INFLUENCE OF EMITTER PROFILE CHARACTERISTICS ON THERMAL STABILITY AND PASSIVIATION QUALITY OF A-SI/SIN$_X$-PASSIVATED BORON EMITTERS

M.Kessler[1], S.Gatz[1], P.Altermatt[2], N.-P.Harder[1,3], and Rolf Brendel[1,2]
[1] Institute of Solar Energy Research Hameln (ISFH), Am Ohrberg 1, 31860 Emmerthal, Germany
[2] Institute of Solid-State Physics, University of Hannover, Appelstrasse 2, 30167 Hannover, Germany
[3] Institute of Electronic Materials and Devices, University of Hannover, Schneiderberg 32, 30167 Hannover, Germany

ABSTRACT

We present emitter saturation current densities (J_{0E}) of different types of BBr_3 furnace-diffused boron emitters for a range of different sheet resistances on planar an textured surfaces: (a) "oxidized" emitters with an extended drive-in phase under oxygen and (b) "industrial" emitters without such additional drive-in step. Upon passivation with amorphous silicon – silicon nitride (a-Si/SiN$_X$) stacks on planar surfaces we measure the J_{0E} as a function of annealing time at 500 and 600°C respectively. The oxidized boron emitters show thermal stability up to 600°C with a stable J_{0E} of 13 ± 2 fA/cm^2 for 90 Ω/□. This is comparable to p^+ emitter performance after passivation by ALD-deposited Al_2O_3. The "industrial type" 90 Ω/□ emitter shows a J_{0E} of 47 ± 5 fA/cm^2 after annealing at 600°C due to a higher boron surface concentration and enhanced recombination within the emitter volume. Our a-Si/SiN$_X$ passivated emitters on textured surfaces exhibit about 50% higher J_{0E} values than emitters on planar surfaces, which corresponds well with the increased area of the KOH-textured wafers.

INTRODUCTION

BBr_3 boron diffused p^+-emitters on *n*-type silicon are suitable for the fabrication of high efficiency solar cells [1]. Cz *n*-type material features some advantages in comparison to *p*-type material in terms of higher minority carrier lifetimes [2,3] and no degradation of the carrier lifetime due to boron-oxygen complexes [4]. Nevertheless *n*-type material is little spread in industrial production, most probably due to the lack of industrial applicable p^+-emitter passivation techniques and the technological complexity of the boron diffusion process which might lead to bulk lifetime reduction for a certain set of process parameters [5,6]. Recently there has been a lot of investigations regarding different passivation schemes on p^+-type emitters showing good passivation qualiy for boron- and also aluminum-doped emitters: Chen [7] (SiN$_X$), Altermatt [8] (*a*-Si,SiO_2) and Plagwitz [9] (*a*-Si/SiN$_X$) showed different techniques which result in emitter saturation current densities comparable to n^+-type emitters. Latest publications on passivation schemes for boron emitters from Hoex *et al.*, Schmidt *et al.* [10,11] (Al_2O_3), and Mihailetchi [12] (chemical SiO_2) show excellent passivation quality. However, the different published values for emitter saturation current densities are difficult to compare between each other, as the corresponding emitter profiles are not shown in some cases. Annealing at temperatures above 350°C, 400°C [8], 425°C [11] and 450°C [7] is necessary in order to reach a good surface passivation. A possible explanation for the need of the annealing step is the diffusion of hydrogen to the silicon interface and a saturation of the dangling bonds for H_2 containing dielectrics. Also for the negatively charged plasma deposited dielectric Al_2O_3 an annealing step is indispensable in order to achieve an optimum surface passivation [13]. All of these passivation schemes have been investigated on planar surfaces and systematic data about textured p^+-type emitters are – to the authors' knowledge - not available in literature. Mönch [14] showed the dependence of *a*-Si passivation quality on the crystallographic orientation of the silicon substrate and found increased passivation quality for <111> oriented material. Si wafers cut along the <100> plane can be etched in KOH to obtain a surface texture of random pyramids with <111> oriented facets. Consequently, one should expect a very high surface passivation quality by *a*-Si locally on the facets of the texture pyramids. This benefit might be slightly mitigated by the enhanced surface area of textured samples and thus the overall ("macroscopic") surface passivation quality could be expected to be essentially identical for planar and textured samples. However, a recent publication of McIntosh *et al.* [15] summarizes studies comparing passivated planar and textured n^+-type emitter and shows that the ratio of measured surface-J_{0E} values ranges between 0.5 and 10 for the different surface topographies.

In this work we investigate the passivation quality of an *a*-Si/SiN$_X$ double layer stack for passivating textured and planar BBr_3 furnace-diffused emitters of two types: (a) "oxidized" emitters with an extended drive-in phase under oxygen and (b) "industrial" emitters without such additional drive-in step. We investigate the thermal stability of the planar emitters and provide data of the saturation current density J_{0E} as a function of emitter sheet resistance for textured surfaces.

EXPERIMENTAL

To analyze the effect of different emitter profile characteristics and silicon surfaces we diffuse boron into n-type wafers in order to prepare symmetrical p^+np^+-samples. We use 125x125 mm^2 <100> oriented Cz *n*-type material with a bulk resistivity of 6-9 Ωcm. Parts of the samples are textured in a KOH-IPA solution. For all samples the boron emitter is prepared by a BBr_3 boron diffusion. We vary the emitter sheet resistance by varying the drive-in diffusion temperature between 850 and 970°C holding all other diffusion parameters constant. Half of the boron-diffused planar samples are oxidized under water steam atmosphere directly after the boron diffusion process at 1000°C for 60min without removing the boron silicate glass (BSG). We call these emitters, that were prepared with this additional oxidizing drive-in step "oxidized" emitters. Similarly to the planar samples, half of the textured samples receive a high temperature drive-in treatment at 1000°C under N_2 and dry O_2 atmosphere for 60 and 30min, respectively. However, in case of the textured wafers we removed the BSG with HF prior to the oxidizing drive-in step. The initial 60 min nitrogen process step for creating "oxidized" emitters on textured surfaces is done in order to achieve deep diffusions, but only little depletion from boron segregation into the SiO_2. For simplicity, we will from hereon refer to all boron emitters prepared with post-diffusion oxidation as "oxidized emitters". As such additional post-diffusion high-temperature step does not appear to be desirable for industrial production, we refer to the non-oxidized emitters by the term "industrial type emitter". Figure 1 shows the resulting characteristics of both emitter types measured by the

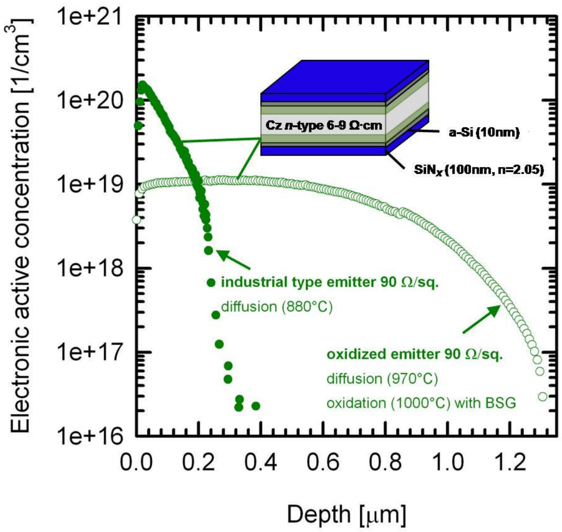

Figure 1 Emitter profiles of oxidized and industrial type emitter for planar samples with a sheet resistance of 90 ± 2 Ω/□ measured by the ECV method [16]. The symmetric sample structure is shown in the inset.

electrochemical capacitance voltage (ECV) method [16]. The sample structure - measured by means of scanning electron microscopy (SEM) – is shown in the inlet of Figure 1. The emitter profiles yield a sheet resistance of 90 ± 2 Ω/□ but differ in terms of surface and peak concentration as well as junction depth. Despite of the identical sheet resistance, the overall amount of electronically active boron atoms for the industrial type emitter is $1.33 \cdot 10^{13}$ and only $8.61 \cdot 10^{12}$ [cm^{-2}] for the oxidized emitter. This is due to the variation in hole mobilities [17] for different hole concentrations. As these emitters are still "transparent emitters" (diffusion length longer than depth of the emitter) we can already conclude that even for perfect surface passivation the 1.54-times higher number of majority charge carriers in the industrial emitter leads to enhanced Auger recombination within the emitter volume: $R_{Auger} \sim n \cdot p^2 = n \cdot N_{ACC}^2$ [18]. Furthermore, the shallow, but locally heavier doped industrial type emitter causes stronger band-gap narrowing and thus higher effective intrinsic charge carrier density $n_{i,eff}$, which also leads to increased recombination.

Prior to *a*-Si deposition the samples are laser cut to 40x40 mm^2, received an RCA clean and are rinsed in deionized water. Amorphous silicon is then deposited onto both sides of the sample by PECVD at a temperature of 225°C [19]. The resulting layer thickness is 10 ± 1 nm as measured by ellipsometry on a planar glass reference. For the enhanced surface area of the textures samples we expect locally an *a*-Si thickness of 7nm, which is still sufficient to provide excellent passiviation [9]. Subsequently, we deposit SiN_X with an refractive index of 2.05 and a thickness of 100 ± 10 nm onto both sides of the wafer at a temperature of 400 °C by PECVD (SiNA, Roth and Rau). Gatz *et al.* have shown previously, that the SiN deposition temperature of 400 °C ensures high thermal stability of the passivation quality of the *a*-Si/SiN_X stack on *p*-type silicon wafer substrates and on phosphorus diffused *n*-type emitters [19].

After passivation, the emitter saturation current densities are measured by means of quasi-steady state and transient photoconductance (PC) measurements [20,21]. The emitter saturation current density is determined by the Kane-Swanson method [22] for symmetrical samples. We assume an intrinsic carrier density of $n_i = 10^{10}$ in the bulk of the wafer and use the Auger-parameterization of Kerr *et al.* [23] in order extract the J_{0E} values. Samples are then annealed on a hotplate at 500°C for different durations up to 15 minutes. After each of these annealing steps we measure the emitter saturation current density. Afterwards, we anneal our samples at 600°C for 45 minutes and measure the J_{0E} value again.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows emitter saturation currents densities of two symmetric samples with planar surfaces determined by means of quasi steady state and transient PC measurements.

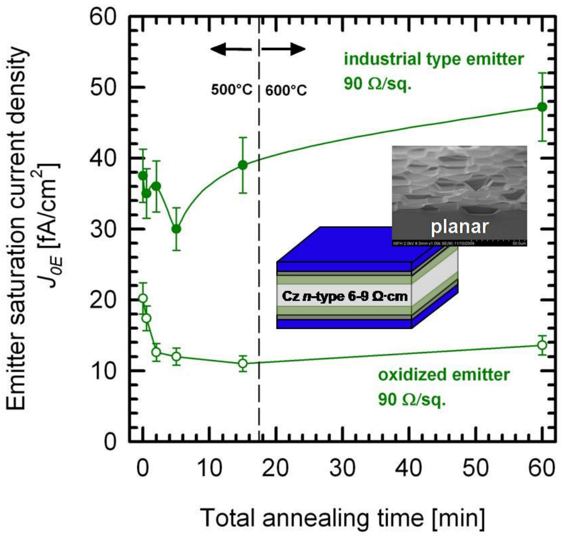

Figure 2 Emitter saturation current density *J_{0E}* of two planar samples with characteristically different emitter profile (see Figure 1). *J_{0E}* is plotted as a function of annealing time at 500 and 600°C. The symetric sample structure as well as the surface structure (SEM image) is shown in the inset. The lines are guides to the eye, only.

After passivation the oxidized emitter shows a low J_{0E} of 20 ± 2 fA/cm^2 whereas the industrial type emitter shows a value of 38 ± 4 fA/cm^2. Optimum passivation quality is achieved in both cases by annealing the sample at 500°C for 5 min: 11 ± 1 fA/cm^2 and 30 ± 3 fA/cm^2 respectively. The improvement of the passivation is assumed to be due to diffusion of hydrogen to the a-Si/Si interface where it saturates dangling bonds [9]. Note that the SiN is an efficient source of hydrogen in addition to the hydrogen within the *a*-Si. We find that annealing at lower temperatures (400 and 450°C) also results in increased passivation quality but the effect is less pronounceed than at 500°C. Interestingly, the two types of samples react differently upon further annealing at 500°C: The saturation current density J_{0E} of the oxidized emitter remains constant or even slightly profits from annealing additional 10 minutes at 500°C (cumulative annealing time 15 minutes). In contrast, the J_{0E} of the "industrial type" emitter with higher surface dopant density increases, that is it becomes worse upon further annealing at 500°C. This effect may be explainable in terms of lower silicon-hydrogen bonding stability in *a*-Si films that are in contact with heavily *p*-type doped material as was shown by De Wolf and Kondo [24]. Annealing at 600°C results in further J_{0E} increase of the industrial type emitter. In contrast to this, the passivation quality of the oxidized emitter stays essentially constant. We find the same phenomenology also for the other emitters of our investigation (not shown in Figure 2):

- General improvement of the passivation quality and thermal stability of the oxidized emitter with moderate surface doping densities
- J_{0E} improvement only in the initial phase of annealing and J_{0E} increase (degradation) upon further annealing for the "industrial type" emitter with high surface doping concentration.

Our results differ significantly to the results shown by Gatz *et al*. on *n*-type surfaces: Gatz *et al*. observed degradation of the passivation quality on phosphorus diffused *n*-type emitters with sheet resistance of 90 Ω/□ n^+pn^+, yielding appr. 200 fA/cm^2 after annealing at 600°C. The reasons for these contrasting results are not yet clear. The comparatively low thermal stability observed by Gatz *et al.* on *n*-type surfaces and our relatively stable J_{0E} values on *p*-type surfaces may contradict attempts to explain the annealing (thermal) stability of the *a*-Si passivation in terms of the lower Si-H bonding stability for *a*-Si films in contact with heavily doped *p*-type silicon [24].

We have also done J_{0E} measurements on textured samples and find that the J_{0E} characteristics as a function of annealing time and temperature is similar to the J_{0E} characteristics of the planar emitters shown in Figure 2. Therefore we use these optimum annealing conditions (500°C for 5 minutes) for annealing our textured samples.

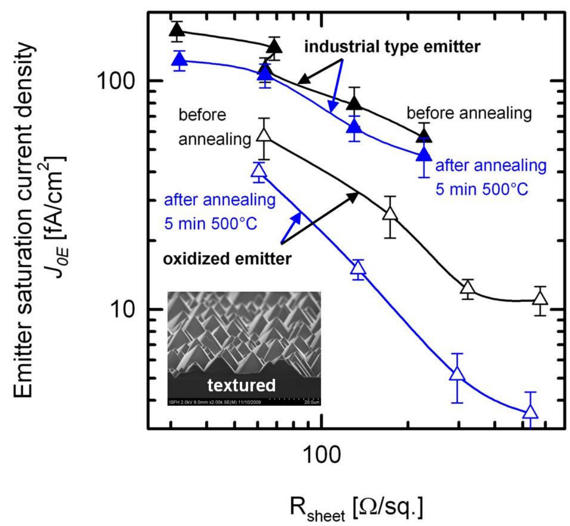

Figure 3 Emitter saturation current density *J_{0E}* of textured samples of industrial type and oxidized emitters as a function of sheet resistance before and after annealing for 5 min at 500°C. A SEM image of the sample surface is shown in the inset of Figure 3. The lines are guides to the eye, only.

Figure 3 shows J_{0E} values of symmetric textured samples before and after annealing for 5min at 500°C, plotted as a function of sheet resistance. Again a SEM image of the surface is shown in the inset of Figure 3. The J_{0E} values for both types of emitters ("oxidized" and "industrial type") decrease (improve) upon annealing at 500°. For all sheet resistances, the oxidized emitter shows lower J_{0E} values, as was also found for the planar samples. In both cases the low J_{0E} values allow to conclude that the *a*-Si/SiN_X stack shows excellent passivation quality on textured surfaces as well. The J_{0E} values are slightly higher compared to J_{0E} values of planar emitters with similar sheet resistance (not shown in Figure 3). This slightly higher J_{0E} values for textured samples can be explained by an increasing number of edges and vertices for a textured surface and is in accordance with other experimental observations summarized by McIntosh and Johnson [15].

Figure 4 shows a summary of different passivation schemes on boron emitters published by Schmidt *et al.* [25] including values from this work for *a*-Si/SiN_X passivated oxidized boron emitters on planar and textured surfaces after annealing at 500°C for 5 min.

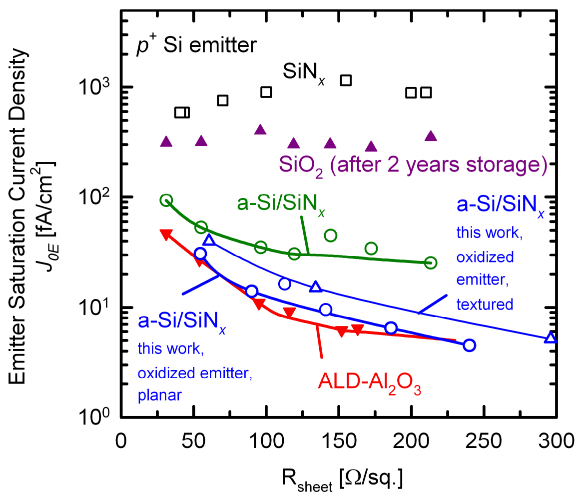

Figure 4 Emitter saturation current density J_{0E} for a-Si/SiN_X passivated oxidized boron emitters on planar and textured surfaces from this work. Values for differrent passivation schemes of planar boron emitters as a function of sheet resistance published by Schmidt *et al.* [25] are included into Figure 4 for comparison. The lines are guides to the eye, only.

The corresponding emitter profiles for the presented J_{0E} data from Schmidt *et al.* in Figure 4 only differ slightly from the emitter characteristics of the "oxidized emitter" we present in this paper: Their emitters feature higher surface doping concentrations (factor 1.25 - 2), lower peak doping concentrations (factor 0.65 – 0.85) and a higher junction depths (factor 1.2 – 1.4) for emitters with comparable sheet resistance. Therefore, the emitter volume recombination is comparable for emitters of the same sheet resistance for both investigations. As the J_{0E} summarizes emitter volume and emitter surface recombination, we are able to compare the emitter surface recombination of Schmidt *et al.* to the emitter surface recombination of samples from this work: We conclude that the emitter surface recombination of the *a*-Si/SiN_X passivated oxidized boron emitters from this work might differ from the emitter surface recombination of ALD-Al_2O_3 passivated boron emitters from Schmidt *et al.,* but – in both cases – can be considered negligible.

SUMMARY

We present excellent saturation current densities J_{0E} of planar and textured boron diffused *p*-type emitters with passivation by a-Si/SiN_X stacks, which are comparable to atomic layer deposited (ALD) Al_2O_3 passivation: The J_{0E} values of our a-Si/SiN passivated boron emitters decrease upon annealing at 500°C and the optimum annealing time was found to be approximately 5min. Upon annealing at 600°C J_{0E} values of the industrial type emitter increase in contrast to the thermally stable "oxidized emitters". We associate this effect of different thermal stability with a higher surface doping concentration. Out diffusion of hydrogen and the possibility of crystallization of the amorphous silicon layer at elevated temperatures appear to be probable mechanisms for the degradation of the passivation.

ACKNOLEDGEMENT

Funding was provided by the German State of Lower Saxony and the German Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU).

REFERENCES

[1] J. Benick, B. Hoex, G. Dingemanns, A. Richter, M. Hermle, and S.W. Glunz, 24th European PVSEC, Hamburg, 2009

[2] A. Cuevas, M. Kerr, C. Ferrazza, and G. Coletti, *Appl. Phys. Lett.* **81**, 4952, 2002

[3] D. MacDonald and L.J. Gerlings, *Appl. Phys. Lett.* **85** 4061, 2004

[4] K. Bothe, R. Sinton, and J. Schmidt, *Prog. Photovoltaics* **13** 287, 2005

[5] M. Kessler, T. Ohrdes, B. Wolpensinger, N.-P. Harder, "Charge carrier lifetime degradation in Cz silicon through the formation of a boron-rich layer during BBr_3 diffusion processes", *Semicond. Sci. Technol.* **25** (2010) 055001.

[6] P. J. Cousins and J. E. Cotter "The influence of diffusion-induced dislocations on high efficiency silicon solar cells" *IEEE T. Electron Dev.* **53** 457-464, 2006

[7] F. Chen, *Appl. Phys. Lett.* **88** 263514, 2006

[8] P.P. Altermatt, H. Plagwitz, R. Bock, J. Schmidt, R. Brendel, M.J. Kerr, A. Cuevas, "The surface recombination velocity at boron-doped emitters: comparison between various passivation techniques", Proceedings 21st European Photovoltaic Solar Energy Conference, 647-650, Dresden, Deutschland, September, 2006

[9] H. Plagwitz, PhD Thesis, ISFH, Leibniz Universität Hannover, 2007

[10] B. Hoex, J. Schmidt, R. Bock, P.P. Altermatt, M.C.M. van de Sanden and W.M.M. Kessles, *Appl. Phys. Lett.* **91**, 112107, 2007

[11] J. Schmidt, B. Veith, R. Brendel, *Phys. Status Solidi RRL* **3**, No. 9, 287–289 (2009)

[12] V.D. Mihailetchi, Y. Komatsu, and L.J. Geerlings, "Nitrid acid pretreatment for the passivation of boron emitters for n-type base silicon solar cells", *Appl. Phys. Lett.* **92**, 063510, 2008

[13] B. Hoex, J.J.H. Gielis, M.C.M. van de Sanden, W.M.M. Kessles, *JAP* **104**, 113703,2008

[14] W. Mönch, Semiconductor surfaces and interfaces, chapter 9 and 14. Springer series in surface science. Springer-Verlag, Belin/Heidelberg, 3rd Edition, (2001).

[15] K. McIntosh and L. Johnson, „Recombination at textured silicon surfaces passivated with silicon dioxide“, *J. Appl. Phys.* **105**, 124520

[16] E. Peiner, *J Electrochem. Soc.* **142**, 576, (1995)

[17] D.B.M. Klaassen, *Solid-St. El.* **35**, 953 (1992)

[18] M.J. Kerr and A. Cuevas, *J. Appl. Phys.* **91**, 2473 (2002)

[19] S. Gatz, H. Plagwitz, P.P. Altermatt, B. Terheiden, and R. Brendel "Thermal stability of amorphous silicon/silicon nitride stacks for passivating crystalline silicon solar cells", *Appl. Phys. Lett.* **93**, 173502 (2008); DOI 10.1063/1.3009571.

[20] R.A. Sinton and A. Cuevas, *Appl. Phys. Lett.* **69**, 2510 (1996)

[21] H. Nagel, C. Berge, and A Aberle, *J. Appl. Phys.* **86**, 6218, 1999

[22] D.E. Kane and R.M. Swanson, in Proceedings of the 18th IEEE PVSC (IEEE, New York, 1985), p.578

[23] M.J. Kerr, A Cuevas, „A general parameterization of Auger recombination in crystalline silicon", *J. Appl. Phys*. **91**(4): 2473-2480

[24] De Wolf and Kondo, J. Appl. Phys. **105**, 103707, 2009

[25] J. Schmidt, A. Merkle, R. Bock, P.P. Altermatt, A. Cuevas, N.-P. Harder, B. Hoex, R. van de Sanden, E. Kessels, R. Brendel, 23rd European Photovoltaic Solar Energy Conference, Valencia, 2008