PHOSPHORIC ANTI-REFLECTIVE COATINGS AS DOPANT SOURCE AND FRONT-SIDE PASSIVATION FOR INDUSTRIAL SILICON SOLAR CELL MANUFACTURING

Daniel Trogus, Johannes Seiffe, Florian Pillath, Marc Hofmann, Andreas Wolf and Jochen Rentsch
Fraunhofer Institute for Solar Energy Systems (ISE),
Heidenhofstrasse 2, D-79110 Freiburg, Germany
Phone: +49 761-4588-5614; fax: +49 761-4588-9250
E-mail: daniel.trogus@ise.fraunhofer.de

ABSTRACT: In this paper, we present the development and investigation of a multifunctional stack-layer plasma deposition for silicon solar cells. The thin stack layer works as phosphorous source in high-temperature diffusion and remains afterwards as front surface passivation and anti-reflective coating (ARC). This way the production of solar cells can be significantly simplified as the wet-chemical removal of phosphosilicate glass (PSG) becomes redundant and the diffusion step could be realised without a $POCl_3$ atmosphere in an open inline furnace system. In this study it is shown that it is possible to deposit such a layer in an industrial-type PECVD system using a double-layer stack of a thin PSG layer and a silicon nitride capping layer. The investigated process steps results in an emitter saturation current $j_{0e} < 120$ fA/cm^2 for a emitter sheet resistance of $R_E < 65$ Ω/sq..

Keywords: Silicon-Nitride, PECVD, Diffusion and Selective-Emitter

1 INTRODUCTION

It is essential to keep process sequences simple and reduce handling steps in manufacturing for high-efficiency silicon solar cells to gain a more cost-effective production. Plasma-deposited PSG layers can provide an effective and homogeneous dopant source as presented in [1]. By adopting such a layer to perform similarly as a passivating ARC after the diffusion step a significant process simplification is possible. Also for the formation of a selective emitter a multifunctional phosphoric ARC will be beneficial, as an opening of the layer by means of laser ablation for galvanic contact formation and laser doping out of the phosphoric layer in the contact area can be done simultaneously [2,3].
In this work, we will present our realization of such a layer. For a double-layer stack system of plasma-deposited SiO_x and SiN_x a high-temperature-stable passivation quality is already known [4]. As will be shown here the oxide layer can be replaced by a PSG layer, which works effectively as dopant source in a following high-temperature diffusion while a good passivation quality is maintained. Additionally industrial-type PECVD equipment is already used in this paper for the deposition of the double-layer enabling a fast implementation of such a process in solar cell mass production.

The developed multifunctional ARC layer has to fulfill several requirements:

- a homogeneous and sufficient doping over the cell area,
- a good surface passivation after the high-temperature diffusion step,
- long-term stability,
- and anti-reflection properties in terms of a λ/4 coating.

Within this paper different deposited stack layers after high temperature diffusion have been investigated concerning the resulting emitter sheet resistance (R_E), and the emitter saturation current density (*j0e*).

2 EXPERIMENTAL DETAILS

2.1 The semi-inline plasma deposition system

All plasma deposition experiments have been performed at a modified SiNA system by Roth&Rau, which provides deposition and etching sources within one vacuum chamber. Figure 1 shows the loading area with a carrier holding 6x6 wafers. For deposition a pulsed microwave (MW) linear plasma source (2.45 GHz) with peak power values up to 3.5 kW has been used.

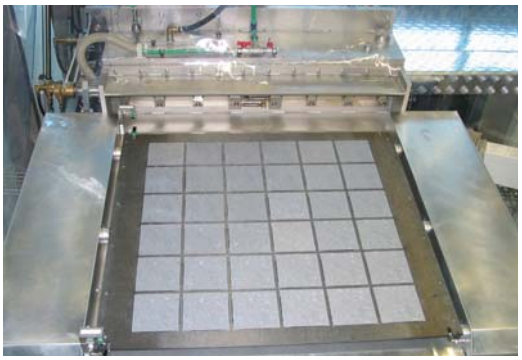

Figure 1: Semi inline plasma system (modified SiNA, Roth&Rau) at Fraunhofer ISE, Freiburg. Wafers can already be processed on a plasma width of 90 cm.

The MW linear antenna consists of a conducting rod into which the MW power is coupled in from both sides. The plasma is excited around the rod and along its entire length (effective width of plasma zone is approx. 0.2 m and length approx. 0.9 m). The deposition duration is adjusted by the speed of the carrier (see Figure 1) transporting the sample below the plasma. Process gases can be introduced either near the substrate or above the linear MW antenna.

2.2 Sample preparation

The deposition of the 2-layer system at the front side involves two different steps of deposition which were combined in the same vacuum. The investigations of carrier lifetime and optical characteristics were performed on p-type samples, a four-inch FZ-Si material with a thickness of 250 µm, resistivity of 1 Ω*cm, exhibiting shiny etched surfaces. For this purpose undiffused wet chemically cleaned (sequence of HNO_3 and HF) samples were used throughout the whole investigation.

Layer stacks of phosphorus-rich silicon oxide (phosphosilicate glass, PSG) and silicon nitride (SiN_x), both deposited by PECVD, with thickness ratios of PSG to SiN_x with 1:1 and 1:3 were processed for 120 nm and 90 nm stacks respectively.

The samples were lying on silicon dummy wafers during the depositions. The carrier speed was varied for the PSG layer and the SiNx capping layer leading to a variation in layer thicknesses. For the PSG layer the precursor gases were silane, nitrous oxide and a varying flux of argon through the liquid source trimethyl phosphite (TMPi).

The SiNx capping was deposited using an ammonia (NH_3) to silane (SiH_4) gasflow ratio of 3:1 for NH_3 to SiH_4. All plasma-deposition experiments were performed at 350°C.

The duration from leaving the vacuum until the high temperature diffusion process was set to approximately 10 minutes for a minimum process gap. Pre-experiments showed that a minimum time gap was beneficial.

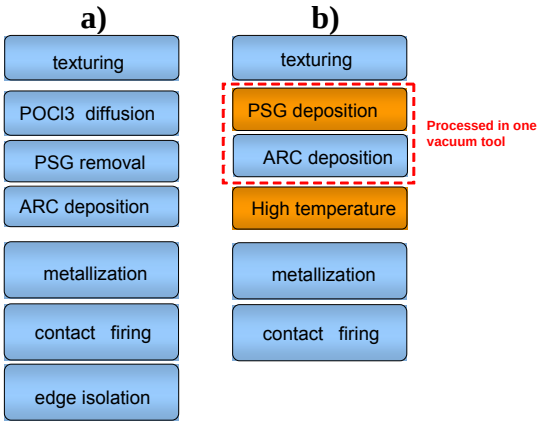

Figure 2: The aspired process sequence in figure 2 equates a standard cell process in a), simplified by redundancy of the PSG removal and $POCl_3$ atmosphere in b). Avoiding the $POCl_3$-gas in the diffusion process the emitter can be realized in a simple high-temperature step, allowing for lower safety requirements and inline processing. The PSG and ARC deposition are implemented in one vacuum tool, the extra deposition can be added very cost effectively to an industrial cell process.

The subsequent diffusion processes were carried out using a constant temperature T within a quartz-tube furnace system (E 2000 XL, centrotherm) for 50 minutes in N_2 atmosphere.

2.3 Characterization methods

The optical constants (refractive index n and extinction coefficient k) of the layers have been determined by spectroscopic ellipsometry (Woollham M-2000).

The layer stack thickness goal is to keep the reflectivity minimum at a wavelength of $\lambda \cong 600$ nm.

$$t = n_1 \cdot d_1 + n_2 \cdot d_2 \cong 150nm$$

Formula 1: Calculation of optical thickness t with n = refractive index and d = layer thickness.

The modelling of the ellipsometric data was performed using two different optical models. A Cauchy model is representing the PSG layer and a Tauc-Lorentz model stands for the SiNx capping. See Fig. 3.

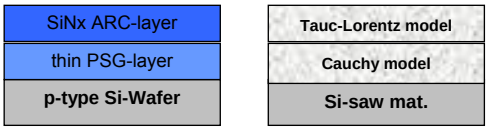

Figure 3: A schematic sketch of the deposited plasma stack system (see figure 3a) which is formed by a thin PSG layer and SiNx capping Two optical models were used for investigation in extract layer thicknesses and optical contants (see figure 3b).

The emitter sheet resistivity R_E has been determined using an inductive coil measurement tool. The samples were measured before plasma step and after diffusion.

Emitter sheet resistance is calculated by simple parallel resistance equation (see formula 2) from base-resistance R_B and the complete resistance R_{All} values after the high temperature step. Since our sample have the layer stack on both sides a factor of ½ has been included.

$$R_E = \frac{1}{2}\left(\frac{1}{R_{All}} - \frac{1}{R_B}\right)^{-1}$$

Formula 2: Calculation of emitter sheet resistance from basic electrical equation.

Former investigations of J. Benick et al. had shown that a homogeneous distribution of a low sheet resistance is possible with a qualified PSG layer thickness [1].

For the evaluation of the effective carrier lifetime τ_{eff} a quasi-steady-state photo conductance (QSSPC) measurement tool has been used. The emitter saturation current density j_{0e} has been calculated from τ_{eff} of symmetrically passivated and diffused samples. For the calculation the following formula was applied:

$$j_{0e} = \frac{qn_i^2 W}{2(N_{dot} + \Delta n)} \left\{ \frac{1}{\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}}} - \frac{1}{D_{\min}} \left(\frac{W}{\pi} \right)^2 \right\}^{-1}$$

Formula 3: The calculation of emitter saturation current from τ_{eff} values.

The calculation of j_{0e} values contains $n_i = 9.728*10^9$ cm^{-3} after Sproul et al. [4]. The Auger recombination in τ_{bulk} was calculated using the model of Kerr and Cuevas [5]. Further quantities are the elementary charge q, the minority diffusion constant $D_{\min}$, the doping concentration N_{dot}, the excess charge carrier density Δn and the wafer thickness W.

3 RESULTS

Serveral variations in plasma deposition parameters were performed such as carrier speed for PSG and ARC layer and Ar gas flow with different flux of TMPi (keeping peak power and process pressure). The approach leading to most promising results was then used for subsequent experiments. The behaviour of plasma stacks were evaluated by means of the emitter saturation-current values.

The resulting sheet resistances R_E were plotted for constant Ar (TMPi) gas flow F and two different carrier speeds for variation in PSG layer thickness, as presented in figure 4. Other parameters for inline plasma deposition were kept constant.

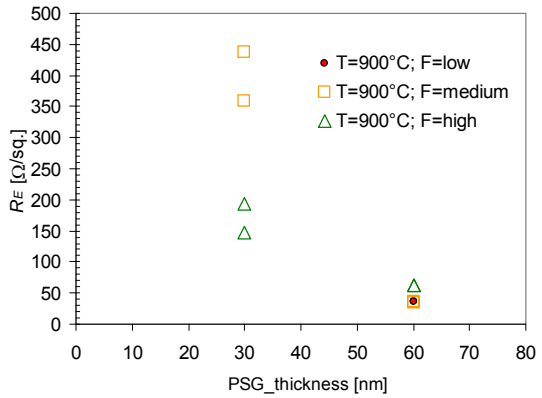

Figure 4: In this graph for constant diffusion temperature T and different TMPi flows F the emitter sheet resistance is plotted in comparison to the PSG thickness.

The effective emitter sheet resistance (R_E) after high temperature diffusion is depending on the layer thickness and the diffusion temperature [1].

Figures 5&6 give an overview of measured τ_{eff} values within the experiments. The results of various stack layers have been compared to R_E values of two different deposited PSG layer thicknesses d (figure 5).

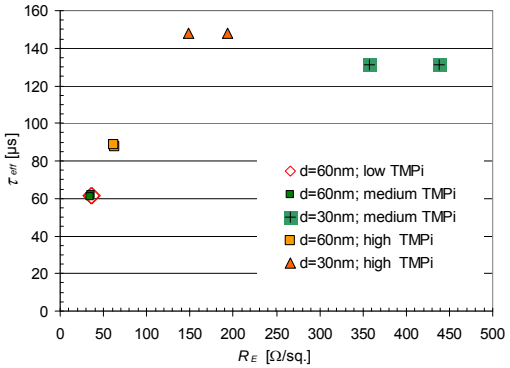

Figure 5: Carrier lifetime τ_{eff} is plotted in relation to sheet resistance R_E for samples which were diffused at 900°C.

It could be seen in figure 6, that remarkable low j_{0e} values could be achieved. $j_{0e} < 100$ fA/cm^2 are possible. Higher sheet resistances are showing the principal passivation quality of the layer.

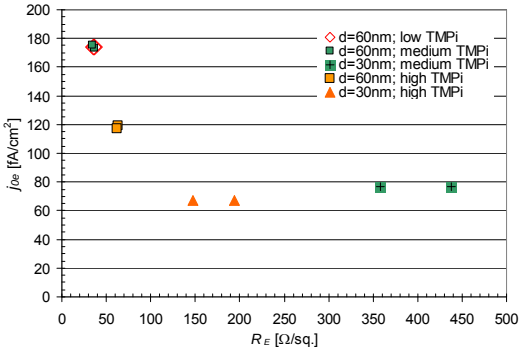

Figure 6: j_{0e} values depending on the sheet resistivity for different PSG layers. All samples exhibited the same capping thickness of 60nm after the diffusion at 900 °C.

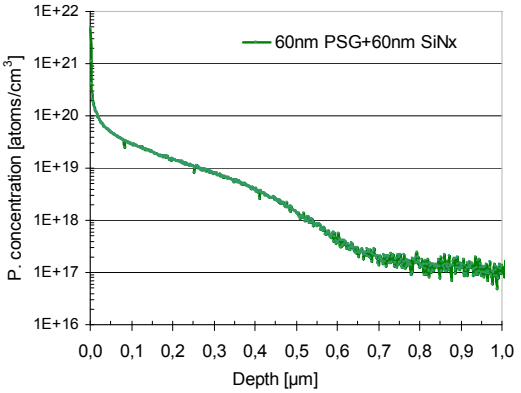

Figure 7: The emitter depth profile of PECVD-deposited stack 60 nm PSG and 60 nm of SiN_x was measured by secondary ion mass spectrometry (SIMS).

Compared to diffusion of a standard $POCl_3$ emitter [6], which is separated in configuration and drive-in phase, the PSG/ SiNx stacks exhibit a nearly double emitter depth. For reaching low contact resistance this type of emitter (see figure 7) is expected to have a positive influence on a possible advanced metallization technique like nickel plating or aerosol jet printing as following process steps [7, 8].

4 SUMMARY

In this work, PECVD stacks of PSG and SiNx were used as phosphorous source in a subsequent diffusion process.

Table 1: Review of the stack results on symmetrical samples. d denotes the PSG thickness. All samples were prepared including a 60 nm SiN_x capping.

d [nm]	R_E [Ω/sq]	τ_{eff} [µs]	j_{0e} [fA/cm^2]	TMPi-flow
60	36	62	174	low
60	37	62	174	mid
60	**63**	**88**	**119**	high
30	398	131	77	mid
30	171	148	67	high

In this study an emitter sheet resistivity of $R_E = (62.5 \pm 0.4)$ Ω/sq., and an emitter saturation current density of $j_{0e} = (118.3 \pm 1.0)$ fA/cm^2 was reached.
So it can already be shown, that in principal a multifunctional dopant source ARC can be realized, but more work is necessary to optimize the thickness of the PSG layer for achieving a more effective anti-reflective characteristic. Testing of the long-time stability of a phosphoric layer within a module is a further important issue, as possible phosphoric acid formation could possibly damage cell or encapsulation materials.
For stack deposition the number of plasma sources would have to be increased for sufficient throughput but is also capable of an industrial production.

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