Passivation of Solar Cell Emitters Using Aluminum Nitride

Georg Krugel, Aashish Sharma, Anamaria Moldovan, Winfried Wolke, Jochen Rentsch, and Ralf Preu

Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, 79110 Freiburg im Breisgau, Germany

Abstract — **Layers of hydrogenated aluminum nitride have proven excellent passivation properties on lowly doped silicon. Effective surface recombination velocities below 8 cm/s have been reached due to a very low interface defect density. In this work, the passivation of highly doped silicon is studied by measuring the emitter saturation current of boron as well as phosphorous emitters. It is shown that hydrogenation is a prerequisite for reaching effective passivation. Emitter saturation current densities of around 100 fA/cm^2 are presented for highly doped p$^+$-type and n$^+$-type silicon allowing maximal open circuit voltages of ~680 mV for silicon solar cells.**

Index Terms — **aluminum nitride, emitter, passivation, photovoltaic cells, silicon, sputtering**

I. INTRODUCTION

One of the key approaches to reach higher efficiencies in silicon photovoltaics is the reduction of recombination losses [1]. As the trend of using thinner silicon wafers is expected to persist, recombination at the surface of the wafers will be even more important in the future.

Hydrogenated aluminum nitride layers have been shown to provide excellent surface passivation on lowly doped p-type silicon. Effective surface recombination velocities of 8 cm/s have been reported for 1 Ωcm p-type FZ silicon wafers [2]. The underlying mechanism of this high level of surface passivation is related to a very low interface defect density in the range of 5×10^{10} eV^{-1} cm^{-2} in combination with a fixed negative charge density of 1×10^{12} cm^{-2} [2].

For some cell concepts highly doped n$^+$-type and p$^+$-type surfaces exist on the same side of the silicon wafer. This is for example the case in back-contact back-junction solar cells [3]. Dielectric layers which can effectively passivate both types of surfaces are needed in these concepts.

a-SiN$_x$:H has proven good passivation for n$^+$ surfaces and is the standard passivation layer of phosphorous emitters. Nevertheless only poor passivation was reached for p$^+$ surfaces due to positive fixed charges in the film [4, 5]. For these p$^+$ surfaces excellent surface passivation was achieved using Al$_2$O$_3$ [6-8]. Hoex showed that Al$_2$O$_3$ grown by plasma-assisted ALD and capped with SiN$_x$:H can also satisfactorily passivate n$^+$ surfaces [9].

Due to the very low interface defect density, AlN:H is an appealing alternative material for the passivation of p$^+$ and n$^+$ surfaces. It has furthermore very interesting optical properties as the refractive index and the extinction coefficient are very similar to SiN$_x$:H [2, 10]. Using Al$_2$O$_3$ as a passivation layer on the front of a solar cell, a capping layer of 75 nm of SiN$_x$:H is needed to ensure good anti-reflective properties. In contrast to this dual layer stack, AlN:H can be used as a combined passivation layer and anti-reflective coating on the front of silicon solar cells.

II. EXPERIMENTAL

Symmetrical lifetime test structures (n$^+$pn$^+$ and p$^+$np$^+$) were fabricated on FZ wafers (1 Ωcm, shiny etched, thickness 250 μm) to investigate the passivation of sputtered AlN:H on three different emitters. The characteristics of the emitters are summed up in Table I.

TABLE I
PROPERTIES OF THE PASSIVATED EMITTERS

	P75	P120	B70
Doping	Phosphorus	Phosphorous	Boron
Sheet resistance	75 Ω/sq.	120 Ω/sq.	70 Ω/sq.
Surface doping	7×10^{20} cm^{-3}	2×10^{20} cm^{-3}	4×10^{18} cm^{-3}
Emitter depth	300 nm	300 nm	400 nm

The diffusion process used for P75 is a typical process for the fabrication of standard solar cells, P120 could be used in solar cells featuring selective emitters [11] and B70 is applicable in the fabrication of n-type solar cells [6]. The samples received a SC1/SC2 clean and an HF dip directly before these diffusions. The AlN:H layers studied in this work were deposited by reactive sputtering of an aluminum target using argon, nitrogen and hydrogen as process gases. An industrial coater manufactured by Applied Materials was used for this purpose. Further information can be found in [2, 12, 13]. The hydrogen content of the layer was controlled precisely by a variation of the H$_2$ flow during sputtering to ensure an optimal passivation of these layers as shown below.

As a reference, some wafers featuring emitter P75 and P120 were coated with PECVD SiN$_x$:H (SiNA, Roth&Rau) which is typically used as a combined anti-reflective coating and passivation layer on phosphorous doped emitters. Reference wafers for the passivation of the boron doped emitter B70 were coated with a laboratory-type ALD reactor (OpAL, Oxford Instruments, plasma-assisted ALD) and capped with PECVD SiN$_x$:H [7].

A firing step in an industrial firing oven at temperatures above 800°C was carried through as such steps are typically used for the contact formation during the fabrication of solar cells. Samples were characterized before and after firing by quasi-steady-state photoconductance decay QSSPC [14] with a Sinton Instruments WCT-120 at an excess carrier density of $\Delta n = 10^{15}$ cm^{-3}. The passivation quality of the different dielectrics was quantified by the emitter saturation current density [15, 16]

$$ J_{0e} = \frac{q n_i^2}{N_{dot} + \Delta n} \frac{W}{2} \left(\left[\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}} \right] - \frac{W^2}{D\pi^2} \right)^{-1} . \quad (1) $$

The parameters used in this equation are the intrinsic carrier concentration n_i, the doping concentration N_{dot}, the sample thickness W and the diffusion constant D. The Auger recombination model of Richter [17] was used for the determination of the bulk lifetime τ_{bulk}, recombination via defects in the bulk is neglected. Furthermore, an upper limit of the attainable open circuit voltage $V_{OC,max}$ for silicon solar cells was determined using the one-diode equation

$$ V_{OC,max} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}}{J_{0e}} + 1 \right) \quad (2) $$

and neglecting recombination losses in the base and on the rear side. $V_{OC,max}$ was calculated for a temperature T = 25 °C and a short circuit density of $J_{SC} = 35$ mA/cm^2.

III. RESULTS

A. Influence of hydrogen on the passivation of AlN:H layers

Recent experiments for reactively sputtered aluminum nitride in silicon photovoltaics reached only a low level of passivation with lifetimes of 12 µs [10]. It has been shown for sputtered SiN$_x$:H that the hydrogen concentration in the layer can significantly influence the obtainable solar cell efficiency [12, 18]. Therefore, hydrogen was added additionally to argon and nitrogen into the sputter chamber during deposition for the here presented AlN:H layers. The hydrogen amount leading to an optimal passivation was determined in a preliminary investigation. For this purpose, lifetime samples (1 Ωcm FZ silicon, p-type, shiny etched) were coated on both sides with AlN:H using different hydrogen flows during sputtering. Fig. 1 shows typical microscopy images before and after the described firing step.

As can be seen, blistering occurs depending on the hydrogen concentration after or even before the firing process. It is believed that the visible structures are caused by a partially delamination of the passivation stack due to the formation of hydrogen blisters at the surface. Such behavior has also been reported for Al$_2$O$_3$ [7, 8, 19].
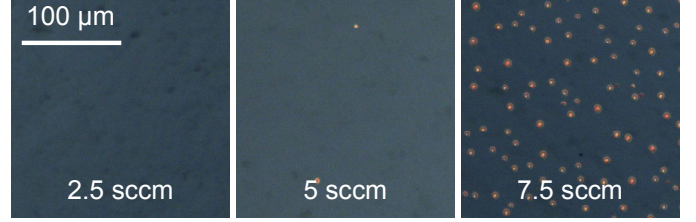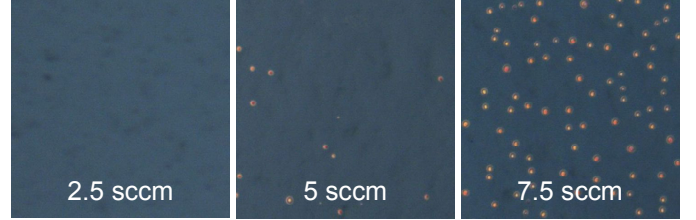

Fig. 1. Typical microscopy images for layers of AlN:H (a) before and (b) after firing at temperatures above 800°C. Hydrogen flows of 2.5 sccm (left), 5.0 sccm (middle) and 7.5 sccm (right) have been used during sputter deposition additionally to argon and nitrogen.

The lifetime τ_{eff} and the interface defect density D_{it} were determined for these samples to get a deeper insight into the influence of hydrogen on the passivation. A COCOS tool (corona oxide characterization of semiconductor) [20] was used for determination of the interface defect density which can be considered as a contactless capacitance voltage measurement. Fig. 2 shows the influence of the hydrogen flow on the passivation of the samples.
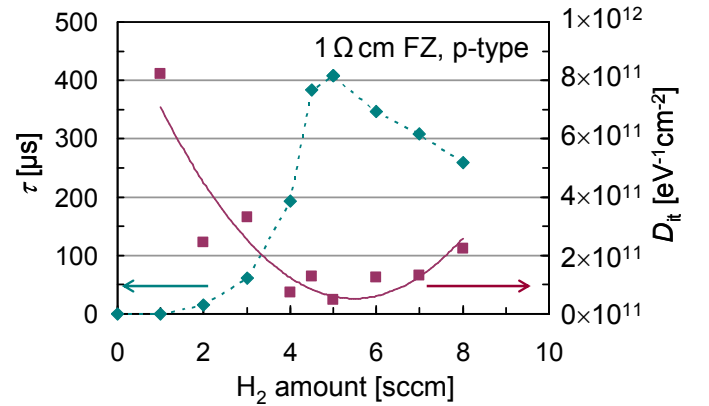

Fig. 2. Influence of the hydrogen flow during sputter deposition of AlN:H on the resulting lifetime τ_{eff} (cyan) and the interface defect density D_{it} (purple) after firing. For an optimized sputter process lifetimes up to 1 ms have been reached [2].

Inserting no hydrogen into the sputter chamber leads only to very low lifetime as can be seen which is correlated with a high interface defect density in the order of 10^{12} eV^{-1} cm^{-2}. Similar high values of D_{it} have also been reported by other groups for non-hydrogenated aluminum nitride [21] and this is

also consistent with the low level of passivation reported by Kaminski [10]. Increasing the hydrogen flow leads to an increase in lifetime accompanied by a decrease of the interface defect density. This can be explained by a diffusion of hydrogen atoms to the interface where dangling bonds are successfully passivated. Similar conclusions have also been drawn for Al_2O_3 [22]. A further increase of the hydrogen flow leads to blistering (Fig. 1) which causes defects at the interface. The lifetime is therefore decreasing at a certain hydrogen flow. The here described preliminary investigation allows the determination of an optimal hydrogen flow which on the one hand lead to optimal passivation of the interface and on the other hand avoids blistering.

B. Emitter passivation using AlN:H

These observations concerning the hydrogen flow carried through on lowly doped silicon have been confirmed for samples featuring highly doped surfaces (emitter P75, P120 and B70) by measuring J_{0e}. Results before and after the firing step for these samples with an optimized AlN:H sputter process are shown in Fig. 3.
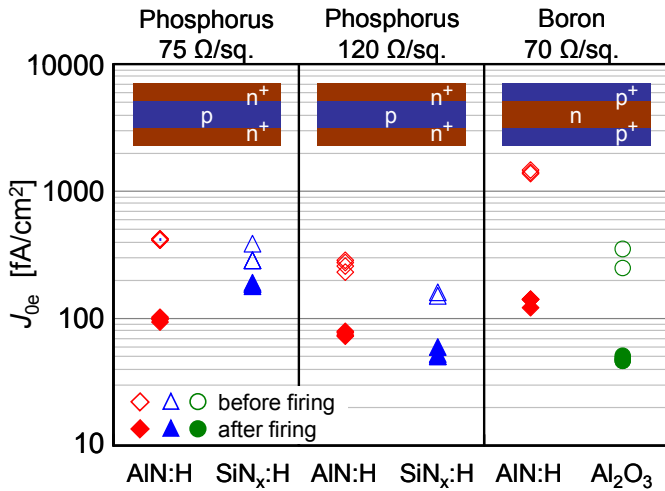

Fig. 3. Emitter Saturation current densities for passivation layers of sputtered AlN:H on three different emitters. Values for reference wafers passivated with PECVD SiN_x:H and ALD Al_2O_3 (with SiN_x:H capping layer) are shown as well.

The passivation quality of the as-deposited AlN:H films is very poor (Fig. 3, open symbols). The corresponding J_{0e} are in the range of a few hundred fA/cm^2 for the two phosphorous emitters P75 and P120 and even above 1000 fA/cm^2 for the boron emitter B70. This is in the range of unpassivated emitters as reported by Kerr [4, 23]. The passivation is activated by the firing step resulting in a low J_{0e} (Fig. 3, filled symbols).

Table II summarizes for AlN:H the emitter saturation current J_{0e} and the corresponding maximal open circuit voltage $V_{OC,max}$ for the best wafer of every group.

TABLE II
EMITTER SATURATION CURRENT AND MAXIMAL OPEN CIRCUIT VOLTAGE USING SPUTTERED ALUMINUM NITRIDE LAYERS AS PASSIVATION LAYER

	P75	P120	B70
J_{0e}	94 fA/cm^2	73 fA/cm^2	120 fA/cm^2
$V_{oc,max}$	685 mV	691 mV	678 mV

IV. DISCUSSION

A. Phosphorous emitters

Sputtering of AlN:H allows emitter saturation currents down to 94 fA/cm^2 (P75) and 73 fA/cm^2 (P120) for the phosphorous emitters studied in this work. The reference wafers coated with SiN_x:H reached emitter saturation currents down 179 fA/cm^2 (P75) and 51 fA/cm^2 (P120) which are typical values for phosphorous emitters passivated with SiN_x:H [4, 23, 24]. For ALD Al_2O_3 Hoex reached emitter saturation currents between 100 fA/cm^2 and 60 fA/cm^2 for the passivation of phosphorous emitters with sheet resistivities in this range [9].

This demonstrates that AlN:H allows effective passivation of the 75 Ω/sq. emitter P75 which is used in standard solar cells. Even lower J_{0e} than for predominantly used SiN_x:H are reached. An explanation is the very low interface defect density of the AlN:H layers which was achieved by a precise control of the hydrogen concentration in the layer. The defect density of AlN:H is in the order of $10^{10}\,eV^{-1}\,cm^{-2}$ and therefore significantly lower than for SiN_x:H where interface defect densities above $10^{11}\,eV^{-1}\,cm^{-2}$ are typically reached for layers applicable as anti-reflective coating in silicon photovoltaics [1]. On the other hand, the passivation of the 120 Ω/sq. emitter P120 is more effective if SiN_x:H is used as a passivation layer rather than AlN:H. A possible explanation is that for the lower doped 120 Ω/sq. emitter P120 the minority carrier density is more affected by the negative fixed charges present in the AlN:H layer compared to the positive fixed charges in SiN_x:H [1] whereas the density might not be significantly affected by the higher doped 75 Ω/sq. emitter.

The passivation quality in this sheet resistance range is similar to ALD Al_2O_3 [9]. This indicates that the passivation of the studied AlN:H layers is not caused by a field effect passivation, but rather by an excellent chemical passivation as ALD Al_2O_3 and AlN:H feature similar interface defect densities below $10^{11}\,eV^{-1}\,cm^{-2}$. However, it should be mentioned that the emitters passivated by ALD Al_2O_3 passivation might have different doping profiles and thus different intrinsic recombination rates [25], e.g. due to Auger recombination. This prevents a direct comparison of emitter saturation currents densities for different emitters.

The reached level of emitter passivation with J_{0e} below 100 fA/cm^2 and $V_{OC,max}$ above 680 mV for both studied phosphorous emitters is sufficient for solar cell efficiencies exceeding 20% in industrial production [26]. Parasitic shunting as observed for SiN$_x$:H on boron emitters [27] could complicate the integration of AlN:H as passivation layer on phosphorous emitters. This effect and the firing through of silver finger will be studied for solar cells featuring an AlN:H layer as a combined anti-reflective coating and passivation layer of a phosphorous emitter.

B. Boron emitter

On highly doped p-type silicon (B70) emitter saturation current densities down to 120 fA/cm^2 were reached using sputtered AlN:H as a passivation layer. For the reference wafers coated with ALD Al$_2$O$_3$ capped with PECVD SiN$_x$:H J_{0e} of 46 fA/cm^2 were measured. This is in the expected range as Richter reported values of 57 fA/cm^2 (75 Ω/sq.) for textured samples which typically have 1.5 to 2.5 higher emitter saturation currents [23].

The difference of the passivation quality of the boron emitter for AlN:H and the Al$_2$O$_3$/SiN$_x$:H stack can be explained by the density of fixed charges at the interface. The interface defect density of both dielectrica is similar whereas AlN:H contains a lower charge density of 1×10^{12} cm^{-2} [2] compared to charge densities up to 10^{13} cm^{-2} reported for ALD Al$_2$O$_3$ [28]. This higher charge density in the Al$_2$O$_3$ layer can repel electrons more effectively and thus reduce the recombination rate.

The effect of the different densities of fixed charges is more prominent for the boron emitter than for the two studied phosphorous emitter as the surface doping concentration is of the order of 10^{18} cm^{-3} for the boron emitter but of the order of 10^{20} cm^{-3} for both phosphorous emitter. For a larger surface doping concentration the density of fixed charges has only a minor impact [9].

Maximal open circuit voltages of 678 mV can be reached using sputtered AlN:H as a passivation layer on the studied 70 Ω/sq. boron emitter. It is believed that an optimization of the sputter process can be carried through so that the efficiency of an industrial n-type solar cell will not be limited by the surface passivation quality of the AlN:H layer.

Results presented here are without the application of an annealing step at moderate temperatures. For Al$_2$O$_3$ it was reported that this can significantly increase the passivation quality [19, 28]. Further increase of the passivation might be achieved by a variation of the preconditioning of the surface. Different cleaning sequences and plasma pre-treatments directly before deposition will be studied in further experiments.

VI. CONCLUSION

In this work, we demonstrate that aluminum nitride prepared by sputtering can provide a good level of surface passivation for highly doped n$^+$-type and p$^+$-type silicon. It is shown that hydrogenation of the layer is an important prerequisite to reach excellent chemical passivation. Emitter saturation currents of ~100 fA/cm^2 and maximal open circuit voltages of around 680 mV are reached for both doping types after an industrial firing step with temperatures above 800°C. This makes AlN:H an interesting material e.g. for the use in back-contact back-junction solar cells where highly doped p$^+$- and n$^+$-type surfaces have to be passivated on the same side of the wafer. In this cell concept AlN:H could be applied as rear side passivation for both types of highly doped surfaces as well as an anti-reflective coating and passivation layer on the front.

REFERENCES

[1] A. G. Aberle, "Crystalline silicon solar cells: advanced surface passivation and analysis of crystalline silicon solar cells," Centre for Photovoltaic Engineering, University of New South Wales, Australia, 1999.

[2] G. Krugel, A. Sharma, W. Wolke, J. Rentsch, R. Preu, "Study of hydrogenated AlN as an anti-reflective coating and for the effective surface passivation of silicon," *Physica Status Solidi RRL*, vol. 7, 2013.

[3] D. De Ceuster, P. Cousins, D. Rose, M. Cudzinovic, W. Mulligan, "Low cost, high volume production of > 22% efficiency silicon solar cells," in *22nd EU PVSEC*, Milan, Italy, 2007.

[4] M. J. Kerr, "Surface, Emitter and Bulk Recombination in Silicon and Development of Silicon Nitride Passivated Solar Cells," Ph.D. Thesis, Australian National University, 2002.

[5] J. Libal, R. Petres, T. Buck, R. Kopecek, G. Hahn, R. Ferre, M. Vetter, I. Martín, K. Wambach, I. Roever, and P. Fath, "N-type multicrystalline silicon solar cells: BBr3-diffusion of p$^+$-diffused silicon surfaces," in *20th EU PVSEC*, Barcelona, Spain, 2005.

[6] J. Benick, B. Hoex, M. C. M. van de Sanden, W. M. M. Kessels, O. Schultz, and S. W. Glunz1 "High efficiency n-type Si solar cells on Al$_2$O$_3$-passivated boron emitters," *Applied Physics Letters*, vol. 92, pp. 253504/1-3, 2008.

[7] A. Richter, S. Henneck, J. Benick, M. Hörteis, M. Hermle, and S. W. Glunz, "Firing stable Al$_2$O$_3$/SiN$_x$ layer stack passivation for the front side boron emitter of n-type solar cells," in *25th EU PVSEC*, Valencia, Spain, 2010.

[8] A. Richter, F. M. M. Souren, D. Schuldis, R. M. W. Görtzen, J. Benick1, M. Hermle and S. W. Glunz, "Thermal stability of spatial ALD deposited Al$_2$O$_3$ capped by PECVD SiN$_x$ for the passivation of lowly and highly doped p-type silicon surfaces," in *27th EU PVSEC*, Frankfurt, Germany, 2012.

[9] B. Hoex, M. C. M. van de Sanden, J. Schmidt, R. Brendel, and W. M. M. Kessels, "Surface passivation of phosphorus-diffused n$^+$-type emitters by plasma-assisted atomic-layer deposited Al$_2$O$_3$," *Physica Status Solidi RRL*, vol. 6, pp. 4-6, 2012.

[10] P. M. Kaminski, K. Bass, and G. Claudio, "High bandgap dielectrics for antireflective coating in silicon solar cells by reactive ion sputtering," *Physica Status Solidi C*, vol. 8, pp. 1311-1314, 2011.

[11] U. Jäger, M. Okanovic, M. Hörtheis, A. Grohe, and R. Preu, "Selective emitter by laser doping from phosphosilicate glass," in *24th EU PVSEC*, Hamburg, Germany, 2009.

[12] W. Wolke, A. Jäckle, R. Preu, S. Wieder, and M. Ruske, "SiN:H anti-reflection coatings for c-Si solar cells by large scale inline sputtering," in *19th EU PVSEC*, Paris, France, 2004.

[13] G. Krugel, W. Wolke, F. Wagner, J. Rentsch, and R. Preu, "Sputtered aluminum oxide for rear side passivation of p-type silicon solar cellsm," in *27th EU PVSEC*, Frankfurt, Germany, 2012.

[14] A. Cuevas, D. Macdonald, "Measuring and interpreting the lifetime of silicon wafers," *Solar Energy*, vol. 76, pp. 255–262, 2004.

[15] A. B. Sproul, "Dimensionless solution of the equation describing the effect of surface recombination on carrier decay in semiconductors," *Journal of Applied Physics*, vol. 76, pp. 2851-2854, 1994.

[16] C. Bertram, "Emitterbildung und -charakterisierung für hocheffiziente Industriesolarzellen," Thesis, Universität Tübingen, Germany, 2009.

[17] A. Richter, F. Werner, A. Cuevas, J. Schmidt, S. W. Glunz, "Improved parameterization of Auger recombination in silicon," *Energy Procedia*, vol. 27, pp. 88-94, 2012.

[18] G. Krugel, W. Wolke, J. Geilker, S. Rein, R. Preu, "Impact of Hydrogen Concentration on the Regeneration of Light Induced Degradation," *Energy Procedia*, vol. 8, pp. 47-51, 2011.

[19] B. Vermang, H. Goverde, A. Lorenz, A. Uruena1, J. Das, P. Choulat, E. Cornagliotti, A. Rothschild, J. John, J. Poortmans, and R. Mertens, "On the Blistering of Al_2O_3 Passivation Layers for Si Solar Cells," in *26th EU PVSEC*, Hamburg, Germany, 2011.

[20] M. Wilson, J. Lagowski, L. Jastrzebski, A. Savtchouk, and V. Faifer, "COCOS (corona oxide characterization of semiconductor) non-contact metrology for gate dielectrics," *AIP Conference Proceedings*, vol. 550, pp. 220-225, 2001.

[21] E. Simoen, D. Visalli, M. Van Hove, M. Leys, P. Favia, H. Bender, G. Borghs, A. P. D. Nguyen, and A. Stesmans "Electrically active defects at AlN/Si interface studied by DLTS and ESR," *Physica Status Solidi A*, vol. 209, pp. 1851-1856, 2012.

[22] G. Dingemans, W. Beyer, M. C. M. van de Sanden, and W. M. M. Kessels, "Hydrogen induced passivation of Si interfaces by Al2O3 films and SiO_2/Al_2O_3 stacks," *Applied Physics Letters*, vol. 97, pp. 152106/1-3, 2010.

[23] M. J. Kerr, J. Schmidt, A. Cuevas, and J. H. Bultman "Surface recombination velocity of phosphorus-diffused silicon solar cell emitters passivated with plasma enhanced chemical vapor deposited silicon nitride and thermal silicon oxide," *Journal of Applied Physics*, vol. 89, pp. 3821-3826, 2001.

[24] C. Schwab, "Entwicklung und Charakterisierung eines PECVD-Schichtsystems zur Emitterpassivierung und Antireflex-beschichtung kristalliner Silicium-Industriesolarzellen," Thesis, Universität Freiburg, Germany, 2010.

[25] P. P. Altermatt, J. O. Schumacher, A. Cuevas, M. J. Kerr, S. W. Glunz, R. R. King, G. Heiser, and A. Schenk, "Numerical modeling of highly doped Si:P emitters based on Fermi–Dirac statistics and self-consistent material parameters," *Journal of Applied Physics*, vol. 92, pp. 3187-3197, 2002.

[26] S. W. Glunz, J. Benick, D. Biro, M. Bivour, M. Hermle, D. Pysch, M. Rauer, C. Reichel, A. Richter, M. Rüdiger, C. Schmiga, D. Suwito, A. Wolf, and R. Preu, "N-type silicon - enabling efficiencies > 20% in industrial production," in *35th IEEE Photovoltaic Specialist Conference*, Honolulu, pp. 50-56, 2010.

[27] S. Dauwe, L. Mittelstädt, A. Metz, and R. Hezel, "Experimental evidence of parasitic shunting in silicon nitride rear surface passivated solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 10, pp. 271-278, 2002.

[28] J. Benick, A. Richter, T.-A. Li, N. E. Grant, K. R. Mc Intosh, Y. Ren, K. J. Weber, M. Hermle, and S. W. Glunz, *35th IEEE Photovoltaic Specialists Conference*, Honolulu, pp. 20–25, 2010.