Presented at the 26th European PV Solar Energy Conference and Exhibition, 5-9 September 2011, Hamburg, Germany

PLASMA DEPOSITION OF AMORPHOUS SILICON DOPANT SOURCES

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ABSTRACT: The basic idea of a dry solar cell process is to minimize the application of wet chemical process steps. By using plasma-enhanced chemical processes, many steps can be converted from wet chemical to dry plasma processes. In previous studies it could be demonstrated, that it is possible to deposit a phosphorus silicate glass (PSG) via plasma-enhanced chemical vapor deposition (PECVD) processes and to use these layers for emitter diffusion in a high-temperature furnace. In order to enable the removal of the dopant source combined with an etch back of the highly phosphorus containing top layer of the emitter (so called “dead layer”) within a single plasma etch step, the use of doped amorphous silicon as dopant source has been investigated throughout this study. To the knowledge of the authors, the application of a-Si as dopant source prior to high temperature diffusion is almost unexplored; therefore the paper investigates the suitability of this approach for industrial solar cell processing. As shown, doped a-Si layers offer a diffusion of phosphorus as well as boron, but an oxidation of the layer while the high temperature diffusion could not be avoided straightforwardly.

Keywords: amorphous silicon, a-Si, Deposition, Diffusion, Doping, PECVD

1 INTRODUCTION

The formation of a pn junction is crucial in a crystalline silicon solar cell process. The standard process to create a n-doped region on a p-doped substrate is the diffusion in a quartz tube furnace using a phosphoryl chloride ($POCl_3$) –containing atmosphere. The resulting dopant source layer on the silicon wafer surface is phosphorus silicate glass (PSG). In previous studies it could be demonstrated, that it is possible to deposit a PSG via PECVD processes [1]. The removing of PSG can be realized in a plasma process, too, by using a dry CF_4 plasma etch process [2]. Using this carbon containing plasma chemistry in a proper composition a good etch selectivity between PSG and c-Si could be realized. However, there are several drawbacks of this process. CF_4 is a gas with a high global warming potential (GWP). Further carbonic residues causing the good selectivity has to be removed in a further step. To avoid the GWP as well as the residues etching in pure fluorine would be advantageous. But a silicon dioxide is very hard to etch only with fluorine plasma.

The new approach is an a-Si dopant source, which could be easily removed in fluorine plasma. Further etching in the same process will improve the emitter by etching the recombination-active high surface concentration of the emitter (dead layer) [3]. By adding this step in the same vacuum chamber as the anti-reflective coating it could be also implemented very cost-effectively in an industrial cell process (see Figure 1). One major challenge of this approach is the avoidance of an oxidation of the amorphous layer structure during the diffusion, to perform the followed combined etch back step of the dopant source and the “dead layer”. Because this oxidation previously could not be prevented, in this publication only the coating process and the diffusion are treated. In Figure 1 the desired process is shown. The $POCl_3$ batch diffusion is replaced by two inline steps;

- PECVD deposition of a-Si:P dopant source
- Inline diffusion for creation of the emitter

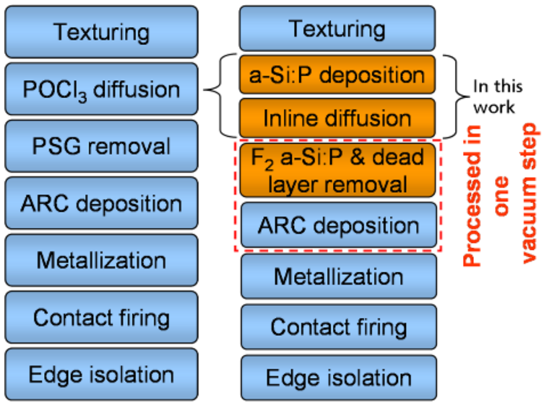

Figure 1: Possible process series to achieve a single-sided emitter with etched-back “dead layer” by adding only one process step to a standard cell production process (left). The edge isolation can potentially be omitted.

2 EXPERIMENTAL

First experiments are performed to develop a PECVD process for an a-Si:P dopant source, which leads to sufficient dopant incorporation enabling a homogenous emitter sheet resistance (R_{sh}) after diffusion. Alkalinely textured 125 x 125 mm^2 Czochralski (Cz) silicon wafers with a specific resistance of 1-3 Ω cm (p-type) were used as substrate material. The saw damage was removed during the texturisation process. To determine thickness and composition, the a-Si:P films were also deposited on shiny-etched float zone (FZ) silicon with a specific resistance of 10 Ω cm (p-type) with a <100> surface crystal orientation and characterized by spectroscopic ellipsometry and Fourier transformed infrared (FTIR) spectroscopy. For the fit of the ellipsometric values Ψ and Δ a Cody-Lorentz oscillator model by Ferlauto et al. [4] was used. a-Si:B layers were also deposited on 125 x 125 mm^2 FZ silicon wafers with a specific resistance of 0.8-1.2 Ω cm (n-type).

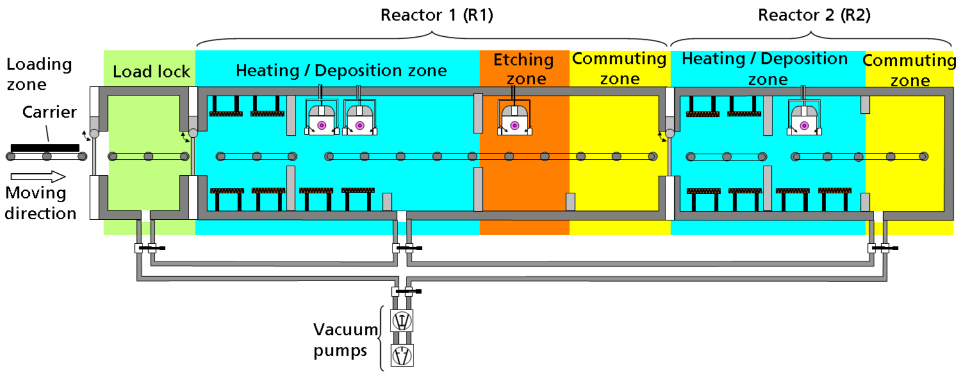

Figure 2: Schematic illustration of the industrial semi-inline microwave plasma tool.

For the plasma deposition of the a-Si dopant sources an industrial-type inline plasma tool (Roth&Rau, see Figure 2) was used applying a microwave plasma (microwave frequency: 2.45 GHz) to a gas flow of silane (SiH_4), phosphine (PH_3 for phosphorus doped amorphous silicon a-Si:P), and diborane (B_2H_6 for boron doped amorphous silicon a-Si:B), respectively. Phosphine was strongly diluted in hydrogen (0.25% [PH_3] in [H_2]), the same holds for diborane (1% [B_2H_6] in [H_2]). The gas ratio r is defined as the amount of pure [PH_3]/[SiH_4], respectively [B_2H_6]/[SiH_4]. The diffusion is realized in an inline furnace in which the a-Si-coated wafers pass through a high-temperature zone. The plateau temperature for phosphorus doped a-Si (a-Si:P) is 910°C, and 940°C for boron doped a-Si (a-Si:B). The plateau time is 25 minutes for both diffusion processes. A nitrogen atmosphere was applied during the diffusion to prevent an oxidation of the a-Si layers. Prior to the a-Si deposition, the textured wafers were cleaned in a HNO_3/HF bath sequence. The process flow is shown in Figure 3.

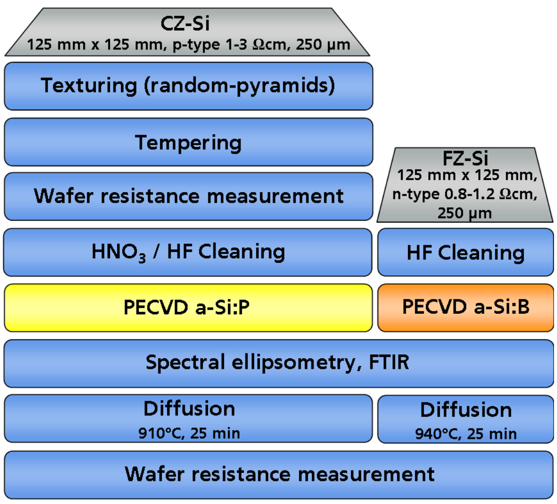

Figure 3: Process flow for wafer treatment before and after dopant source deposition and diffusion

3 RESULTS

Measurement of the a-Si dopant source after deposition by spectral ellipsometry reveals a thickness of 195 ± 6 nm (± 3.1%) (absolute deviation over 49 measurement points distributed over a 60 x 60 mm^2 shiny-etched FZ wafer). The deposition homogeneity over the plasma length of around 90 cm is shown in Figure 4. Here six samples were distributed over the plasma length and were coated with a-Si:P and measured by spectral ellipsometry. The deposition parameters are shown in Table I.

Table I: Process parameter for the evaluation of the deposition homogeneity of a-Si:P (see Figure 4): effective MW power P_{MW}, process pressure p and ratio of PH_3 and SiH_4 r.

Process	P_{MW} (W/cm^2)	r	p (µbar)
A	1.1	1/26	200
B	0.9	1/20	150
C	1.1	1/20	150
D	0.9	1/20	200

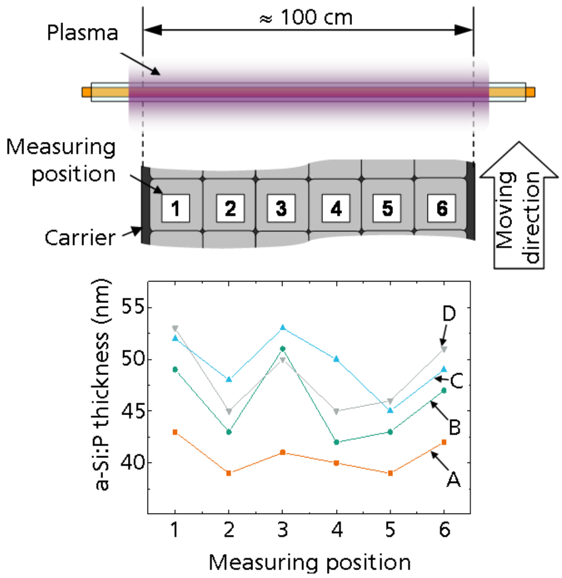

Figure 4: Homogeneity of a-Si:P deposition over carrier width.

Process A shows the best homogeneity of around 4% relative deviation of a-Si:P thickness over the carrier. Process B has the worst homogeneity with a deviation of 8% over the plasma width. It can be said, that a higher microwave power (P_{MW}) and a higher pressure (p) is advantageous for the homogeneity of the a-Si:P deposition. The better homogeneity with higher power can be explained by a homogeneous plasma density over the entire length of the linear plasma source.

It was found that an increase of phosphine gas flow leads to a reduction of R_{sh} and reciprocal to a linear increase of the conductivity (Figure 5) (R_{sh}^{-1}). This indicates that the adsorption capacity of a-Si for phosphorus has not been reached.

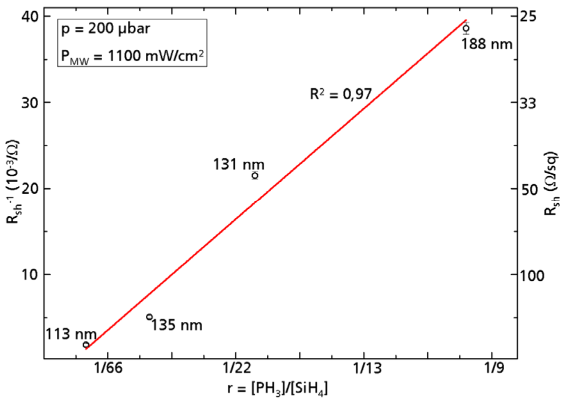

Figure 5: Emitter sheet conductivity $(R_{sh})^{-1}$ in dependence of the gas flow ratio r on textured CZ silicon wafers (ρ=1-3 Ωcm, p-type) measured by inductive coil method. The a-Si:P thicknesses after deposition are written next to the symbols.

Using an inductive coil resistivity measurement tool it could be shown, that it is possible to diffuse a homogeneous emitter with a sheet resistance R_{sh} down to 26 ± 1.2 Ω/sq (absolute deviation over 54 measurement points distributed over a 125 x 125 mm^2 pseudo-square wafer). Figure 6 shows a spatially resolved R_{sh} map of this wafer measured by 4-point probe method.

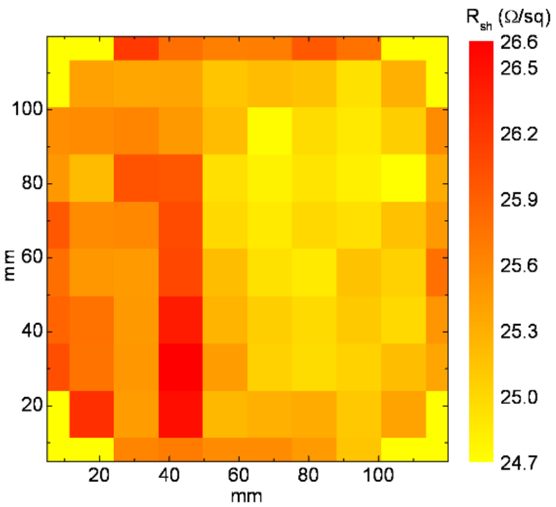

Figure 6: Emitter sheet resistance (R_{sh}) on a textured CZ silicon wafers (ρ = 1-3 Ωcm, p-type) for a gas flow ratio of r = $[PH_3]/[SiH_4]$ = 1/10, measured by 4-point probe method

A variation of the dopant source thickness is shown in Figure 7. What we see here is a decrease of the diffused emitter sheet resistance depending on the thickness. This behavior can be explained by an exhaustible source of dopants [5] at low a-Si thicknesses.

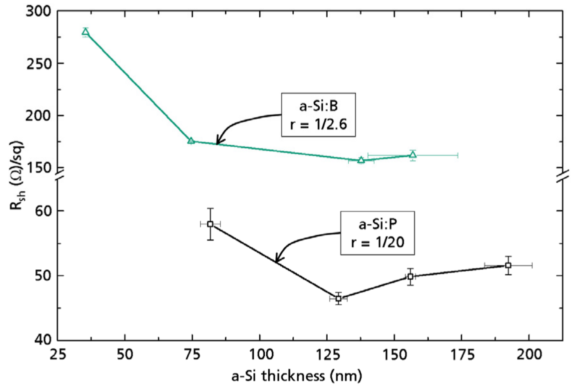

Figure 7: Emitter sheet resistance (R_{sh}) diffused at 910°C (a-Si:P) and 940°C (a-Si:B), respectively, for 25 min for different dopant source thicknesses

The minimum of the resistance for phosphorus-doped silicon at a-Si:P thicknesses of around 125 nm can be interpreted by the oxidation of the dopant source during diffusion. The resulting a-SiO_x layer causes a separation of phosphorus at the a-Si/a-SiO_x interface because of the smaller solid solubility of phosphorus in silicon dioxide, which is known as segregation during thermal oxidation [6]. The phosphorus is pressed into the crystalline silicon by the a-SiO_x interface, when the entire a-Si layer is oxidized. As shown by secondary electron microscopy (SEM), the formed a-SiO_x layer is in the range of 100 nm (Figure 8), and thus in the range of the dopant source thickness.

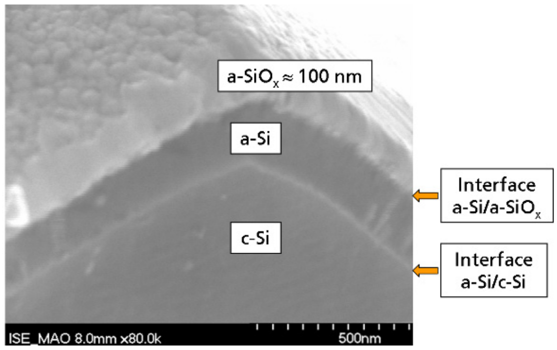

Figure 8: SEM image of an oxidized a-Si:P layer after diffusion

The sheet resistance of boron doped n-type wafers is three times larger than the R_{sh} of phosphorus doped p-type wafers (see Figure 7). The reason for this is the higher solid solubility (C_P) for electrically active phosphorus in silicon, given by the following equation [7], with k = 8.617 eV/K [8] as Boltzmann constant and T as temperature in Kelvin.

$$C_P = 1.8 \cdot 10^{22} \cdot e^{-\frac{0,4eV}{k \cdot T}} (cm^{-3}) \qquad (1)$$

At the given diffusion temperature of 1183 K, the concentration of electrically active phosphorus in silicon results in $3.6 \cdot 10^{20}$ atoms/cm^3. In contrast, the concentration of boron in silicon at 1213 K is $1.3 \cdot 10^{20}$ atoms/cm^3 [9]. From the given diffusion time (t = 1500 s) and the diffusion coefficient for boron at 1213 K ($D_B = 1.9 \cdot 10^{-14}$ cm^2/s [9]) the diffusion length (x_L) can be calculated [5].

$$x_L = 2\sqrt{D_B t} \qquad (2)$$

Using a complementary error function shaped diffusion profile for boron in silicon [9] with this diffusion length and solubility and calculating the corresponding sheet resistance with PC1D [10] results in a sheet resistance of 151 Ω/sq for a boron-doped emitter with a phosphorus background doping density of $5 \cdot 10^{15}$ atoms/cm^3 This is close to the measured minimum value of 157 Ω/sq. The sheet resistance of the boron emitter thus can only be raised by increasing the diffusion temperature and/or the diffusion time. E.g. a temperature of 1273 K and a diffusion time of 1800 s should result in a sheet resistance of less than 45 Ω/sq, simulated by PC1D and the boron-specific diffusion parameters by Vick et al. [9].

In Figure 9 FTIR spectra of as-grown a-Si:P layers deposited in the PECVD reactor 1 (R1) are shown. The FTIR spectra were interpreted here by using the absorption peaks from Pai et al. [11], Bustarret [12], and Tsu et al. [13]. However, these peaks are not clearly assignable to these absorption modes, but obvious at present deposition gases. As can be seen, in the deposited a-Si:P a high amount of oxygen is incorporated. It was found that a higher oxygen concentration in the deposited a-Si:P dopant source has a deteriorating influence on the resulting sheet resistance after diffusion. This may be due to a smaller diffusion constant for phosphorus in oxygen-rich amorphous silicon, since it is known that phosphorus has a lower diffusivity in silicon dioxide [14].

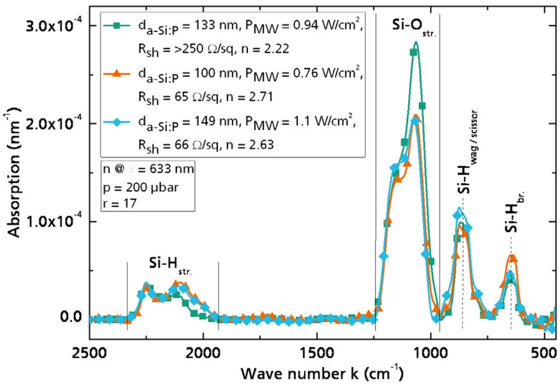

Figure 9: FTIR spectra of a-Si:P deposited in the PECVD reactor 1 (R1, see Figure 2)

In Figure 10 the FTIR spectra of an a-Si:B layer deposited in the PECVD reactor 2 (R2) is shown. The additional B-H absoption peaks are given by Zedlitz et al. [15]. But even here the association with the absorption modes is a matter of interpretation. In contrast to samples that were produced in the reactor 1, the absorption by oxygen compounds is significantly smaller. For the given spectra the Si-O absorption at k = 1070 cm^{-1} is > 2×10^{-4} nm^{-1} in R1 and 1.5×10^{-4} nm^{-1} in R2. Also the disorder-induced shoulder at around 1150 cm^{-1} [11] at the Si-O$_{str}$ absorption peak is not seen in the a-Si:B FTIR spectra. The greater oxygen content in the reactor 1 can be traced back to a higher reactor base pressure, and contamination of the reactor walls, by oxygen-containing processes. Therefore, it is important to pay attention to the conditions during the coating.

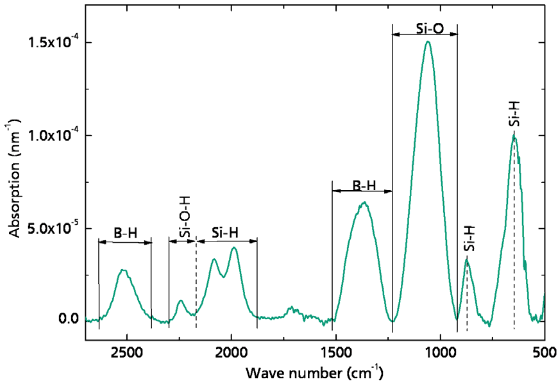

Figure 10: FTIR spectra of a-Si:B deposited in the PECVD reactor 2 (R2, see Figure 2)

4 SUMMARY

It was shown that doped amorphous silicon layers, deposited by microwave-induced plasma CVD can be used as a dopant source for thermal diffusion. A homogeneous phosphorus-doped emitter down to a resistivity of 26 ± 1 Ω/sq, and a boron-doped emitter down to 157 ± 3 Ω/sq were produced.

To perform a simple dry back etch step of the dopant source and the dead layer after diffusion, the oxidation of the a-Si layer during the diffusion process must be prevented. To achieve this, a temperature step with complete absence of oxygen seems necessary.

An oxygen contamination of the PECVD reactor affects the diffusivity of dopants in the a-Si layer, and should therefore be prevented.

5 ACKNOWLEDGMENTS

The authors are grateful to Rainer Neubauer and Heike Furtwängler for the wet chemical process steps, Andreas Müller, Udo Belledin and Antonio Leimenstoll for the diffusion, Jutta Zielonka for SEM measurements, and Daniel Trogus and Bertrand Bremen for support and work on the PECVD system.

This work has been supported by the German Federal Ministry of Education and Research (BMBF) under contract no. 13N11838.

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