

PASSIVATION QUALITY OF WET OXIDES GROWN FROM PURIFIED STEAM

J. Benick¹, K. Zimmermann¹, J. Spiegelman², M. Hermle¹ and S. W. Glunz¹

¹Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, D-79110 Freiburg, Germany

²RASIRC, 11760 Sorrento Valley Road, Suite E, San Diego, Ca, USA

Phone +49-761-4588-5493; Fax +49-761-4588-9250; email: jan.benick@ise.fraunhofer.de

ABSTRACT: An effective passivation of the rear surface is a prerequisite to considerably improve the conversion efficiency of industrial solar cells. An excellent level of surface passivation on lowly doped *p*-type surfaces is provided by thermal grown silicon oxides. However, dry thermal oxidation processes require relatively high temperatures (~1000°C) and, due to the low growth rate, long process times. To decrease both oxidation temperature and process time the dry oxidation process can be replaced by a wet oxidation. The most common way to introduce high purity water vapor into the oxidation tube is the pyrolytic generation from high purity gases (H₂ and O₂). A more easy and cost effective option for the supply of water vapour that was applied within this work is the direct purification of steam. The passivation quality of dry and wet oxides, the latter grown from pyrolytic generated water vapor and purified steam was compared within this work. The passivation quality obtained for the wet oxides grown from purified steam was found to be comparable to those oxides grown from pyrolytic generated water vapor. On LFC solar cells conversion efficiencies well above 20% could be reached independent of the oxide that was applied for the rear side passivation.

Keywords: Silicon, High-Efficiency, Passivation, Silicon Oxide

1 INTRODUCTION

Cost reduction is one of the major targets for the technological development in the field of photovoltaics. One way for the cost reduction of crystalline solar cells is the improvement of the conversion efficiency. Thus, particularly at the actual trend towards thinner wafers the application of a PERC-type [1, 2] solar cell structure with a passivated rear side becomes crucial. An economically feasible way to create a PERC-type rear structure has been developed by the application of laser technology. This laser fired contacts (LFC) process is based on the local alloying of Al through an insulating passivation layer [3]. However, an industrial feasible rear surface passivation layer is still needed.

Using silicon nitride excellent surface recombination velocities have been achieved on *p*-type surfaces [4]. However, the relatively high density of fixed positive charges within this layer creates a shunt like behaviour when integrated as the rear side passivation of PERC-type solar cells [5]. To overcome this also layer stack systems combining silicon nitride and silicon oxide are under investigation [6].

The negative charge dielectric Al₂O₃ recently has been proven to be an effective passivation layer on *p*-type surfaces and excellent results have been reported for PERC-type solar cells [7].

The highest conversion efficiencies so far have been realized for cells with a rear surface passivated by a thermal SiO₂ [8]. The introduction of thermal oxidation into industrial production processes therefore is investigated [9-11]. However, the high temperatures (~1000°C) that are needed for dry thermal oxidation do not perfectly fit in the solar cell production process. Above all, multicrystalline silicon substrates demand low temperatures for oxide growth to avoid minority carrier lifetime degradation [12]. By replacing dry oxidation with wet oxidation, process temperatures can be lowered from ~1000°C to below 900°C. The most common way to introduce high purity water vapor into the oxidation

tube is the pyrolytic generation from high purity gases (H₂ and O₂). The direct purification of steam is an easier and cost effective way for introducing ultrapure water vapor into the oxidation tube. With the applied system steam generated from DI water is purified from dissolved gases and metals by a non-porous hydrophilic membrane that selectively allows water vapour to pass.

A comparison of the passivation quality of dry and wet oxides, the latter grown from pyrolytic generated water vapor and purified steam, is presented within this work.

2 LIFETIME INVESTIGATION

2.1 Experimental

Dry and wet silicon oxide layers have been grown on 250 μm thick 1 Ω cm *p*-type FZ silicon wafers. Wet oxides were grown at 850°C under H₂O ambient (80 nm: 60 min, 200 nm: 150 min). The water vapor for the wet oxidation was introduced into the tube at two different ways:

- purified ultrapure steam (RASIRC[®] Steamer)
- pyrolytic generation from ultrapure gases H₂ and O₂

The steam generator and the torch for the pyrolytic generation of water vapor were not installed in the same tube, thus wet oxidations were performed at different furnaces. Dry oxidations were grown at 1050°C under oxygen ambient (80 nm: 40 min, 200 nm: 150 min) in the same tube as the wet oxidation using purified steam. After oxide growth all samples received a forming gas anneal (FGA) at 425°C for 25 min. The QSSPC method (Lifetime tester WCT 120) is used to measure the injection dependent effective lifetime τ_{eff} [13].

2.2 Results

The measured lifetimes (at an injection level of $\Delta n = 10^{15} \text{ cm}^{-3}$) of the samples passivated by the different oxides are shown in Fig. 1. As expected, after the post

oxidation anneal in forming gas atmosphere the measured lifetime of all samples increases significantly. With a measured lifetime of $\sim 300 \mu\text{s}$ the dry thermal oxide shows the highest passivation quality. Nevertheless, also the wet oxides show a sufficient level of surface passivation in the range of ~ 150 to $\sim 200 \mu\text{s}$. Herewith the wet oxides grown from purified steam seem to provide a higher level of surface passivation compared to the process where the water vapor was introduced by pyrolytic generation. However, different oxidation tubes of different furnaces have been applied for the wet oxidations, leading to an uncertainty of the direct process comparison. Nevertheless, it can be said that both processes for the wet oxidation should be well suited for the passivation of the solar cell rear side.

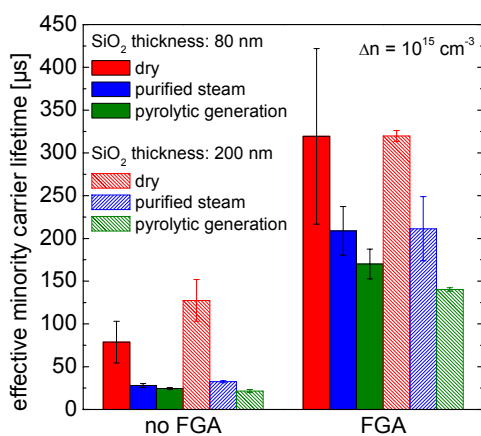


Fig. 1 Comparison of the surface passivation quality of dry and wet thermal oxides. The wet oxides were grown from purified steam as well as from pyrolytic generation of water vapor.

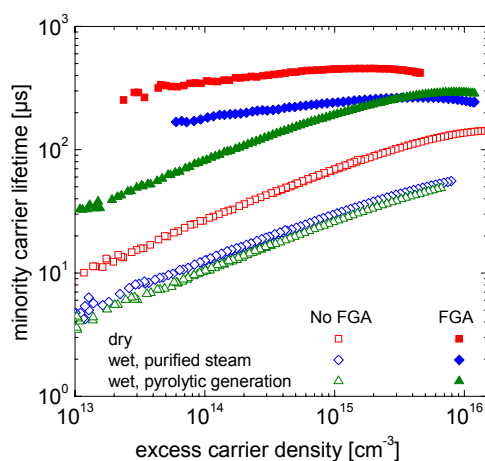


Fig. 2 Injection dependent lifetime of dry and wet ~ 100 nm thick thermal oxides. The wet oxides were grown from purified steam as well as from pyrolytic generation of water vapor.

The injection level dependence of the oxidized samples is shown in Fig. 2. The samples passivated by the wet oxide grown from pyrolytic generated water vapour show a more pronounced injection level dependence compared to the other oxides after FGA. For the operation at the solar cell rear side under one-sun

illumination (i.e. low level injection) such a behaviour might alter the efficiency potential. However, the rear side of a common high efficiency solar cell is covered by aluminium and thus at the device level the rear side oxides receive an anneal process [14] which considerably enhances the passivation quality compared to the anneal in forming gas. Therefore all oxides are expected to perform a sufficient level of rear side passivation for the applied LFC solar cell structure.

3 SOLAR CELLS

3.1 Experimental

In order to investigate the rear surface passivation quality of the different dry and wet oxides, LFC solar cells were fabricated on $\langle 100 \rangle$ $1 \Omega \text{ cm}$, FZ, p -type c -Si wafers with a thickness of $250 \mu\text{m}$. These cells (area = 4 cm^2) feature a front surface with inverted pyramids and evaporated Ti/Pd/Ag front contacts which are thickened by light-induced plating [15]. The rear surface is passivated by the respective ~ 100 nm thick thermally grown silicon oxides that have been presented in section 2. This oxide also acts as the diffusion mask for the front side phosphorus diffusion. The rear side metallization is realized by a $2 \mu\text{m}$ thick aluminum layer that is contacted by the laser-fired contacts (LFC) process which leads to the formation of a local Al-BSF underneath the contacts.

POCl_3 diffusion at 810°C results in a homogenous phosphorus emitter with a sheet resistance of $\sim 110 \Omega/\text{sq}$. This front side phosphorus emitter is passivated by a 70 nm thick SiN_x ($n \approx 2$). To ensure the electrical contact and to remove the damage introduced by the x-rays during the e-gun evaporation processes the samples achieved an annealing step at 425°C in forming gas ambient. The structure of the applied LFC solar cell is shown in Fig. 3.

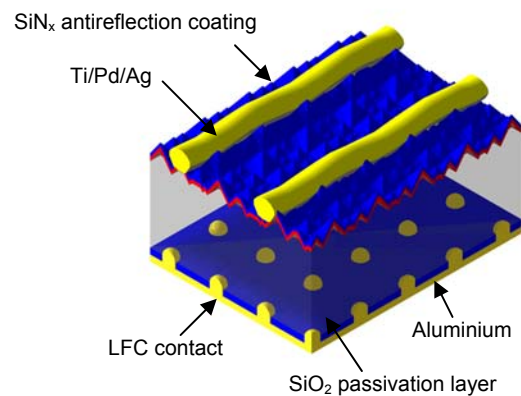


Fig. 3 Applied LFC solar cell structure.

3.2 Results

The one-sun parameters of the LFC solar cells featuring the rear side passivation by the different dry and wet thermal oxides are summarized in Table I. It can be seen that the open-circuit voltage of the solar cells (the most sensitive one-sun parameter with respect to the surface passivation) with the different oxides for the rear side passivation is comparable. With an average of 650.6 mV and a maximum of 652.4 mV the highest V_{oc} could be reached with the rear side passivated by the dry SiO_2 . However, also for the wet oxides average open-

circuit voltages of 648.4 mV and 649.3 mV for the oxides grown by purified steam and pyrolytic generation of water vapor respectively have been reached. Also the short-circuit current density of 39.8 – 39.9 mA/cm² is comparable for all cells. Thus, a high conversion efficiency >20% could be obtained for all cells. However, a significant difference can be observed for the fill factor, i.e. the FF of the cells featuring the wet oxide grown from purified steam is considerably lower. The average FF of these cells of 78.1% is 2 %_{abs} below that of the cells passivated by the dry oxide and ~1.5%_{abs} below that for the cells where the oxide was grown from pyrolytic generated water vapor and this effect is linked to an increased series resistance. The series resistance was determined by comparing the illuminated and dark *I-V* curves [16]. For cells passivated by the wet oxide grown from purified steam an average series resistance of ~0.8 Ω cm² was determined. For the other cells a considerably lower series resistance of ~0.5 Ω cm² could be measured. Due to a slightly increased thickness of 110 nm for the wet oxide grown from purified steam the LFC process for these cells did not work as well as for the cells with the optimum oxide thickness of ~100 nm, as can be seen by the micrographs of the LFCs in Fig. 4. For the 110 nm thick SiO₂ the contact region in the middle of the contact only is connected to the rear side metal by narrow metal bridges.

Table I One-sun parameters of LFC solar cells with different rear surface passivations: (i) dry SiO₂, (ii) wet SiO₂ (purified steam), (iii) wet SiO₂ (pyrolytic generation of water vapor).

	V_{oc} [mV]	J_{sc} [mA/cm ²]	FF [%]	η [%]
dry oxidation (1050°C)				
Average (28 cells)	650.6 ± 1.3	39.8 ± 0.3	80.1 ± 0.7	20.7 ± 0.2
Best	652.4	39.9	80.5	21.0
wet oxidation, purified steam (850°C)				
Average (28 cells)	648.4 ± 3.4	39.9 ± 0.5	78.1 ± 1.0	20.2 ± 0.3
Best	650.7	40.1	79.1	20.6
Wet oxidation, pyrolytic generation (850°C)				
Average (28 cells)	649.3 ± 1.8	39.8 ± 0.2	79.5 ± 1.5	20.5 ± 0.4
Best	651.7	39.9	80.5	20.9

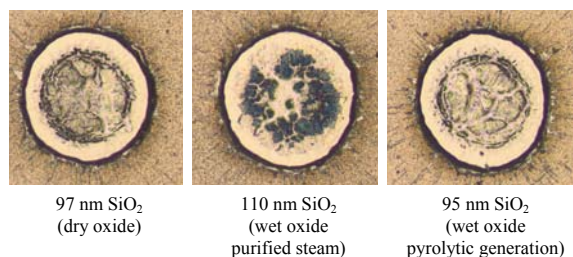


Fig. 4 Micrographs of the rear side LFCs. Due to the increased thickness of the wet oxide grown by purified steam (exceeding the optimum thickness of ~100 nm) the LFC of these cells did not work properly.

The measured external and internal quantum efficiencies as well as the reflection of the cells are shown in Fig. 5. As can be seen, the quantum efficiencies of all cells are

very close. The strong decrease of the IQE in the short wavelength range is due to the insufficient passivation of the front side by the low refractive index SiN_x. Thus, in particular the open-circuit voltage is limited by the front side recombination. Hence, to be able to quantify the rear side passivation the measured EQE data is simulated with PC1D [17]. The calculated EQE together with the measured data for the long wavelength range above 800 nm is shown in Fig. 6.

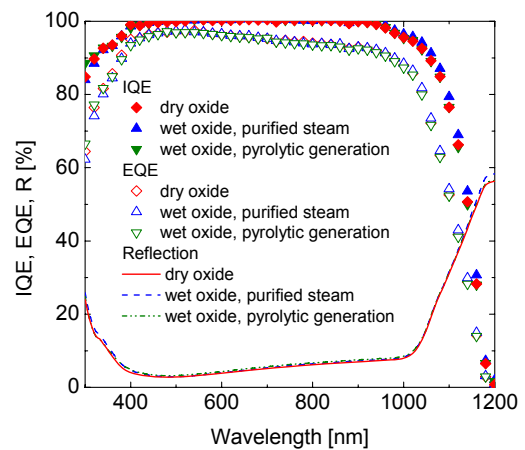


Fig. 5 IQE, EQE and reflection of the LFC solar cells with different rear side passivations: (i) dry SiO₂, (ii) wet SiO₂ (purified steam), (iii) wet SiO₂ (pyrolytic generation of water vapor).

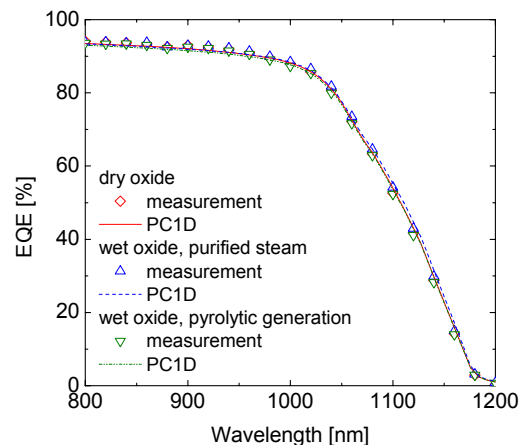


Fig. 6 Measured external quantum efficiency. The lines show the fitted EQE curves (PC1D) for the extraction of the surface recombination velocity of the rear side.

The measured EQE can be perfectly reproduced by the simulation. For the front side the simulation of the cells results in a surface recombination velocity of approximately 4×10^4 cm/s. From the measured quantum efficiency in the long wavelength range it is evident that the passivation quality of the different oxides basically is the same. Table II summarizes the effective surface recombination velocity of the rear that has been extracted by the PC1D simulation. As would be expected from the EQE measurement of the extracted effective surface recombination velocities (including recombination at the metal contacts) for the respective oxide passivation

layers are in a very close range of 80 to 100 cm/s. Thus, within the measurement accuracy of the EQE as well as the simulation that was applied for the extraction of the SRV (contribution of the rear side LFC contacts can not be extracted) it can be stated that the quality of the rear side passivation of the different oxides seems to be the same.

Hence, the wet oxide grown from purified steam is well suited for the application as the rear side passivation of high-efficiency LFC solar cells.

Table II Effective surface recombination velocity of the rear (including recombination at the metal contacts) extracted from the EQE measurements shown in Fig. 6.

Rear side	Effective surface recombination velocity of the rear [cm/s]
Dry SiO ₂ (97 nm)	90
Wet SiO ₂ (110 nm) purified steam	80
Wet SiO ₂ (95 nm) pyrolytic generation	100

4 CONCLUSIONS

Wet oxides grown from purified steam have been shown to provide a high level of surface passivation that at least is comparable to wet oxides grown by the standard process, where the water vapor is introduced by the pyrolytic generation from high purity gases (H₂, O₂). The rear side of laboratory type LFC solar cells has been passivated by a wet oxide grown from purified steam at a temperature of 850°C. As a reference also a standard wet oxide grown at the same temperature as well as a dry oxide grown at 1050°C has been applied for the LFC solar cells. For all cells conversion efficiencies well above 20% could be achieved. The average open-circuit voltages for the different rear side passivation layers lie in a very close range of 648.4 mV for the wet oxide grown from purified steam to 650.6 mV for the dry oxidation. The effective rear surface recombination velocity that was extracted from the measured quantum efficiency for all oxides is in the range of 80 to 100 cm/s. Thus, the wet oxides grown from purified steam seem to be well suited for the rear side passivation of LFC solar cells.

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6 REFERENCES

- [1] A.W. Blakers, A. Wang, A.M. Milne, J. Zhao and M.A. Green, *Applied Physics Letters* 55 (1989) 1363.
- [2] G. Agostinelli, P. Choulat, H.F.W. Dekkers, S. De Wolf and G. Beaucarne, *Proceedings of the 20th European Photovoltaic Solar Energy Conference, Barcelona, Spain (2005)* 647.
- [3] E. Schneiderlöchner, R. Preu, R. Lüdemann and S.W. Glunz, *Progress in Photovoltaics: Research and Applications* 10 (2002) 29.
- [4] J. Schmidt and A.G. Aberle, *Journal of Applied Physics* 85 (1999) 3626.
- [5] S. Dauwe, L. Mittelstädt, A. Metz and R. Hezel, *Progress in Photovoltaics: Research and Applications* 10 (2002) 271.
- [6] M. Hofmann, S. Kambor, C. Schmidt, D. Grambole, J. Rentsch, S.W. Glunz and R. Preu, *Advances in OptoElectronics* 2008 (2008) 1.
- [7] J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M.C.M. van de Sanden and W.M.M. Kessels, *Progress in Photovoltaics: Research and Applications* 16 (2008) 461.
- [8] J. Zhao, A. Wang and M.A. Green, *Progress in Photovoltaics: Research and Applications* 7 (1999) 471.
- [9] D. Biro, S. Mack, A. Wolf, A. Lemke, U. Belledin, d. Erath, B. Holzinger, E.A. Wotke, M. Hofmann, L. Gautero, et al., *Proceedings of the 34th IEEE Photovoltaic Specialists Conference, Philadelphia, USA (2009)*.
- [10] A. Wolf, A. Walczak, S. Mack, E.A. Wotke, A. Lemke, C. Bertram, U. Belledin, D. Biro and R. Preu, *Proceedings of the 34th IEEE Photovoltaic Specialists Conference, Philadelphia, USA (2009)*.
- [11] S. Mack, A. Lemke, A. Wolf, B. Holzinger, M. Zimmer, D. Biro and R. Preu, *Proceedings of the 34th IEEE Photovoltaic Specialists Conference, Philadelphia, USA (2009)*.
- [12] O. Schultz, S.W. Glunz and G. Willeke, *Progress in Photovoltaics: Research and Applications* 12 (2004) 553.
- [13] R.A. Sinton, A. Cuevas and M. Stuckings, *Proceedings of the 25th IEEE Photovoltaic Specialists Conference, Washington DC, USA (1996)* 457.
- [14] A. Cuevas, P.A. Basore, G. Giroult-Matlakowski and C. Dubois, *Journal of Applied Physics* 80 (1996) 3370.
- [15] A. Mette, C. Schetter, D. Wissen, S. Lust, S.W. Glunz and G. Willeke, *Proceedings of the 4th World Conference on Photovoltaic Energy Conversion, Waikoloa, Hawaii, USA (2006)* 1056.
- [16] M. Wolf and H. Rauschenbach, *Advanced Energy Conversion* 3 (1963) 455.
- [17] P.A. Basore and D.A. Clugston, *Proceedings of the 25th IEEE Photovoltaic Specialists Conference, Washington D C (1996)* 377.