mentioned before. Here thermal oxide thicknesses are illustrated using different analysis methods such as ellipsometry and GD-OES. The ellipsometry data seem to match quite good with the position of the max. P measured with GD-OES. However, the position of the Si-O intersection points differ to the ellipsometry data in a range between 5 nm in case of weakly P-precipitated emitter and 8 nm in case of strongly P-precipitated emitter.

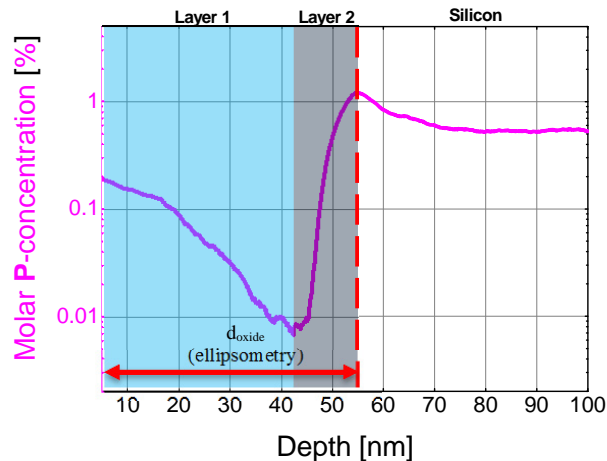


Fig. 6. Thermal oxide on a strongly P-precipitated emitter as a bilayer system.

The thickness of the SiO_2 layer is strongly correlated with the electrically non-active P concentration of the emitter which is adjusted by variation of the $\text{POCl}_3\text{-N}_2$ gas flow during the POCl_3 diffusion process. In Fig. 6 two regions of the thermal oxide layer are illustrated. The left side of the P concentration profile can be related to a standard SiO_2 layer with a gradient of molar P concentration within this layer. The molar P concentration in this layer (Layer 1) is in the range of 0.19% to 0.007%, corresponding to P concentrations of $9.5 \cdot 10^{19} \text{ cm}^{-3}$ to $3.5 \cdot 10^{18} \text{ cm}^{-3}$. In the next layer (Layer 2) the molar P concentration increases from 0.007% to 1.24%, corresponding to P

concentrations of $3.5 \cdot 10^{18} \text{ cm}^{-3}$ to $6.2 \cdot 10^{20} \text{ cm}^{-3}$. In case of the Layer 2 it is assumed that a SiO_x layer exists which at least partly includes a high amount of P. Taking into account that the ratio of the minimal and maximal molar P concentration in the oxide is about 100, the strong accumulation of P at the Si surface can not only be linked to segregation. The well-known segregation coefficient of P in Si/SiO₂ is about 10 [10]. The profile of the P-concentration in Layer 2 is similar to ToF-SIMS measurements of highly doped PSG layers [11]. This indicates that a thermal oxidation on a strongly P-precipitated emitter leads to a bilayer which contains a huge amount of P close to the SiO_x/Si interface similar to PSG/Si interfaces.

3.3. Variation of electrically non-active P by emitter etch-back

The last investigation in this study deals, analogous to the experiment presented in section 3.2, with the correlation between the electrically non-active P concentration of the emitter and the layer characteristics of the thermally grown SiO₂ layer. The variation of the electrically non-active P concentration was here realized through a homogenous EEB. Thereby it can be guaranteed that all emitter structures display almost the same electrically active peak P concentration. Here the EEB procedure makes possible a reduction of the electrically non-active P concentration with a constant maximal carrier concentration.

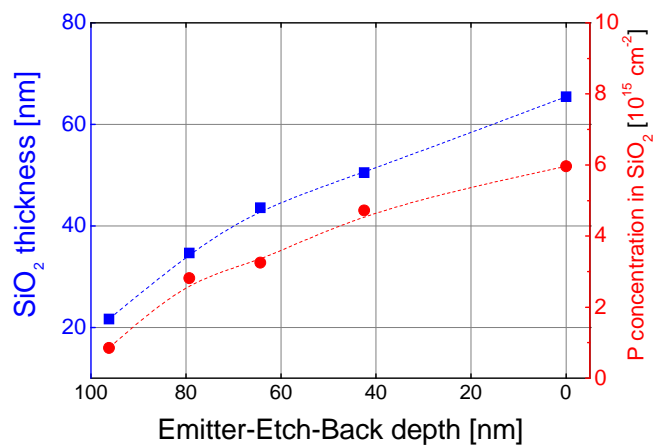


Fig. 7. SiO₂ thickness and P concentration in the SiO₂ layer as a function of EEB depth (measured by ICP-OES). The depth of the EEB indicates the reduction of peak concentration of electrically non-active P.

Fig. 7 shows how strongly the layer characteristics of the SiO₂ layer are influenced by variation of the total P concentration of the emitter using the EEB procedure. From the diagram we can deduce that not only the layer thickness of the SiO₂ layer, but also the measured P concentration in the oxide layer depends significantly on the emitter substrate and steadily decreases with decreasing plateau depth of the emitter. The fact that in the SiO₂ layer a significant concentration of P was measured, and this depends on the P concentration of the emitter, further supports the assumption that a considerable amount of P-O bonds are present close to the interface between the thermal oxide and Si. In order to further support this hypothesis, the following illustrations show, analogous to section 3.2, concentration profiles of O, Si and P in SiO₂ layers measured by GD-OES.

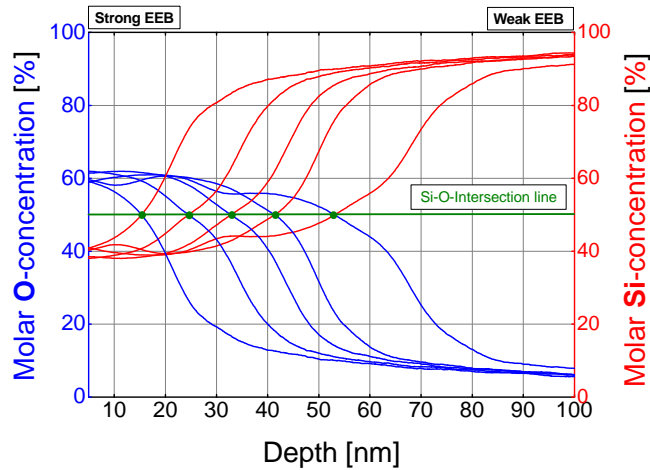


Fig. 8. Molar concentration profiles of O and Si in SiO_2 layers measured by GD-OES. The variation of electrically non-active P was realized by the wet-chemical EEB process.

As was already described in section 3.2, the different emitter structures influence via variable P concentrations the profiles of O and Si in the SiO_2 layer.

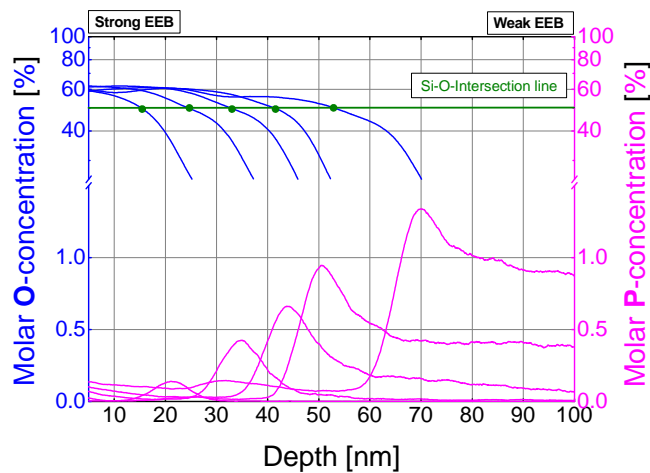


Fig. 9. Molar O and P concentration profiles of SiO_2 layers measured by GD-OES. The variation of electrically non-active P was realized by the wet-chemical EEB process.

The increase of the total P concentration with constant maximal carrier concentration influences not only the profiles of the O concentration in the thermally grown SiO_2 but also the accumulation of P close to the SiO_2/Si interface. Through this investigation, independently of the first experiment in section 3.2, we can support our hypothesis that the existence of electrically non-active P at the emitter surface and in the emitter bulk has a direct influence on the growth behavior and layer composition of the oxide layer. The existence of P-O bonds on the $\text{SiO}_2\text{-Si}$ interface might play a significant role in the dielectric passivation of emitter structures and will continue to be a topic of future investigations.

4. Conclusion

In this study we showed that the oxidation rate of a thermally grown SiO₂ layer on a heavily doped emitter not only depends on carrier concentration. Rather the concentration of electrically non-active P, like in form of P precipitates, plays a significant role in case of the increased oxidation growth rate. Based on ICP-OES, analysis we propose the existence of P-O bonds in SiO₂ layer. Because of that the SiO₂ layer on a highly doped emitter cannot be regarded as a uniform layer. Depth resolved element profiling using GD-OES gave us more detailed information about layer composition of the investigated SiO₂. The shift between intersection points of Si and O concentrations in the thermally grown SiO₂ layer and the position of maximum P concentration in SiO₂ layer highlight our hypothesis of a SiO₂ bilayer system.

Acknowledgements

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