

**BULK AND SURFACE PASSIVATION BY SILICON NITRIDE GROWN BY REMOTE MICROWAVE PECVD**

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**ABSTRACT:** Surface and bulk passivating properties of SiN<sub>x</sub>:H layers deposited by Remote Microwave PECVD are investigated. We found that the N/Si ratio of the layers is dependent of the substrate temperature, which suggests that the layer growth is dominated by the arrival of separate SiH and NH species at the surface and not by the arrival of SiN<sub>x</sub>H<sub>y</sub> clusters formed in the plasma. SiN<sub>x</sub>:H layers with good surface passivating properties require different deposition conditions than layers with good bulk passivating properties. For good surface passivation, Si-rich layers are needed with relatively low H-concentrations. For layers which can provide good hydrogenation through firing, more stoichiometric and hydrogen rich layers are required in which the hydrogen is predominantly bonded to N-atoms. For p-type mc-Si Baysix wafers we found that SiN<sub>x</sub>:H induced hydrogenation can improve the bulk lifetime of charge carriers by more than 20 %. No synergistic effects of an Al BSF on this hydrogenation process, however, were observed.

Keywords: Passivation - 1: PECVD - 2: Silicon-Nitride - 3

**1. INTRODUCTION**

The efficiency of multicrystalline silicon solar cells can be significantly improved by applying SiN<sub>x</sub>:H as a passivating layer. SiN<sub>x</sub>:H namely not only acts as a surface passivating layer, but it can also induce bulk passivation of the silicon wafer. The latter effect can be accomplished by a thermal activation of the layer (e.g. during firing of a screen-printed metallisation) during which hydrogen diffuses from the SiN<sub>x</sub>:H into the silicon wafer where it passivates crystal defects and impurities.

Because of these outstanding properties of SiN<sub>x</sub>:H, a strong demand has grown for the development of industrial scale systems, capable of deposition of such layers. Recently, some different types of such high throughput PECVD systems have become available.

One of these systems is a Remote Microwave PECVD system, developed in co-operation between ECN and the company Roth&Rau. Two prototypes of such a system have been installed at ECN; one in which batches of 6 wafers can be processed (Reactor A) and one which is capable of continuous processing of 200 wafers per hour (Reactor B). We have shown that with such systems it is possible to grow SiN<sub>x</sub>:H layers with excellent passivating properties [1] and that the deposition process is robust when applied on industrial scale; i.e. when a large number of wafers is being processed [2].

In this paper we will address two specific aspects of the passivation provided by the SiN<sub>x</sub>:H layers, namely the effect of the substrate temperature on surface and bulk passivation properties and the possible assistance of an Al BSF to the bulk passivation. Both aspects are very relevant for the industrial application of SiN<sub>x</sub>:H layers grown by PECVD [3].

**2. REMOTE MICROWAVE PECVD**

The plasma source in the reactors is a new remote microwave plasma source, developed by Roth&Rau,

consisting of a quartz tube with a Cu antenna inside. The source is operated at a microwave frequency of 2.45 GHz. The source also includes an arrangement of permanent magnets for electron confinement in the plasma (see Figure 1). Different gasses can be used depending on the plasma technologic demands in the pressure range of about 0.01 to 500 mbar[4].

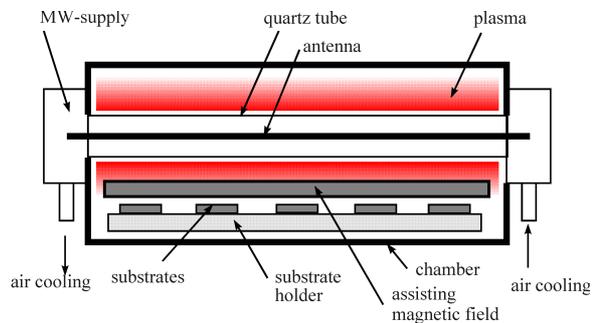


Figure 1: Schematic view of the microwave plasma source.

For the deposition of SiN<sub>x</sub>:H, NH<sub>3</sub> is injected close to the quartz tube. The strong EM field there causes an almost complete dissociation of the gas (by means of electron impact). The dissociation of the NH<sub>3</sub> is typically more than 95%. Somewhat more downstream, SiH<sub>4</sub> is added to the plasma. The silane gas is almost completely dissociated too (between 97 and 99% dissociation) by excited NH<sup>\*</sup> species, but also by electron impact and by thermal dissociation. Residual gas analysis by means of QMA did not provide any evidence for the presence of SiN<sub>x</sub>H<sub>y</sub> compounds in the plasma, as found for RF-PECVD [5].

The plasma source is truly remote in the sense that the plasma is independent of the substrates, and that no ion bombardment of the substrate occurs.

### 3. PASSIVATION: EFFECTS OF SUBSTRATE TEMPERATURE

#### 3.1 Experimental setup

SiN<sub>x</sub>:H coatings were deposited on the frontside of 10x10 cm<sup>2</sup> multicrystalline Si wafers, with an emitter. The emitter has a sheet resistance of about 40 Ohm/sq and a relatively high P concentration (>10<sup>20</sup> cm<sup>-3</sup>) at the surface.

The depositions of the SiN<sub>x</sub>:H layers took place in Reactor A. We varied the deposition temperature and kept all other parameters (pressure, flow rates etc.) constant. Note that we did not use optimised deposition conditions for either bulk or surface passivation.

After the depositions the cells obtained a front and a rear side metallisation by means of screen printing, and were subsequently co-fired in a belt furnace. Information on the passivating effect of the SiN<sub>x</sub>:H on these cells was obtained by evaluating the IV characteristics and by spectral response measurements.

In each deposition run we also included a piece of a FZ wafer. This FZ material obtained an RCA clean plus an HF etch prior to deposition of SiN<sub>x</sub>:H. Each deposition was repeated once with the same conditions in order to coat the rear side of these FZ samples.

The FZ samples were analyzed by Quasi Steady State Photo Conductance (QSSPC) measurements [6] to obtain information on the surface passivation. These samples were also analyzed by Elastic Recoil Detection (ERD) [7] and FTIR to obtain information on the structural properties of the SiN<sub>x</sub>:H coatings.

#### 3.2 Results

The substrate temperature appears to have a significant impact on the structure of the SiN<sub>x</sub>:H layers. ERD measurements show that the hydrogen concentration decreases with increasing temperature (see Fig. 2). This phenomenon, due to enhanced Si-N cross linking, can also be observed if SiN<sub>x</sub>:H layers grown at low temperatures are heated up to higher temperatures [8].

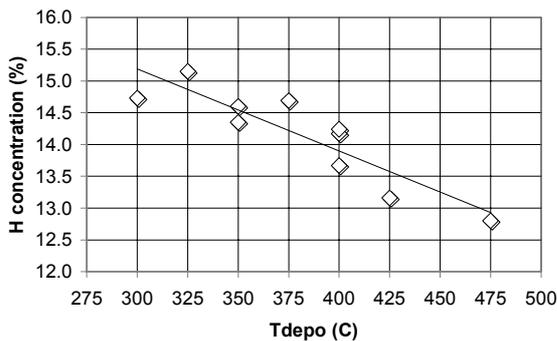


Figure 2: Hydrogen concentration in SiN<sub>x</sub>:H layers as a function of the deposition temperature.

At the same time we see that the stoichiometry of the films changes. The N/Si ratio decreases with increasing temperatures; i.e. the films become more silicon rich (see Fig 3). As a result the refractive index *n* increases with increasing deposition temperature also from 2.0 to 2.3 (values at 614 nm). FTIR measurements show that in these films the hydrogen atoms are predominantly bonded to Si atoms; i.e. the Si-H/N-H ratio is larger than the Si/N ratio.

The surface passivation of the films, in terms of effective lifetime of charge carriers in the FZ wafers is displayed in Figure 4. We can observe that the best surface

passivation is obtained at the highest deposition temperatures.

The maximum substrate temperature is 475 C for this reactor, so we were unable to see whether the surface passivation would reach a maximum at higher temperatures.

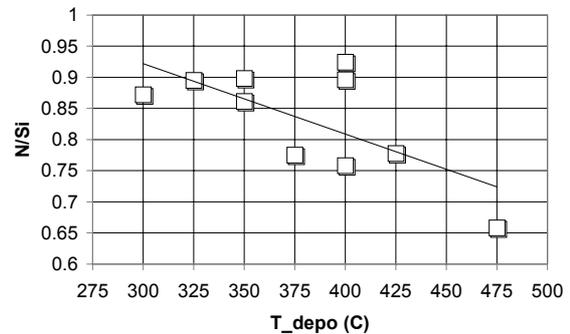


Figure 3: Ratio of Nitrogen/Silicon concentrations in SiN<sub>x</sub>:H as a function of the deposition temperature.

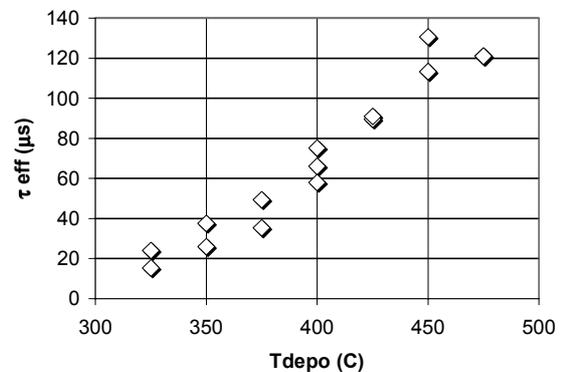


Figure 4: Effective lifetime of charge carriers in FZ wafers as a function of the deposition temperature of the SiN layers.

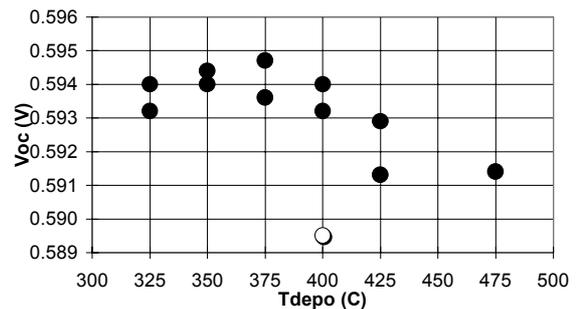


Figure 5: Voc of neighbour cells for various SiN deposition temperatures (filled circles). The open circle refers to a reference sample in which the SiN<sub>x</sub>:H layer is deposited after the printing of metallization and firing.

If we take a look at the cell performance in terms of V<sub>oc</sub>, we see that a maximum is obtained in the investigated temperature region (See Figure 5). The data plotted in this figure refer to cells made from mc-Si wafers which were adjacent in the ingot. Spectral response measurements revealed that the gain of the Voc with respect to the process sequence in which the SiN<sub>x</sub>:H was deposited after metallization and firing (open circle in Fig. 5) was entirely due to an increase of IQE at larger wavelengths. The V<sub>oc</sub> in this figure thus can be considered as a fingerprint of the

bulk passivation of mc-Si by a sequence of SiN<sub>x</sub>:H deposition and co-firing of a Ag-front side and an Al rear side metallisation.

### 3.3 Discussion

The substrate temperature dependence of the composition of the SiN<sub>x</sub>:H layers indicates that the growth of the layers by MW-PECVD is a result of a reaction of separate NH and SiH species at the surface and not a result of sticking of SiN<sub>x</sub>H<sub>y</sub> clusters formed in the plasma. Formation of latter clusters, namely, would be independent of the substrate temperature. This conclusion is supported by the fact that we do not find any traces of cluster formation in the plasma by residual gas analysis.

The results of the temperature dependence of the surface passivation are to some extent in contrast with findings for another remote MW-PECVD source [9] where an optimum temperature of about 375 C is reported. We have to be aware, however, of the fact that plasma and growth conditions of both systems are quite different. In our systems, the silane is injected in the NH<sub>3</sub> plasma whereas in the system of Lauinger et al. the silane is injected far downstream. As a consequence, in the latter system the silane is dissociated only by NH<sup>+</sup> species and not by electron impact. Therefore, the SiN layer growth mechanisms will be quite different for the system of Lauinger and our system. This difference is e.g. also expressed by the fact that quite different NH<sub>3</sub>/SiH<sub>4</sub> gasflow ratios have to be used in order to obtain films with the same N/Si ratio.

On the other hand for both MW PECVD systems (but also for RF-PECVD systems) an increase of the surface passivation with a decrease of the N/Si ratio has been observed. CVMIS experiments on RF-PECVD grown layers have shown that decreasing the N/Si ratio in the layer (by means of decreasing the ratio of the gasses NH<sub>3</sub>/SiH<sub>4</sub>) leads both to an increase of the number of interface defects  $D_{it}$  and to an increase of the positive fixed charge  $Q_f$  at the Si-SiN interface[10]. The relative changes of both quantities are almost equal but since, roughly,  $S_{eff} \propto D_{it}/Q_f^2$  the increase of  $Q_f$  is dominant.

A disadvantage of the best surface passivation at low N/Si ratios in the films is that these low ratios lead to SiN layers with a relatively small bandgap. We measured an optical bandgap ( $E_{opt}$ ) of 2.5 eV for these films where for stoichiometric Si<sub>3</sub>N<sub>4</sub> the bandgap is typically larger than 3.5 eV. As a result, the absorption of these silicon rich films is rather large, which makes them unsuitable as front-side anti-reflection coating. A practical solution for this is to apply a multi-layer structure in which thicknesses, refractive indices and bandgaps are optimised for anti-reflectivity and bulk- and surface passivating properties.

## 4. ALUMINIUM ENHANCED BULK PASSIVATION OF SILICON NITRIDE

### 4.1 Experimental set-up

Five groups of 10 mc-Si p-type Baysix wafers were selected, with wafers from adjacent positions in the ingot (neighbour wafers) equally divided over each group. All wafers obtained an emitter by spin-on coating and diffusion in a belt furnace, resulting in a sheet resistance of about 50 Ohm/sq. We processed the five groups then as follows:

Group I: emitter stripping by wet chemical etching (about 40 micron in total was removed).

Group II: firing process in belt furnace as for co-firing of front and back side metallisation (but this metallisation was not present), followed by emitter stripping as for Group I.

Group III: SiN layer deposition, followed by firing. The SiN layer is an optimised layer for bulk passivation[1]. Emitter plus SiN layer were subsequently removed by wet chemical etching.

Group IV: SiN layer deposition at front side plus a screenprinted Al layer at rear side, followed by firing. Emitter, SiN layer and Al BSF layer were subsequently removed by wet chemical etching.

Group V: as group IV, but no layer removal.

Finally, all wafers from groups I-IV obtained a SiN layer with good surface passivation properties on front and rear side. All SiN<sub>x</sub>:H layer depositions took place in Reactor B. Wafers of groups I-IV were used for the determination of effective lifetime of the minority charge carriers by the QSSPC method. The cells of group IV were used for the determination of the I-V characteristics.

### 4.2 Results

The effective lifetime of the charge carriers after the various treatments is shown in Figure 6. The group which did not obtain any treatment after the phosphorous diffusion (group I) had a mean charge carrier lifetime of about 24 μs. An additional firing step (group II) does not have any detrimental or beneficial effect on the lifetime. Firing of a good silicon nitride layer, though, does increase the lifetime significantly to 29 μs. We see that this improvement is already obtained without an Al rear side during firing (group III). Application of an Al rear side (group IV) appears to have no additional effect on the bulk passivation.

This last finding seems to be in contrast with observations made at IMEC and GeorgiaTech [3,11]. These authors found a clear synergistic effect of Al and SiN<sub>x</sub>:H co-firing.

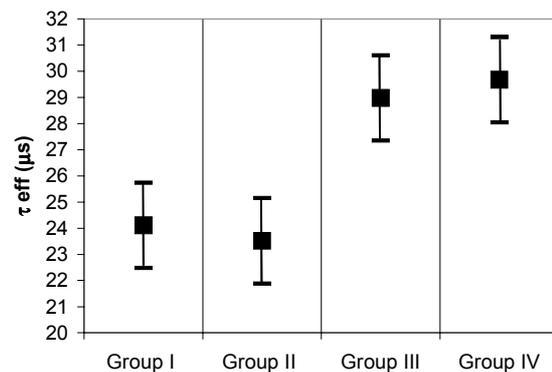


Figure 6: Effective lifetime of charge carriers after various treatments. Upper and lower boundaries are 95% confidence intervals.

If we look at the results for the individual wafers (Figure 7), we see a remarkable difference between passivation effects on wafers with a lower quality at the beginning and wafers with a better starting quality.

Wafers with a low charge carrier lifetime prior to the SiN<sub>x</sub>:H deposition (wafers no. 1 and 4, presumably originating from the top or the bottom of the ingot) do not benefit at all from the SiN<sub>x</sub>:H hydrogenation. On the other hand, the rest of the wafers, all with an initial bulk lifetime of more than 15 μs, show an increase from an average of 29 μs to an average of 36 μs before and after the SiN<sub>x</sub>:H

hydrogenation. The short lifetimes of the 'bad' material are probably determined by the presence of impurities, which can not be passivated by hydrogen.

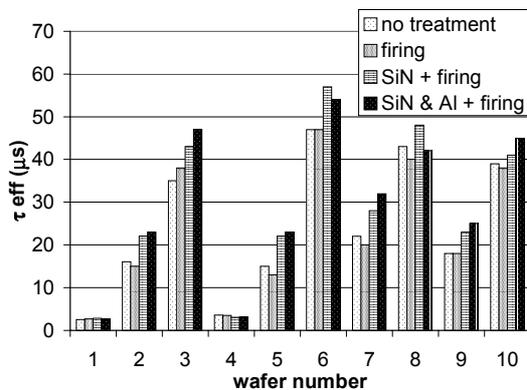


Figure 7: Effective lifetimes of the individual wafers before and after SiN passivation.

The cells which were made from neighbour wafers (group V) show  $V_{oc}$  values which are in first approximation in line with the measured values of  $\tau_{eff}$  (see Figure 8). The cells made from wafers with the low initial lifetimes (cells 1 and 4) produce a low  $V_{oc}$  (lower than 580 mV).

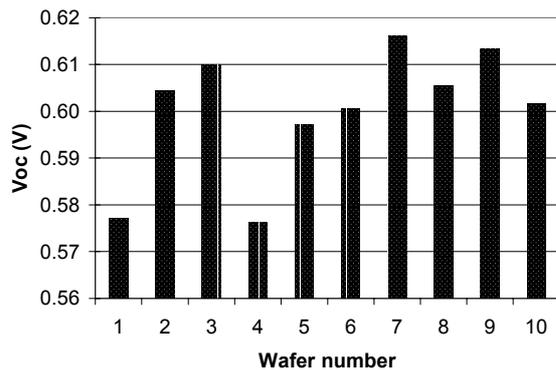


Figure 8: Voc results for cells of group V

The performances of cells made from wafers with medium or good initial lifetimes are somewhat less predictable. The correlation between the initial  $\tau_{eff}$  and  $V_{oc}$  is not exactly one to one, and is probably effected by small variations in one or more steps of the total processing.

#### 4.3 Discussion

The experiments have shown a clear improvement by about 20% of the lifetime of charge carriers by SiN<sub>x</sub>:H induced hydrogenation. However, we don't observe any additional effect of an Al enhanced hydrogen diffusion, as reported by other authors. The reason for this is not clear at the moment. It could be that the observed improvement by an Al BSF is only obtained if the SiN layers are deposited by a RF-PECVD method. It is known that a RF-plasma causes surface damage due to ion bombardment and it could be that the 'synergistic effect' of an Al BSF is just the repair of this surface damage. As noted before, such surface damage does not occur for a micro-wave plasma. Another explanation could be that we have not used an optimised firing process to obtain the best Al enhanced bulk passivation of SiN<sub>x</sub>:H.

In any case, more insight in the underlying mechanism's of bulk passivation by SiN<sub>x</sub>:H hydrogenation in combination with an Al BSF is strongly desired.

## 5. CONCLUSIONS

Remote Microwave PECVD of SiN<sub>x</sub>:H is an excellent method to obtain surface and bulk passivation of mc-Si solar cells. SiN<sub>x</sub>:H layers with the best surface passivating properties, however, require different deposition conditions than layers which are optimised for obtaining bulk passivation of mc-Si wafers. Good bulk passivation by co-firing of the SiN<sub>x</sub>:H layers requires a relatively high H-concentration in the layers, where the hydrogen is predominantly bonded to N-atoms. Good surface passivation is obtained for silicon-rich layers, with lower H-concentrations, where the H-atoms are predominantly bonded to Si-atoms. These Si-rich layers are characterised by a relatively high absorption coefficient which makes them less suitable as anti-reflection layers. Future research will be directed to optimisation of the optical properties of SiN<sub>x</sub>:H layers for bulk passivation.

We did not find any evidence for an Al enhanced bulk passivation for the silicon-nitrides grown with the MW-PECVD system. We have shown that the process of firing an optimised SiN layer leads to an increase of the effective lifetime of charge carriers in mc-Si wafers by more than 20%. The SiN<sub>x</sub>:H induced hydrogenation appears to improve the bulk life time of wafers with a medium or good initial lifetime only. Wafers with a low initial lifetime, probably dominated by a high impurity concentration, could not be improved by the SiN<sub>x</sub>:H induced hydrogenation in this experiment.

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