Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 8 (2011) 47–51

Energy Procedia

SiliconPV: 17-20 April 2011, Freiburg, Germany

Impact of Hydrogen Concentration on the Regeneration of Light Induced Degradation

Georg Krugel*, Winfried Wolke, Juliane Geilker, Stefan Rein, Ralf Preu

Fraunhofer ISE, Heidenhofstr .2, 79110 Freiburg, Germany

Abstract

The permanent deactivation called regeneration of light induced degradation in p-type Czochralski silicon solar cells is analyzed in this paper. Industrial solar cells were fabricated with varying hydrogen concentration in the silicon nitride anti-reflection layer but with an otherwise identical setup. They are subsequently degraded, annealed and regenerated by simultaneous illumination and heating. Measurements of cell parameters reveal the crucial effect of hydrogen on the regeneration.

Keywords: degradation; regeneration; passivation

1. Introduction

Efficiencies of advanced cell concepts strongly depend on high carrier diffusion length. In boron-doped Czochralski silicon solar cells light induced degradation leads to a fundamental limitation of the bulk lifetime and consequently to a limited efficiency [1]. This is caused by the formation of recombination-active boron-oxygen complexes under illumination [2-5]. At higher temperatures these complexes reconstruct, thus a short anneal in the dark is a possibility to reverse the degradation. However, under illumination the recombination-active complexes form again. A permanent reversion of this degradation, which is called regeneration, can be achieved by simultaneously illuminating and heating the cell [6, 7].

* Corresponding author. Tel.: +49-761-4588-5829; fax: +49-761-4588-9250.
E-mail address: georg.krugel@ise.fraunhofer.de.

1876–6102 © 2011 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of SiliconPV 2011.
Open access under CC BY-NC-ND license. doi:10.1016/j.egypro.2011.06.100

This leads to an almost complete recovery of open circuit voltage and of the bulk carrier lifetime. A complete understanding of this process on the atomic level remains unclear.

It has been presumed that hydrogen diffusing out of the a-SiN:H anti-reflection layer into the bulk plays an important role during regeneration [8]. These attempts compare degradation and regeneration behavior from solar cells coated with hydrogen containing PECVD (plasma-enhanced chemical-vapor deposition) and hydrogen-free LPCVD (low pressure chemical-vapor deposition) silicon nitride. But apart from the difference in hydrogen concentration, temperature ramps for example also differ for both processes. Other experiments comparing cells coated with PECVD silicon nitride and cells with PA-ALD (plasma-assisted atomic layer deposition) aluminum oxide questioned the role of hydrogen during regeneration [9].

In the experiment presented here an identical setup is used to fabricate solar cells with different hydrogen concentrations in the silicon nitride layer. In this way different regeneration behaviors can be traced back directly to the hydrogen content.

2. Approach

Solar cells are fabricated on p-type Czochralski wafers with a resistivity of 3.2 Ohmcm and a thickness of 200 µm (Fig. 1). After the formation of random pyramids with an alkaline texture a phosphorus emitter (sheet resistance R_{sh}= 65 Ohm/sq.) is established using $POCl_3$, followed by a PSG etch.

The deposition of a SiN:H anti-reflection coating is used to achieve different hydrogen concentrations on the wafer surface and via a subsequent diffusion also in the silicon bulk. The silicon nitride anti-reflection layer is deposited by a twin magnetron mid-frequency sputter coater manufactured by Applied Materials. The hydrogen content of the layer can be varied by using different ammonia fluxes (high/medium/no) and by using an optional ammonia plasma pre-treatment [10, 11]. Cells with hydrogen containing PECVD silicon nitride coatings are fabricated as a reference. A standard screen printing and subsequent fast firing step is carried out for the contact formation.

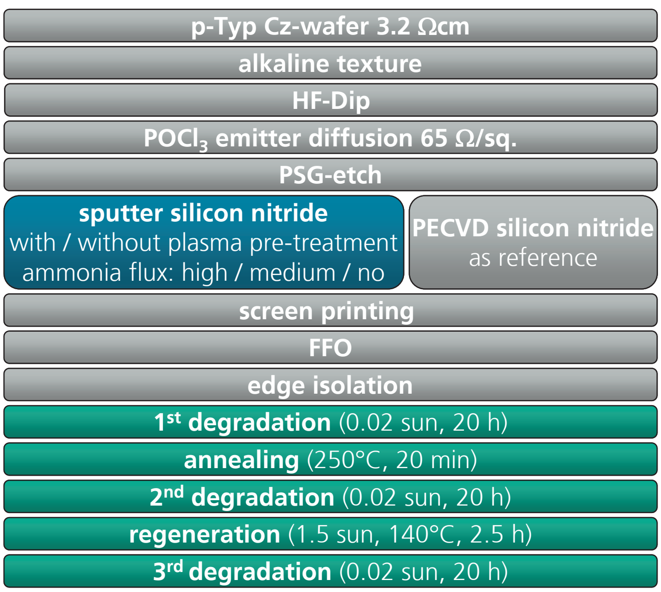

Fig. 1. Approach for analyzing the degradation, annealing and regeneration behavior.

A first degradation is followed by an annealing step to reconstruct the boron-oxygen complexes and determine the highest achievable open circuit voltages. After a second degradation the starting point for regeneration is reached. Cell parameters are measured before and after each degradation and annealing step and during regeneration.

For degradation the cells are illuminated with 50 W/m² (0.02 sun) for 20 hours. Annealing is done at 250°C for 20 min and regeneration is a combination of heating and illumination at 1.5 sun. The regeneration temperature is set to 140°C which is within the temperature range from 50°C to 220°C used in similar experiments [6-8]. Preliminary investigations show that a regeneration time of 2.5 h is sufficient.

3. Results and discussion

First the results in regard to the processed and degraded cells with varying silicon nitride coatings are shown in Fig. 2. It can be seen that a higher flux of ammonia leads to higher open circuit voltages and efficiencies which can be explained by a passivation of impurities and defects at the surface and in the bulk through hydrogen diffusion [10, 11]. Only cells with lower hydrogen content benefit from an additional plasma pre-treatment. Cells already containing higher fractions of hydrogen are not further improved. For reliable statistics every group consists of 14 wafers. Therefore differences observed between the groups are statistically relevant, even though they are only in the range of a few mV.

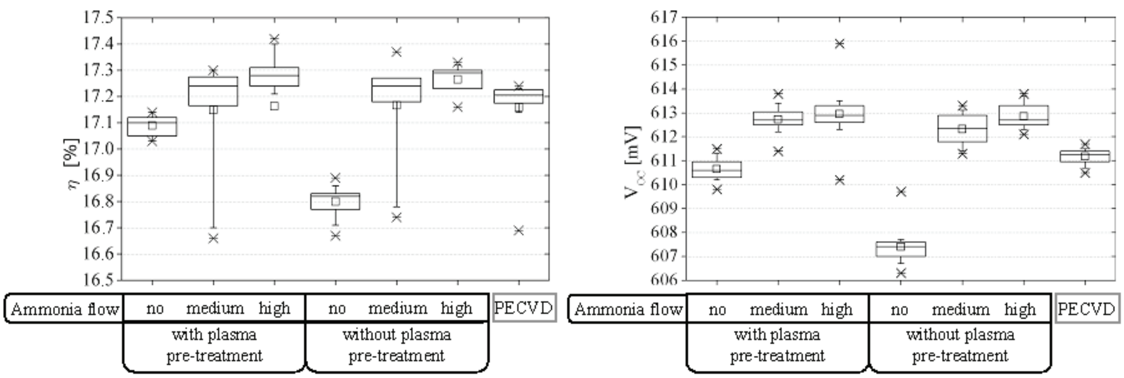

Fig. 2. Efficiency and open circuit voltage of degraded Cz solar cells with sputtered silicon nitride. Results for hydrogen containing PECVD wafers are shown as reference. Higher hydrogen concentration caused by higher ammonia flux leads to higher values. Only cells containing less hydrogen benefit from additional plasma pre-treatment.

For annealing, degradation and regeneration groups without and with high ammonia flux during sputtering of the silicon nitride layer (without plasma pre-treatment) are compared. Both groups consist of three wafers; three PECVD wafers are investigated as a reference. Fig. 3 shows the evolution of open circuit voltage and efficiency during this procedure.

In the first degradation and annealing cycle the typical decrease and increase in cell parameters is observed for all cells. The cells reach a metastable configuration after the annealing step and cell parameters decrease as a consequence in the following second degradation. A higher amount of hydrogen in the silicon nitride layer amplifies these effects. After the second degradation the starting point for the regeneration procedure is reached.

For wafers with high ammonia flux and thus high hydrogen concentration the highest increase in V_{OC} of 3.3 mV and efficiency of 0.3%^{abs} (averaged for three wafers) during the regeneration process is observed. In contrast, wafers without ammonia flux neither improve in V_{OC} (below 0.5 mV) nor in efficiency (0.0%^{abs}), nor in fill factor, nor in I_{SC}. For hydrogen containing PECVD wafers an increase of 2.9 mV and 0.2%^{abs} respectively is observed. These values stay nearly on the same level after a subsequent degradation.

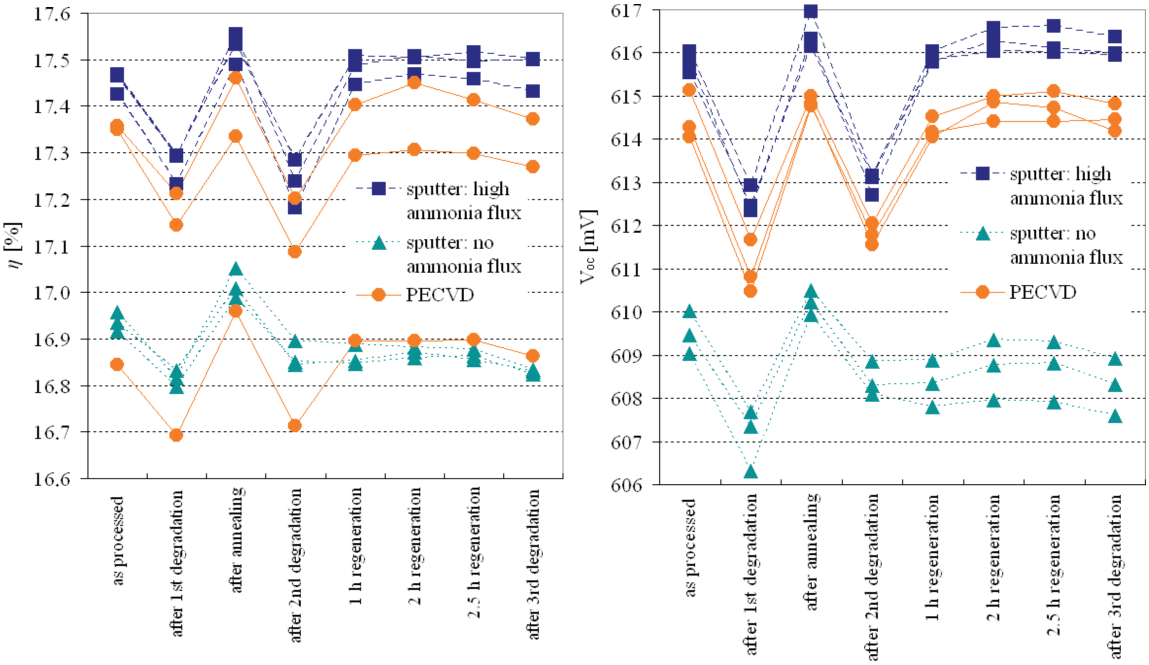

Fig. 3. Comparison during annealing, degradation and regeneration of cells with sputtered silicon nitride (high and no ammonia flux; without plasma pre-treatment) and PECVD silicon nitride coating; each group consists of three wafers. Cells containing a high hydrogen concentration benefit from the regeneration step and recover nearly completely. Cells without additional hydrogen in the silicon nitride layer do not regenerate and stay on the degraded level. Hydrogen containing PECVD cells also regenerate. One PECVD cell suffers from parasitic shunting and reaches only low efficiencies; nevertheless the regeneration behavior is identical.

This confirms the hypothesis that besides the passivation of interface and bulk defects hydrogen is also important for the regeneration of light induced degradation. This can be explained by a diffusion of hydrogen into the bulk material and interaction with harmful boron oxygen complexes during simultaneous illumination and heating. The observed effect would be even more eminent if material with a higher boron concentration is used. Nevertheless, the effect is clearly observable even at low concentrations.

4. Conclusion

An identical experimental procedure was used for the fabrication of industrial type solar cells from Cz wafer material with high and without hydrogen content in the silicon nitride layer. The regeneration of light induced degradation by simultaneously illuminating and heating was analyzed. A strong dependence on the hydrogen content in the silicon nitride layer for the regeneration behavior was observed. Open circuit voltage as well as efficiency of cells with high hydrogen concentration was improved. Cells containing hardly any hydrogen in the silicon nitride layer stayed in the degraded state. Therefore this experiment clearly supports the assumption that hydrogen plays a key role during regeneration. This can be used for further optimization of Czochralski silicon solar cells.

Acknowledgements

Parts of this work have been funded by Applied Materials, Alzenau. Support of Deutsche Bundesstiftung Umwelt is gratefully acknowledged.

References

[1] Bothe K, Sinton R, Schmidt J. Fundamental boron-oxygen-related carrier lifetime limit in mono- and multicrystalline silicon. *Progr Photovolt Res App l*2005;**13**:287-96.

[2] Schmidt J, Aberle AG, Hezel R. Investigation of carrier lifetime instabilities in Cz-grown silicon. *Proceedings of the 26th IEEE Photovoltaic Specialists Conference* 1997, Anaheim, California, USA, p. 13-18

[3] Glunz SW, Rein S, Warta W, Knobloch J, Wettling W. On the degradation of Cz-silicon solar cells. *Proceedings of the 2nd World Conference on Photovoltaic Energy Conversion* 1998, Vienna, Austria, p. 1343-6

[4] Rein S, Diez S, Falster R, Glunz SW. Quantitative correlation of the metastable defect in Cz-silicon with different impurities. *Proceedings of the 3rd World Conference on Photovoltaic Energy Conversion* 2003, Osaka, Japan, p. 1048-52

[5] Voronkova VV, and Falster R. Latent complexes of interstitial boron and oxygen dimers as a reason for degradation of silicon-based solar cells. *J Appl Phys* 2010;**107**,053509.

[6] Herguth A, Schubert G, Kaes M, Hahn G. Avoiding boron-oxygen related degradation in highly boron doped Cz silicon. *Proceedings of the 21st European Photovoltaic Solar Energy Conference* 2006, Dresden, Germany, p. 530-7

[7] Lim B, Hermann S, Bothe K, Schmidt J, Brendel R. Permanent deactivation of the boron-oxygen recombination center in silicon solar cells. *Proceedings of the 23rd European Photovoltaic Solar Energy Conference* 2008, Valencia, Spain, p. 1018-22

[8] Münzer KA. Hydrogenated silicon nitride for regeneration of light induced degradation. *Proceedings of the 24th European Photovoltaic Solar Energy Conferenc*e 2009, Hamburg, Germany, p. 1558-61

[9] Lim B, K Bothe, Schmidt J. Impact of oxygen on the permanent deactivation of boron–oxygen-related recombination centers in crystalline silicon. *J Appl Phys* 2010.**107**,053509.

[10] Wolke W, Kathodenzerstäubung zur Beschichtung von kristallinen Silizium-Solarzellen, Dissertation, Universität Freiburg, 2005

[11] Wolke W, Jäckle A, Preu R, Wieder S, Ruske M. SiN:H anti-reflection coatings for c-Si solar cells by large scale inline sputtering. *Proceedings of the 19th European Photovoltaic Solar Energy Conference* 2004, Paris, France, p. 419-22