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New method for determination of electrically inactive phosphorus in n-type emitters

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Abstract

The precise knowledge of the amount and the location in depth of inactive phosphorus in an n-type emitter is still a challenge. As a new approach, we determine the total amount of phosphorus (P dose) in the emitter stepwise in dependence of etching depth with the characterization tool ICP-OES. A comparison of the data with the electrically active P concentration profile measured by ECV allows to determine in which depths electrically inactive phosphorus is present. For a highly doped emitter, we show that most of the inactive P dose is located next to the sample surface. Furthermore, we compare the determined P dose in dependence of depth with the P dose extracted from a SIMS profile. In a second experiment, we investigate the amount of inactive phosphorus in the whole emitter for various n-type emitters, depending on the $POCl_3$-N_2 gas flow as a significant diffusion parameter. It is shown that an increase of the $POCl_3$-N_2 gas flow results in a saturation effect of the active phosphorus, while the amount of inactive phosphorus is strongly increasing.

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Keywords: electrically inactive phosphorus; dead layer; P dose; n-type emitter; ICP-OES; ECV; SIMS

1. Introduction

A homogenous n-type emitter is most commonly formed by $POCl_3$ diffusion. During the diffusion process PhosphoSilicate Glass (PSG) grows on the silicon wafer and acts as dopant source. Because of the solubility limit of phosphorus in crystalline silicon, highly doped emitters have normally a so-called dead layer next to the surface.

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This electrically inactive phosphorus acts as recombination center and increases emitter saturation current density [1]. The amount and the location of the inactive phosphorus is of great interest to understand phosphorus precipitate formation. Standard analytical methods currently applied are Secondary Ion Mass Spectrometry (SIMS) for the total phosphorus concentration profile or an Electrochemical Capacitance-Voltage profiler (ECV) [2] for an electrically active P concentration profile. However, the comparison of ECV and SIMS profiles and therefore the detection of the location in depth of inactive phosphorus is often difficult [3]. In this study, we used the wet-chemical emitter etch-back procedure to remove the emitter stepwise [4] and analyze the etch solution with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [5] to determine the total amount of phosphorus per unit area (P dose) in the emitter. With this analytical method sputtering effects are avoided, which are part of SIMS measurements. On the other hand, the electrically active P dose of the emitter was measured by ECV. The knowledge of the total and the active P dose finally allows the determination of the inactive P dose.

2. Method and experimental details

2.1. Determination of the P dose in the whole emitter

The base material is p-type, 5x5 cm^2 Czochralski silicon wafers with a bulk resistivity of 2 Ωcm. The wafers are wet chemically cleaned before the $POCl_3$ diffusion process. Different types of the emitters have been created by changing the $POCl_3$-N_2 gas flow Φ_{POCl3} as a significant diffusion parameter. Afterwards, the PSG is removed in lowly concentrated hydrofluoric acid. Finally, the *whole* emitter is removed (2 µm per wafer side) in an etching solution of hydrofluoric and nitric acid. This etching solution of a defined volume is investigated by ICP-OES to determine the total amount of phosphorus Q_{total} within the whole emitter (m_P: mass of phosphorus in the total etching solution, A: surface area of the etched wafer (both sides), N_A: Avogadro constant, M_P: molar mass):

$$Q_{total} = \frac{m_P}{A}\frac{N_A}{M_P} \tag{1}$$

On the other hand, the same unetched emitters have been measured by ECV to determine an active doping profile. The integration of the ECV profile yields the active P dose Q_{active} of the whole emitter (C: phosphorus concentration, x: depth, compare Fig. 1):

$$Q_{active} = \int_0^\infty C(x)dx \tag{2}$$

The difference in the emitter P dose determined by ICP-OES (Q_{total}) and ECV (Q_{active}) indicates the electrically inactive phosphorus dose ($Q_{inactive}$). Furthermore, we compare the Q_{total} determined by ICP-OES with the Q_{total} extracted from SIMS profiles [6] of the same emitters using equation (2), (see Fig. 2, left).

2.2. Determination of the P dose stepwise for one emitter-type

The samples are prepared, as described in the first part, using just one emitter type (Φ_{POCl3}=const.). In contrast to the first investigation, the emitter is only partly removed. The challenge was to find the right etching solution, with low etching rate, high homogeneity and suitable background signal for the ICP-OES measurement (see e.g. the problem with carbonate [7] based acid). As the etched area is necessary to be known for the calculation of Q_{total} (see equation (1)), it is also important that no porous silicon is formed durig etching. We successfully found an etching solution with an etching rate of 0.5 nm/s. For the stepwise analysis of the P dose, several samples with the same emitter profile have been etched down to different depths. Each etching solution is analyzed by ICP-OES. To determine the *total* P dose of the remaining emitter profile $\Delta Q_{total,\ unetched}$, the P dose $Q_{total,\ etched}$ is subtracted from the *total* P dose of the *whole* emitter depth Q_{total} (compare Fig. 1). The active P dose $Q_{active,\ unetched}$ of the remaining emitter profile is determined by ECV. The etching depth is determined by comparing the depths values at a defined

P concentration of 10^{20} cm^{-3} (or maximum if less) of each profile with the original profile (42 Ω/□), see Fig. 3 (right). For comparison, we also determine the $Q_{total,\ unetched}$ of the SIMS profile, using the etching depth as lower integration limit for equation (2) (see Fig. 4). The sheet resistance (R_{Sheet}) of the remaining emitters is measured by a Four-Point-Prober (4PP).

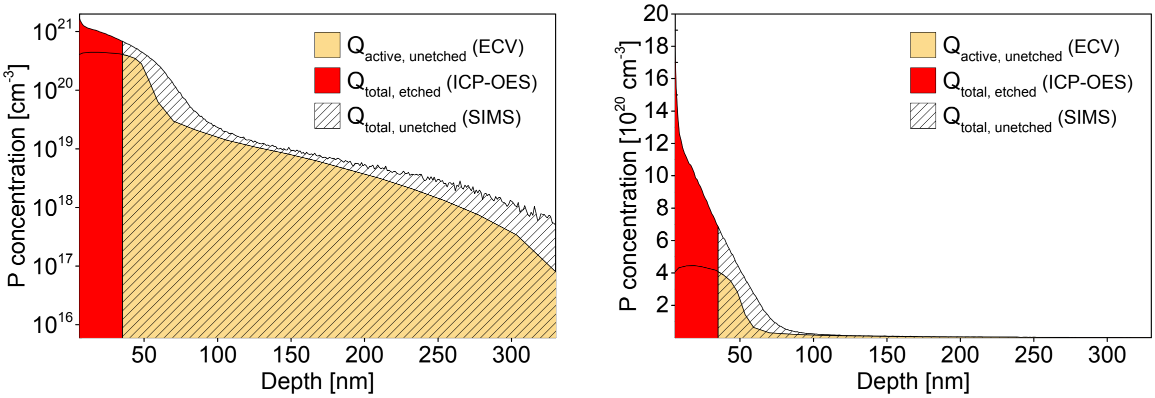

Fig. 1. Typical n-type emitter profile for the total (SIMS measurement) and the electrically active phosphor concentration (ECV measurement). The area under the ECV curve indicates the active P Dose, while the area under the SIMS curve indicates the total P dose. The removed emitter part is analyzed with ICP-OES to determine $Q_{total,\ etched}$ and should be identical with the removed area of the SIMS profile. The left graph shows the usual logarithmic scaling for the concentration, while the right graph shows the linear scaling.

3. Results and discussion

3.1. Determination of the P dose in the whole emitter

The P dose in the whole depth of the emitter in dependence of the $POCl_3$-N_2 gas flow diffusion parameter is shown in Fig. 2 (left). The total P dose is measured by ICP-OES, while the electrically active P dose is determined by the ECV profiles (see Fig. 2, right) of the unetched wafers. The total P doses of emitters created with $POCl_3$-N_2 gas flows of 250 sccm, 375 sccm, 500 sccm and 750 sccm are additionally determined by SIMS profiles. The Q_{total} determined by ICP-OES is in good agreement with the Q_{total} extracted from SIMS profiles.

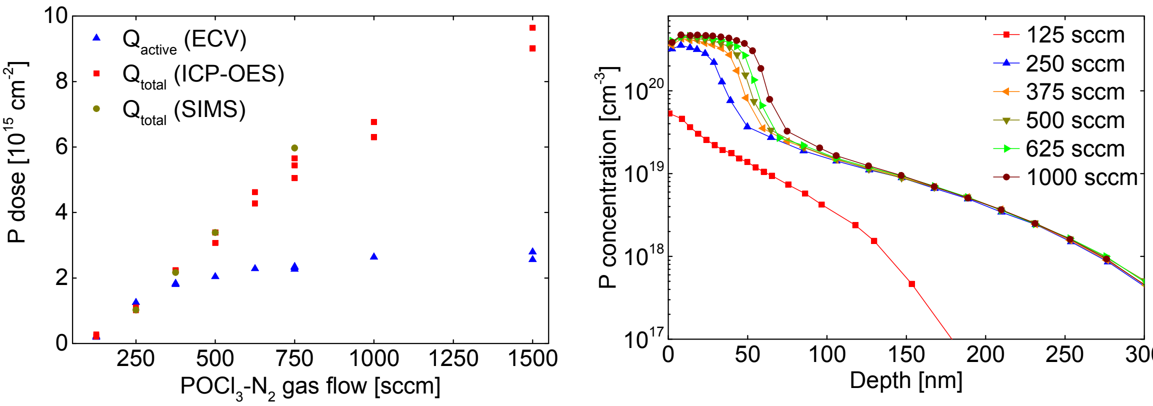

Fig. 2. P dose in the whole emitter in dependence of the $POCl_3$-N_2 gas flow (left graph). To make sure the whole emitter is etched, at least 2 µm per side have been removed from the silicon wafer. The total P dose is measured by ICP-OES, while the electrically active P dose is determined by the ECV profile (right graph) of the unetched wafer. In addition, the total P dose is also extracted from SIMS profiles.

For low $POCl_3$-N_2 gas flows of 125 sccm and 250 sccm the P dose determined by ECV and ICP-OES is similar, which means that there is low density of inactive phosphorus. For a higher gas flow, the difference between the P dose determined by ECV and ICP-OES increases, which means that the amount of electrically inactive phosphorus is increasing. At Φ_{POCl3}=625 sccm only half of the total phosphorus is electrically active. Q_{active} saturates at a value of $2.3 \cdot 10^{15}$ cm^{-2}.

3.2. Determination of the P dose stepwise for one emitter type

The total and the active P dose of a stepwise etched-back emitter (unetched 42 Ω/□, see Fig. 2: Φ_{POCl3}=750 sccm) in dependence of the etching depth is shown in Fig. 3 (left). After each etching step, R_{Sheet} and the ECV profile (see Fig. 3 right) were measured. Most of the inactive phosphorus is located next to the surface. With increasing etching depth, the total amount of phosphorus atoms approaches the number of active phosphorous atoms. The slope of the P dose function gives the P concentration. In Fig. 4, the total P dose extracted from the SIMS profile is also shown. SIMS and ICP-OES measurement show the same trend for the total P dose.

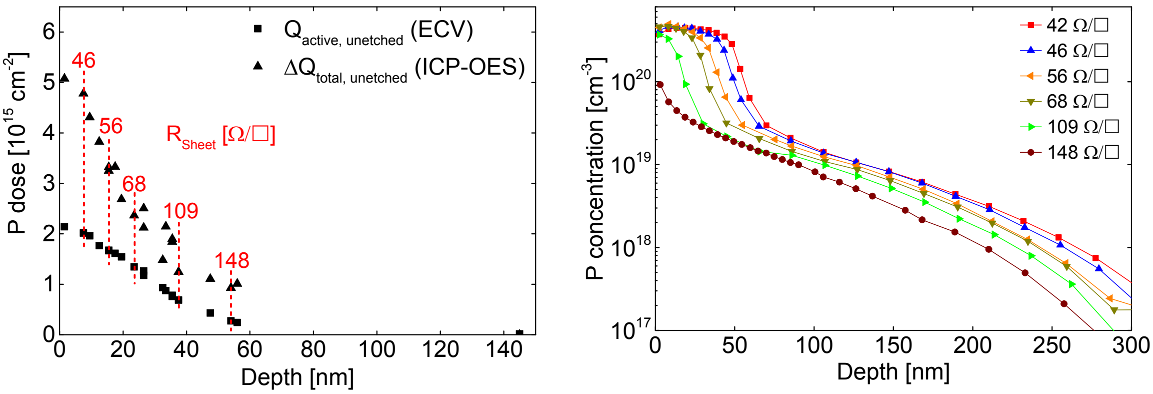

Fig. 3. P dose of a stepwise etched emitter (42 Ω/□). To determine the total P dose of the remaining emitter, the measured P dose is subtracted from the total P dose of the whole emitter. The remaining emitters are measured by ECV to determine the active P dose. The ECV profiles (right graph) are indicated by the corresponding R_{Sheet} in the left graph. The etching depth is determined by the ECV profiles. Therefore, the plateau at a defined P concentration of 10^{20} cm^{-3} (or maximum if less) is extracted for each profile and subtracted from the depth of the original profile (42 Ω/□).

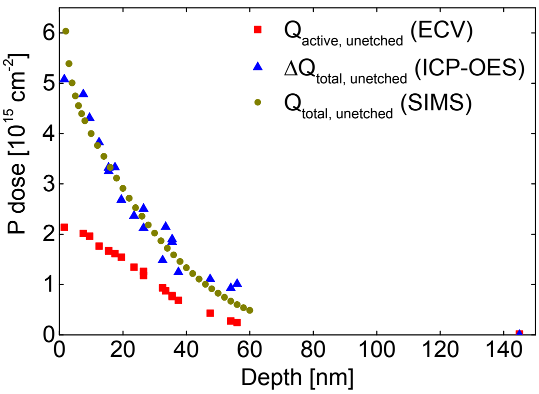

Fig. 4. P dose of a stepwise etched emitter, as in Fig. 3 left. Additionally, we determined the total P dose of the SIMS profile, using the etching depth as lower integration limit for equation (2).

Further experiments can be improved by determining the etching depth not by ECV, but by the etching rate (0.5 nm/s). In this case, only one ECV profile of the reference emitter is needed. The active P dose depending on the depth can be calculated by using the etching depth as lower integration limit for equation (2) (as already demonstrated for the SIMS measurement). Furthermore, only one sample is needed for the ICP-OES measurement: After each etching step, the etching solution is decanted and the sample is used for the next etching step.

4. Conclusion

In the first experiment, we investigated the amount of electrically inactive phosphorus in the emitter systematically in dependence of the $POCl_3$-N_2 gas flow. We showed that the electrically active P dose saturates for high $POCl_3$-N_2 gas flows, while the total P dose is continuously increasing. This successfully demonstrated method can help to optimize $POCl_3$ diffusion parameters by keeping the active P dose constant and minimize the inactive P dose, e.g. by performing a design of experiment.

In the second experiment, we successfully determined the inactive P dose depending on the emitter depth. We showed that most of the inactive phosphorus is located next to the surface. This is already considered in solar cell production to improve the electrical performance of a crystalline silicon solar cell [4]. Our new method allows to quantify the removed inactive phosphorus and to optimize the etching depth for different emitter types.

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