PASSIVATION ON MC-SI SOLAR CELLS WITH PECVD SiN_X:H USING N_2 AND SIH_4

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ABSTRACT: Application of N_2 instead of NH_3 as precursor gas in Plasma Enhanced Chemical Vapor Deposition (PECVD) of SiN_x:H can have significant advantages with respect to safety and environment. In this paper we will show that for MicroWave-PECVD, SiN_x:H with good bulk passivating properties can be obtained if only N_2 and SiH_4 are used as process gasses. A drawback of the current SiN_x:H grown with N_2 as precursor gas is the higher absorption at shorter wavelengths with respect to SiN_x:H grown with NH_3 as precursor gas.

Keywords: Passivation, PECVD, Silicon-Nitride.

1 INTRODUCTION

Plasma Enhanced Chemical Vapor Deposition (PECVD) of amorphous, hydrogenated silicon nitride (a-SiN_x:H) can be obtained with various precursor gasses but most commonly used are combinations of either SiH_4 & N_2 or SiH_4 & NH_3. So far, the first combination has mainly been applied in order to obtain chemically and electrically insulating SiN_x:H layers [1]. The resulting layers are usually stoichiometric and hydrogen-poor. The second combination is commonly applied in the PV industry, where in order to obtain passivating layers, the SiN_x:H usually has to be hydrogen- and silicon-rich. From the environmental and safety point of view, the usage of N_2 instead of NH_3 would be preferable. Recently it has been shown that by usage of a precursor gas mixture of N_2, SiH_4 and NH_3, in which N_2 was the most abundant species, excellent surface-passivating SiN_x:H layers could be obtained by rf (13.56 MHz) PECVD [2]. SiN_x:H layers which provide good surface passivation on FZ wafers, however, are not per definition good for bulk passivation of mc-Si wafers too. Generally bulk passivation requires SiN_x:H with somewhat different physical properties than needed for surface passivation [3].

Kessels et al. [4] and Hong et al. [5,6] showed that bulk passivation can be obtained by using N_2 and SiH_4 in an Expanding Thermal Plasma (ETP) system. However, the bulk passivating properties were not as good as for layers deposited with NH_3 and SiH_4. The purpose of our investigations was to find SiN_x:H with good surface **and** bulk passivating properties, using MW-PECVD and N_2 & SiH_4 as the only precursor gasses.

2 EXPERIMENTAL SETUP

2.1 Depositions

The microwave (MW) PECVD system at ECN which has been used for depositions of the SiN_x:H layers has been described in detail in previous papers [7,8]. With this MW plasma-source we have developed an optimal SiN_x:H layer for surface passivation by systematically varying the deposition conditions: substrate temperature, pressure, MW power and gas flows. Microwave power can be varied by two means: by peak power and by the duty cycle. In order to obtain a homogeneous deposition over the whole width of the linear plasma source (and wafer carrier), the peak power has to be larger than a certain minimum (typically larger than 1 kW). We applied t_{on} and t_{off} times of the duty cycles typical in the range of 10 ms.

Plasma properties have been investigated by Residual Gas Analysis (RGA) using a Prisma 200 mass spectrometer. Optical properties of the SiN_x:H layers were measured with Spectroscopic Ellipsometry (SE) and with a Filmetrics Reflectometer.

2.2 Cell processing

An industrial processing scheme, as depicted in Table I, was used to make cells using 10×10 cm^2 mc-Si wafers.

Table I : Applied process scheme.

Applied process scheme
Alkaline saw damage etch
Industrial emitter processing (50 • /•)
P-glass removal
MW PECVD of SiN_x:H
Front side metallization by screen printing
Drying front side metallization
Screen printing Al on rear side
Simultaneous firing of the front and rear side metallization
Edge isolation

Three groups of 6 wafers were processed and we selected the wafers such that each wafer had an ingot-neighbour wafer in the other groups. The three groups obtained a SiN deposition according to Table II.

Prior to the depositions of group 1, some initial test depositions were performed in order to evaluate the optical properties of the layers. Final gas flow ratios for the depositions on this group were chosen such that the refractive index of the layers was about 2.1.

The conditions for group 1 were determined after optimization of optical properties of the layers, and therefore these conditions cannot be considered as completely optimized for cell processing. The conditions of group 2 – in contrast – are well optimised for mc-Si cell passivation as reported in a previous paper [3]. The cells of group 3, finally, obtained a SiN_x:H layer after metallization, so that we can exclude bulk passivation for the cells of this group.

3 RESULTS AND DISCUSSION

3.1 Plasma characteristics

In Figure 1 the residual gas analysis spectrum, during a typical deposition run using N_2&SiH_4 is shown. It can be observed that the depletion rate of SiH_4 is very high: about 95 %. This is almost the same as for a NH_3&SiH_4 plasma created with this MW plasma source. The depletion rate of N_2, though, is appreciably smaller: about 40 %, where in an NH_3&SiH_4 plasma the depletion of NH_3 is more than 90 % [7]. The lower dissociation rate of N_2 is in line with the bond strength: for N-N the bond energy is 9.81 eV, for H-NH_2 this value is 4.65 eV (for H-SiH_3 the bond strength is 3.89 eV) [9].

Since the depletion rate of N_2 is about half of that for NH_3, the contribution of nitrogen atoms to film growth per mole of gas is approximately the same for both precursor gasses. This means that the deposition rate should be comparable for N_2 and NH_3 when the same gas flows are used. Indeed the deposition rate with MW-PECVD for the N_2/SiH_4 combination is about the same as for the NH_3/SiH_4 combination: approximately 1 nm/s.

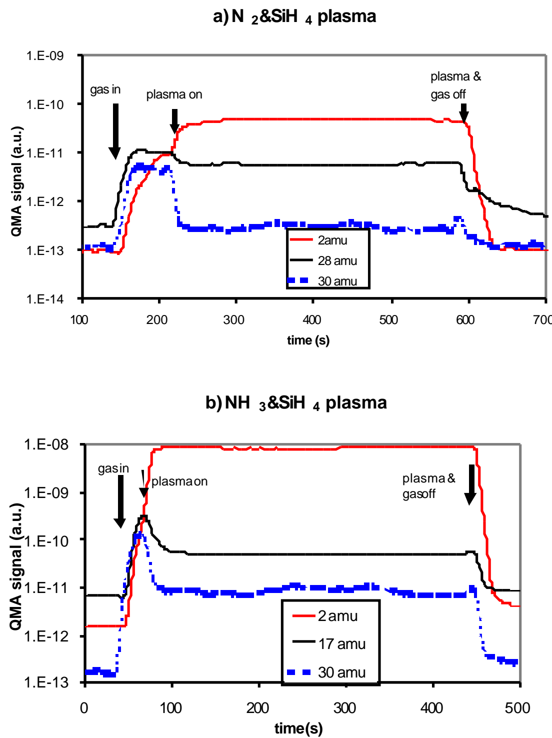

Figure 1: Residual Gas Analysis spectrum of typical depositions. a): N_2&SiH_4 plasma; b) NH_3&SiH_4 plasma. Concentrations of masses 2 (H_2), 17 (NH_3), 28 (N_2), and 30(SiH_4) are shown.

3.2 Optical properties

Refractive index and absorption of the SiN_x:H layers can be tuned by the flow ratio N_2/SiH_4. Smaller ratios generally lead to the growth of Si richer films with higher refractive indices and with higher absorption coefficients. This trend can also be observed in Figure 2 and Figure 3. From Figure 3 it can also be seen that the absorption of SiN_x:H layers deposited with N_2 will have a higher absorption at shorter wavelengths than layers deposited using NH_3 and using similar gas-flow ratios.

The gas composition to obtain n = 2.1 - 2.2 using N_2&SiH_4 can be found using the data of both optical characterization techniques presented in Figure 2. Note that ellipsometry measurements of n lead to higher values than for reflectometry measurements. We determined by interpolation of data from both methods, that in order to obtain a refractive index of about 2.1, the ratio N_2/SiH_4 has to be about 1.6 and thus comparable to the NH_3/SiH_4 gas-flow ratio. These flow ratios have been applied for processing of cells (see Table II).

Residual gas analysis has shown that the ratio of amounts of active N* and Si* species is linearly correlated with the ratio of N_2 or NH_3 and SiH_4. Probably, the N/Si ratio in the deposited layer will also be the same for layers with the same refractive index irrespective of the precursor gas N_2 or NH_3. This has to be confirmed by detailed characterisation of the layers.

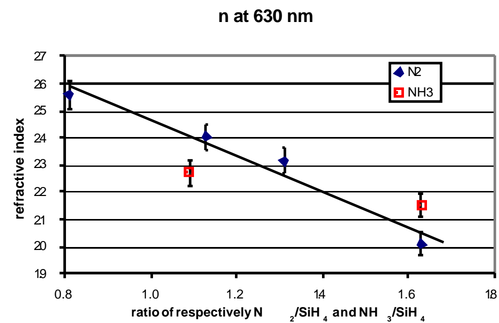

Figure 2: Refractive index versus the N_2/SiH_4 and NH_3/SiH_4 flow ratio.

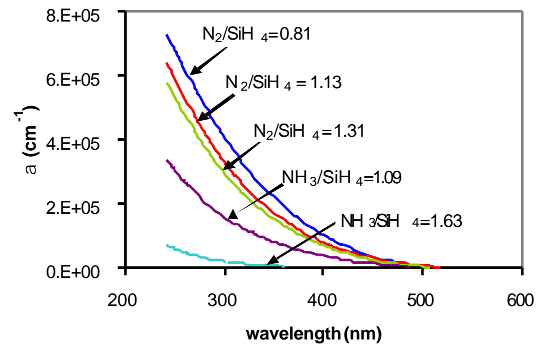

Figure 3: Absorption coefficient of SiN_x:H for various N_2/SiH_4 and NH_3/SiH_4 ratios.

Table II : PECVD conditions

Group	deposition conditions
#1	N_2/SiH_4 = 1.63
#2	NH_3/SiH_4 = 1.63
#3	reference scenario without passivation: SiN_x:H after metallization

3.3 Cell results

Mean IV results for cells of the three groups are shown in Table III. The results of both the N_2&SiH_4 (group #1) and the NH_3&SiH_4 (group #2) group are better than those of group #3 (not-passivated reference group). Since the firing conditions for group #1 and #3 are not completely optimized, *FF* is somewhat lower for these groups. Because of this it is better to determine the passivation effect from $J_{sc}\times V_{oc}$. For the NH_3&SiH_4 group the gain in $J_{sc}\times V_{oc}$ is 13% with respect to the group without passivation, and for the N_2&SiH_4 group the gain is 6%. The increase for the N_2&SiH_4 group is less because of a lower V_{oc} (1%) and a lower J_{sc} (5%) compared to group #2.

Table III : mean IV results

group	V_{oc} (mV)	J_{sc} (mA/cm^2)	$J_{sc}\times V_{oc}$ (mW/cm^2)	*FF* (%)	• (%)
#1	602	29.3	17.6	72.2	12.4
#2	608	30.9	18.8	75.3	14.1
#3	589	28.2	16.6	72.2	12.0

Spectral response measurements (see Figure 4) show what the origin is of the arrears of J_{sc} for group #1: it is a lack of blue response in the range 350 – 500 nm. From the measurements of the optical properties it can be seen that the absorption for the SiN_x:H layer deposited with N_2&SiH_4 is higher at those shorter wavelengths. However, the higher absorption cannot explain the lack in blue response completely, and the 6 mV lower V_{oc}. Therefore the surface recombination velocity for group #1 must be higher than that of group #2. PC1D5.5 and a best estimate for the absorption in the SiN_x:H layer deposited with N_2&SiH_4 were used to fit the IV results and the IQEs for group #1 and #2. A 3 mV lower V_{oc} and a 1% lower J_{sc} were found for group #1 by increasing the surface recombination velocity at the front side. A 4% lower J_{sc} caused by absorption will result in a 1 mV lower V_{oc}. These results are summarized in table IV and the lower V_{oc} determined with PC1D is within the experimental error of the IV results presented in table III.

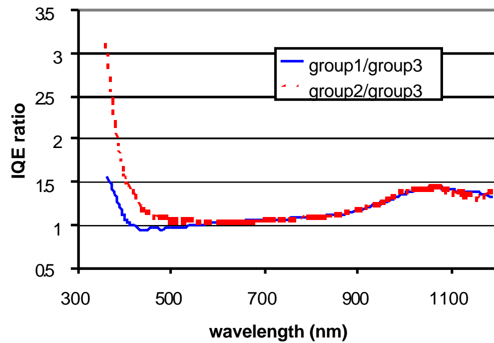

Figure 4: Internal Quantum Efficiency of cells of group 1 and 2 relative to the IQE of the neighbour cell in group 3.

Table IV: Effects of a higher absorption and higher surface recombination velocity on V_{oc} and J_{sc} determined with PC1D.

	ΔV_{oc} (mV)	ΔJ_{sc}
absorption	-1	-4%
higher surface recombintion	-3	-1%
total	-4	-5%

In the longer wavelength regime between 900 and 1200 nm we see that the spectral response of group #1 is the same as that of group #2 and both are appreciably larger than that of the reference group #3. This shows that the bulk passivation, which is caused by hydrogenation of the cells during the firing of the metallization, is excellent and the same for both groups. These results differ somewhat from passivation experiments performed by Hong et al. [4,5]. They used an ETP system and N_2&SiH_4 as precursor gasses. In their experiment the bulk passivation using N_2 was not as good as for using NH_3 and the absorption at shorter wavelengths was significant. In our experiment the bulk passivation is as good as that of NH_3 and we only observed a lack of IQE at shorter wavelengths. From the above we may conclude that it is possible with MW-PECVD to grow SiN_x:H layers with N_2&SiH_4 which are as good for bulk passivation as layers grown with NH_3&SiH_4.

Further research will be performed on how the absorption at shorter wavelengths can be reduced. It is expected that reducing the absorption will result in cells that have comparable output as when NH_3 is used.

Also the surface recombination velocity, the composition and thermal stability of the layers will be investigated and compared to layers deposited using NH_3. Lenkheit and Hezel [10] have shown that for SiN_x:H grown with NH_3 as precursor gas, the effective lifetime of charge carriers in FZ wafers can decrease significantly for Si rich layers after thermal aneal, probably due to thermal degradation of the surface passivation.

4 CONCLUSIONS

4.1 Optical properties

- The refractive index *n* of SiN_x:H deposited using N_2&SiH_4 can be easily tuned between about 2.0 and 2.5 by changing the gas composition. Increasing the amount of N_2 results in a lower refractive index.
- The absorption of SiN_x:H layers at shorter wavelengths is higher for the layers using N_2. For the same *n* the use of NH_3 will result in less absorption at shorter wavelengths.
- For higher values of *n* the absorption increases even further for SiN_x:H layers deposited using N_2.

4.2 Solar cell results

A not completely optimized PECVD process was used for the deposition of SiN_x:H with N_2 as precursor gas. IQE measurements show that the obtained bulk passivation is the same as for layers deposited with NH_3 as precursor gas. The optical properties of SiN_x:H deposited using N_2 - that is: the transmission at shorter wavelengths - should be improved to obtain comparable IV results. Further, the thermal stability of the surface passivation has to be investigated.

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REFERENCES

[1] J. Batey, E. Tierney, J. Stasiak and T.N. Nguen, Applied Surface Science, 39 (1989) 1.
[2] J. Schmidt and M. Kerr, Solar Energy Materials & Solar Cells 65 (2001) 585.
[3] W. J. Soppe, J.Hong, W.M.M. Kessels, M.C.M. van de Sanden, W.M. Arnoldbik, H. Schlemm, C. Devilée, H. Rieffe, S.E.A. Schiermeier, J.H. Bultman and A.W. Weeber, Proceedings 29th IEEE P VSC, New Orleans (2002) in press.
[4] W.M.M. Kessels, J. Hong, F.J.H. van Assche, J.D. Moschner, T. Lauinger, W.J. Soppe, A.W. Weeber, M.C.M. van de Sanden, J. Vac. Sci. Technol. A 20 (2002) 1704.
[5] J. Hong, W.M.M. Kessels, F.J.M. van Assche, H.C. Rieffe, W.J. Soppe, A.W. Weeber, M.C.M. van de Sanden, Prog. Photovoltaics: Research and Applications, in the press.
[6] J. Hong, W.M.M. Kessels, F.J.H. van Assche, W.M. Arnold Bik, H.C. Rieffe, W.J. Soppe, A.W. Weeber, and M.C.M. van de Sanden, Proceedings 29th IE EE PVSC, New Orleans (2002) in press.
[7] W.J. Soppe, B.G. Duijvelaar, S.E.A. Schiermeier, A.W. Weeber, A. Steiner and F.M. Schuurmans, Proceedings 16th European Photovoltaic Solar Energy Conference, Glasgow (2000) 1420.
[8] W.J. Soppe, C. Devilee, S.E.A. Schiermeier, J. Hong, W.M.M. Kessels, M.C.M. van de Sanden, W.M. Arnoldbik and A.W. Weeber, Presented at the 17th European Photovoltaic Solar Energy Conference and Exhibition, Munich, 2001.
[9] D.L. Lide, CRC Handbook of Chemistry and Physics, (1994), CRC Press, Boca Raton.
[10] B. Lenkheit and R. Hezel, Proc. 17th EPVSEC, Munich (2001), p. 343.