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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 PECVD of SiN_x:H can have significant advantages with respect to safety and environment. In this paper we will show that for MicroWave-Plasma Enhanced Chemical Vapor Deposition, 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 – so far – of 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 (is dat zo?) 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 in stead 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 Microwave (MW) PECVD [2]. SiN_x:H layers which provide good surface passivation, 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 of FZ-wafers [3].

Kessels et al. [4] and Hong et al. [5] presented 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 that for layers deposited with NH_3 and SiH_4. The purpose of our investigations, was to find means for MW-PECVD of SiN_x:H with good surface **and** bulk passivating properties, using only N_2 and SiH_4 as precursor gasses.

2 EXPERIMENTAL

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 [6,7]. With this MW plasma-source we have developed an optimised SiN_x:H layer for surface passivation by systematically varying the deposition conditions: substrate temperature, pressure, MW power and SiH_4 and N_2 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).

2.2 Cell processing

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

Table I: Applied process scheme.

Applied process scheme
Alkaline saw damage etch
Industrial emitter processing (50 Ω/□)
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 choosen 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.

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

Surface passivation was established by growing identical SiN layers on front and rear side of 1.5 Ohm.cm p-type FZ wafers and subsequent measurement of τ_{eff} by Quasi Steady State Photo Conductance (QSSPC) [8] and Modulated Free Carrier Absorption (MFCA).

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 % [6]. 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]. (op zich niet onwaar, maar om er zo diep op in te gaan hier?)

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. (op zich ook wel aardig gevonden maar of het nu zo overtuigend is... het hangt ook af van de N/Si ratio etc.)

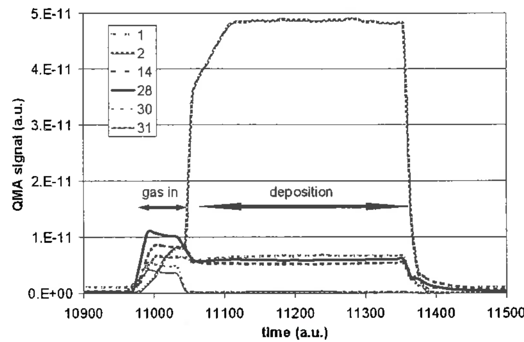

Figure 1: Residual Gas Analysis spectrum of a typical deposition. Concentrations of masses 1, 2 (hydrogen), 14, 28 (nitrogen), 30 and 31 (SiH_4) are shown. (lijnen in zwart-wit niet duidelijk)

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 (as for the NH_3/SiH_4 case) using N_2&SiH_4 can be found by extrapolation of the data in Figure 2. The ratio will be about 1.6 and thus comparable to the NH_3/SiH_4 gas-flow ratio. From the plasma characteristics it was shown that similar gas-flow ratios will result in a similar ratio of active N* and Si* species. Probably, the N/Si ratio will also be similar in the deposited layer with a similar refractive index. This has to be confirmed by detailled characterisation of the layers.

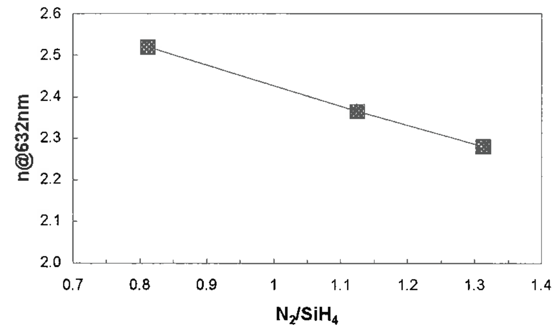

Figure 2: Refractive index versus the N_2/SiH_4 flow ratio.

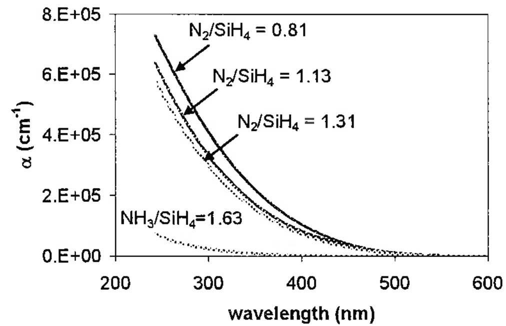

Figure 3: Absorption coefficient of SiN for various N_2/SiH_4 ratio's. The absorption coefficient for a SiN_x:H layer (n=2.1) grown with NH_3&SiH_4 is also shown.

3.3 Cell results

Mean I-V results for cells of the three groups are shown in Table III. We see that the V_{oc} for the N_2&SiH_4 group (#1) is 1 % smaller than for the NH_3&SiH_4 group (#2). The difference in the short circuit current is much larger: here the mean value for group 1 is about 5% smaller than for group 2.

Table III: mean IV results

group	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
#1	602	29.3	72.2	12.4
#2	608	30.9	75.3	14.1
#3	589	28.2	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 experiments with FZ wafers we know that the surface passivation of the SiN_x:H layers as deposited on group 1 is good, and it is mostly absorption in the SiN_x:H layers which is responsible for the low blue response. This absorption also will cause a lower short circuit current density. The somewhat lower J_{sc} of group 2 will hardly affect V_{oc}. Since V_{oc} is about 6 mV lower for group 1 compared to group 2, there must be some extra recombination. Because the light absorption at shorter wavelengths cannot explain the lack in IQE completely the surface recombination for group 1 must be higher than that of group 2.

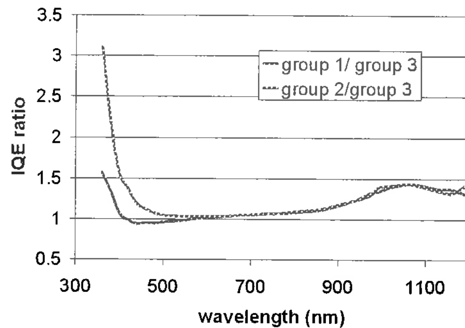

Figure 4: Internal Quantum Efficiency of cells of group 1 and 2 relative to the IQE of the neighbour cell in group 3.

duidelijk in zwart-wit?

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 with an ETP system and using N_2&SiH_4 that were published by Hong et al. [4,5]. 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 significantly. (hetzelfde als hier ook) In our experiment the bulk passivation is as good as that of NH_3 and we only observed an 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 composition and thermal stability of the layers will be investigated and compared to layers deposited using NH_3.

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.

nodig?

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 comparable to the one using 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. Lenkheit and Hezel [10] have shown that for SiN_x:H grown with NH_3 as precursor gas, 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. This thermal stability will be one of the subjects of further research of layers grown with N_2 as precursor gas.

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