IMPROVEMENTS IN THE PASSIVATION OF P$^+$-SI SURFACES BY PECVD SILICON CARBIDE FILMS

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ABSTRACT

We present further results of a surface passivation study of p$^+$-Si emitters by both intrinsic and boron-doped amorphous SiC$_x$ films, deposited in two different standard PECVD reactors. For comparison, thermally grown SiO$_2$ and PECVD-SiN$_x$ layers with refractive indices of n=2.0 and n=2.4 were examined on the same test structures. While thermal SiO$_2$ exhibits passivating properties comparable to those on n$^+$-Si emitters, PECVD-SiN$_x$ is found to even deteriorate the surface passivation, especially after firing (without metal contacts).

On the other hand, PECVD-SiC$_x$ yields, to our knowledge, the best p$^+$-Si passivation so far obtained by an industrially relevant low temperature process. It is expressed by an implied V$_{oc}$ of 635 mV for a symmetrically 60 Ω/sq BBr$_3$-diffused n-type Cz-wafer with a base resistivity of 4.6 Ωcm.

INTRODUCTION

There are two important applications for the passivation of p$^+$-silicon surfaces: one is the diffused back side of p-type Si solar cells in cell concepts with open rear contacts and rear side passivation.The second is the emitter of n-type Si solar cells which might, for several reasons, hold a major and possibly even the dominant share in silicon solar cell production in the future [1,2].

REVIEW OF P$^+$ SURFACE PASSIVATION

Thermally grown SiO$_2$ has shown excellent surface passivating properties of both n$^+$- and p$^+$-Si layers, but does not provide hydrogen for defect passivation which is especially important for the industrially dominating mc-Si and therefore requires an additional annealing step under H-atmosphere. Another drawback is the high temperature needed to achieve acceptable growth rates, as it usually deteriorates the bulk lifetime and increase the thermal budget of the device. Using wet oxidation, this effect is reduced, but still present in mc-Si like for the recently presented record-efficiency mc-Si solar cell from the Fraunhofer ISE [3]. The high growth temperatures also cause a surface depletion in the doping concentration of the emitter, assumed to reduce the cell efficiency due to increased surface recombination and to deteriorate the long-term stability [4]. The problem of the low refractive index of SiO$_2$ (n=1.5) can indirectly be solved by growing very thin oxides (10 to 15 nm) and depositing an additional single or double layer ARC of different materials on the top. This yields very good results, but increases the number of necessary processing steps even further.

Another principal drawback for industrial mass production is the necessity for sophisticated surface cleaning and the fact that a thermal oxide requires tube furnace processing due to the sensitivity of its passivating quality to a very well cleaned surface. Both are disadvantageous for industrial mass-production.

For those reasons, PECVD-SiN$_x$ is the present industrial standard for the n$^+$-emitter of p-type Si solar cells, as it combines the advantages of good surface passivation of n$^+$-emitters, low deposition temperatures (usually approx. 400°C), bulk hydrogenation and a refractive index which can be adapted for various purposes by altering the Si-content of the deposited layer. However, reported experiments on PECVD-SiN$_x$ for the passivation of p$^+$-Si surfaces by Kerr [5] and Fischer [6] were unsatisfactory when using different sets of parameters approved for n$^+$-Si surfaces. As an explanation, both Kerr and Dauwe et al. [7] supposed independently the formation of an n-type inversion layer underneath the SiN$_x$ due to the high fixed positive charge density within the SiN$_x$ films, even under illumination. This leads to an injection-level dependent "depassivating" effect which could also be observed in experiments of our group (see Fig. 2b and 2c for an example).

EXPERIMENTS

Symmetrical p$^+$np$^+$ test structures as depicted in Fig.1 were prepared using two of our standard tube-furnace BBr$_3$-diffusions on shiny etched n-type Cz-Si wafers with resistivities of 2.8 and 4.6 Ωcm and thicknesses of 260-280 µm. They exhibited sheet resistances of 60 and 90 Ω/sq, respectively, and a surface boron doping concentration of about $4 \cdot 10^{19}$ cm^{-3}, determined by the Electrochemical Capacitance Voltage (ECV) method.

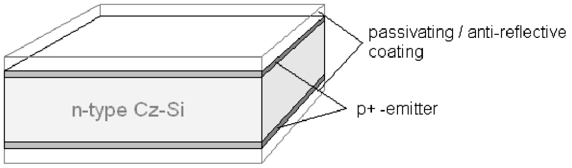

Fig. 1. Structure of the samples used for the experiments

A symmetrical sample allows easier and more precise extraction of passivation relevant parameters (e.g. implicit open circuit voltage (V_{oc}) by the QSSPC measurement method introduced by Sinton et al. in 1996 [8]. As the J_{oe} determined from QSSPC data using the “slope-method” does not make sense for SiN_x due to its special behaviour on p^+ Si (see Fig.2b, 2c and also [5]), the implied V_{oc} at 1-sun illumination was used as an indicator of the surface passivation quality for comparison of the applied passivation schemes.

RESULTS

Three different categories of samples (A, B, C) were used as described in table 1. The samples were measured with native oxide on the surface prior to the application of the different passivation schemes and exhibited the following characteristics, averaged over 10 samples:

Category – • $_{base}$ [Ωcm]	**R_{sheet} [Ω/sq]**	**implied V_{oc} $V_{oc,i}$ [mV]**	**j_{oe} [fA/cm²]**
A) – 2.8	90±5	596±5	1000±80
B) – 4.6	90±5	588±6	1000±90
C) – 4.6	60±4	596±6	960±90

Tab.1. Characteristics of the unpassivated samples. The difference in the implied V_{oc} between Category A) and B) is due to the different base doping of the wafers

Thermal SiO_2 and PECVD-SiN_x

As reference, a 10 nm thin thermal oxide was grown on both sides of two samples of category A), resulting in a j_{oe} of 80 fA/cm^2 and implied V_{oc}’s of 650 and 647mV, respectively.

Two samples received a PECVD-SiN_x coating with refractive indices of n_1=2.0 and n_2=2.4 in a direct-plasma reactor used for industrial solar cell production where the applied layers usually provide good surface passivation of n^+-emitters. The samples exhibited no improvement when measured directly after deposition, but showed clear deterioration after the usual contact firing step (without the metallic paste!). The implied V_{oc}’s decreased by 21 mV for the n=2.0 SiN_x covered sample and 29 mV for the one with the n=2.4 SiN_x which - on n^+-Si - provides better passivation than the n=2.0 SiN_x.

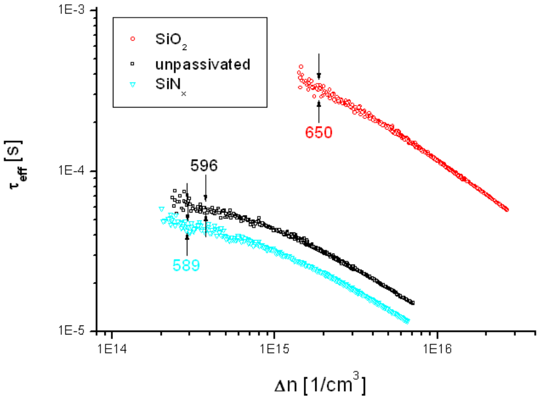

Fig. 2a. Deterioration of p^+-surface quality after deposition of SiN_x with n=2.0 on a sample of Category A). Arrows indicate 1-sun illumination, numbers at arrows indicate the corresponding implied V_{oc}

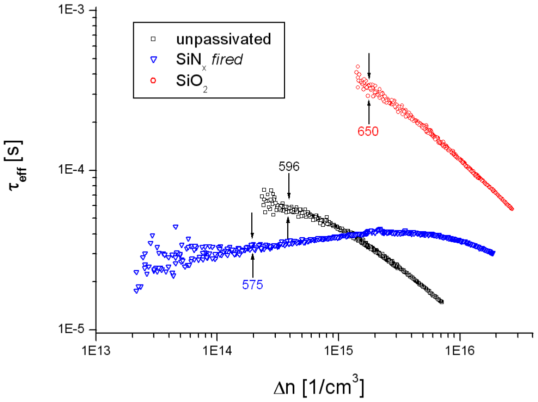

Fig.2b. Behavior of the same SiN_x-layer after a standard firing step (without metal paste). While there is a visible improvement in high injection, the injection level at 1-sun illumination (arrows), being relevant for solar cells, is now even further below that of the unpassivated sample.
According to simulations, this is most likely due to the counter-action of a) a reduction of the interface state density D_{it} by hydrogen, causing an improvement independent from the injection-level, and b) the formation of a high fixed positive surface charge of $>10^{12}$ cm^{-2}, especially detrimental for p^+-surfaces in lower injection.

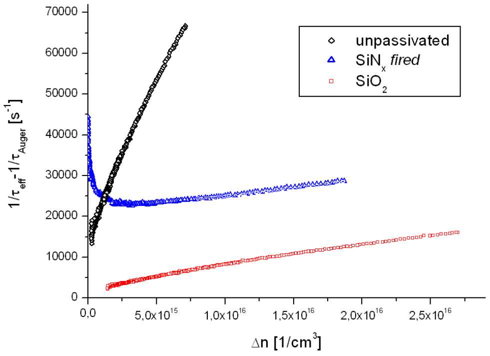

Fig. 2c. Values from Fig. 2b, displayed in the way usually applied to determine the j_{oe} of the emitter by the “slope-method”. The strong decrease of the lifetime in low injection of the fired SiN_x covered sample does not correspond with the j_{0e} calculated from the high injection region; therefore the slope method is not applicable here.

PECVD-SiC$_x$

In the PECVD-SiC_x experiments, silicon carbides of three different compositions were applied: a Si-rich intrinsic SiC_x which exhibited excellent surface passivation of p-type substrates [9] and also yielded the highest implied V_{oc}-value achieved with intrinsic SiC_x in our experiments so far. However, it shows, due to its higher silicon content, relatively high absorption for wavelengths $\lambda < 500$ nm when depositing films with thicknesses of 60 nm and more as would be required for ARC. Secondly, a stoichiometric SiC_x which is transparent down to below 400 nm wavelength and has a refractive index n around 1.97. This film provides less surface passivation of p- and n-type Si wafers than Si-rich films, but is excellent for anti-reflection coating. The third is similar to the intrinsic silicon-rich one but has an additional boron-doping, implemented by using diborane or trimethyl-borane (TMB) as dopand gas.

In order to combine the different advantages of the mentioned layers, we used stacks of the Si- and the C-rich film (Fig.3) for further investigations.

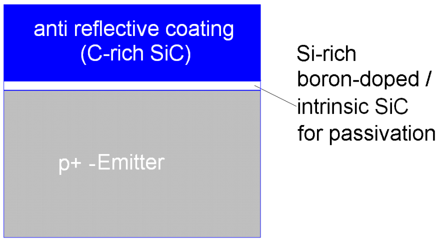

Fig. 3. Structure of the applied PECVD-SiC_x-stacks

SiC_x stacks prepared in the past with the thin Si-rich film deposited at 300 or 350°C and the C-rich layer on top deposited at 300°C showed a color-change after forming-gas annealing (FGA) and even more after firing. We attributed this to a loss of hydrogen from the layer, as past experiments had shown that deposited layers are less dense and contain more hydrogen the lower the applied deposition temperature [10]. However, this problem could be solved by optimizing deposition conditions and applying the higher deposition temperature of 350°C to both the C-rich and the Si-rich film.

In prior experiments depositing the intrinsic and the B-doped stack on the 90 Ω/sq emitter with 2.8 Ωcm base resistivity [11], implied V_{oc}‘s of 619 and 627 mV have been found (see Fig.6), respectively. The Si-rich part of these stacks was about 20 nm thick.

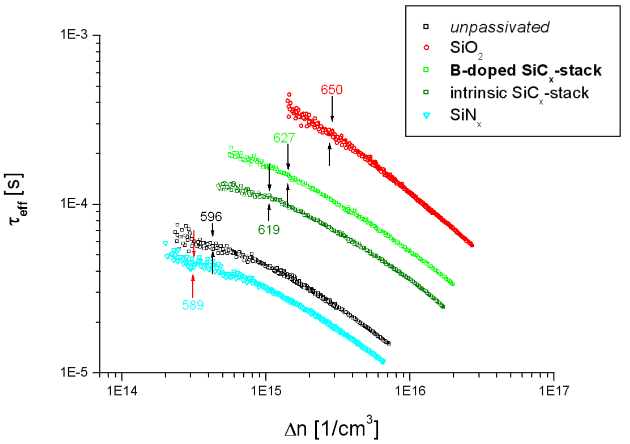

Fig. 4. Overview of the best results with PECVD-SiC_x on 90 Ω/sq on 2.8 Ωcm n-type Cz to PECVD-SiN_x and 10nm thin thermal SiO_2. Arrows indicate 1-sun illumination, numbers at arrows display the corresponding implied V_{oc}

When decreasing the thickness of the Si-rich part of the stack to 10 nm and thus reducing the absorption of this film by about 50 percent, a further improvement in the passivating quality could be found; it was achieved on the 60 Ω/sq emitter with 4.6 Ωcm base resistivity (see Fig. 5).

The best passivation applying the intrinsic stack is expressed by an implied V_{oc} of 632 mV and an effective lifetime τ_{eff} of 177 μs, that of the B-doped stack by $V_{oc,i}$ = 635 mV and τ_{eff} = 183 μs.

The influence of the two different thicknesses of the Si-rich film can be seen in Fig. 5. The lower implied V_{oc} of the 90 Ω/sq-sample with 20nm of Si-rich SiC_x compared to that in Fig. 4 can partially be explained by the lower base doping of the wafer, to which a drop of 10 mV is attributed.

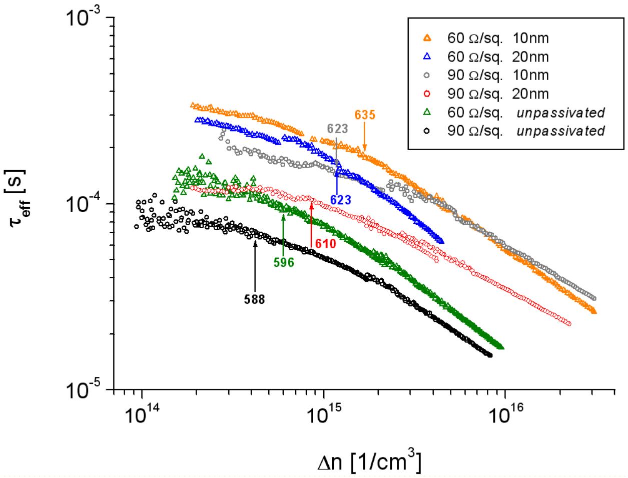

Fig. 5. Comparison of B-doped stacks with thicknesses of 10 and 20nm for the Si-rich layer on 4.6 Ωcm n-type Cz. Arrows indicate 1-sun illumination, numbers at arrows display the corresponding implied V_{oc}

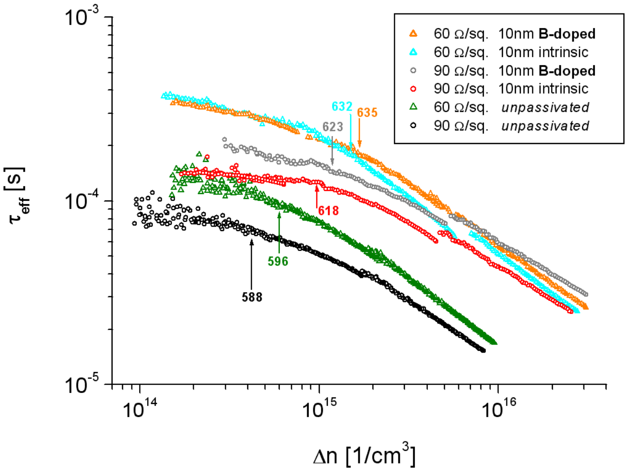

Fig. 6. Best passivation so far observed with intrinsic and B-doped SiC_x-stacks, resulting from 50% thinner Si-rich layer (10 nm) on 4.6 Ωcm n-type Cz Si-wafers with 60 and 90 Ω/sq. Arrows indicate 1-sun illumination, numbers at arrows display the corresponding implied V_{oc}

The reason for the better performance of the B-doped stack is not yet clear. It is assumed that the B-doping lowers the effect of the fixed positive charge Q_f within the SiC_x close to the p^+-Si which, in the intrinsic SiC_x, is about one order of magnitude lower than that in PECVD-SiN_x[10]. Future measurements of the effective Q_f might help to clarify this as well as further experiments with variations of the boron-concentration.

Concerning the contact resistance,the firing of screen-printed contacts through different SiC_x-anti reflection coatings, an important criterion for the application of PECVD-SiC_x in industrial mc-Si solar cell production, was recently investigated and works out well. Using the same firing parameters as for PECVD-SiN_x leads to a comparably low contact resistivity of around 6 mΩcm².

CONCLUSIONS AND OUTLOOK

PECVD-SiC_x was shown to passivate effectively p^+-Si surfaces, here surpassing PECVD-SiN_x and, to our knowledge, yielding the best passivation so far reported for p^+-Si using a low temperature process. B-doping of the Si-rich SiC_x yielded better results than the intrinsic one. A thinner and thus less-absorbing layer gives better passivation. It can be calculated that the best SiC_x -stack so far should be capable of an implied V_{oc} of almost 660 mV on 1 Ωcm n-type Si with the investigated 60 Ω/sq B-emitter. The problem of a color-change of the SiC_x-stack after firing, most likely attributed to a loss of hydrogen from the layer which causes deterioration of its surface passivation, can be avoided through higher deposition temperatures of 350°C and above.The firing of screen-printed contacts through different SiC_x-anti reflection coatings was investigated and works well using standard SiN_x firing parameters, yielding an equally low contact resistivity.

Further experiments will be performed to explore the potential of PECVD-SiC_x-layers, especially B-doped ones, balancing in between optimum surface passivation and best optical properties. PECVD-SiC_x has similar advantages like PECVD-SiN_x: low deposition temperatures, high deposition rates, an adjustable refractive index, and it can be deposited by the same high-throughput in-line PECVD processing reactors. We therefore consider it to be a promising candidate for future industrial silicon solar cell applications.

ACKNOWLEDGEMENTS

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