MW PECVD A-$SI_XN_YH_Z$: THE ROAD TO OPTIMUM SILICON NITRIDE COATINGS

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ABSTRACT: Amorphous silicon nitride (a-$Si_xN_yH_z$) layers are widely used in the solar cell industry because they are cost effective and they offer an efficient solution for three critical aspects within the solar cell fabrication process sequence at the same time: While acting as an excellent anti-reflection coating (ARC) they also supply very good bulk and surface hydrogen passivation. It is widely accepted that the a-$Si_xN_yH_z$ layer should have a refraction index of $n \approx 2.1$ and low absorption to behave as a good ARC, and in previous publications it was pointed out that the Si-N bond density of the layer should be around $13*10^{22}$ cm^{-3} to enable good bulk and surface passivation.

This work intends to study the factors determining the structural and optical properties of the silicon nitride layers deposited with large industrial remote MW PECVD systems, using NH_3 and SiH_4 as precursor gasses. While in most studies the changes of Si-N bond densities are achieved irrespectively of the refractive index of the layer, we will investigate how the Si-N bond density and passivation capability of the silicon nitride layer can be optimized while maintaining an optimum refractive index of 2.08+/-0.02.

Keywords: Silicon-nitride, Passivation, PECVD

1 INTRODUCTION

The role of silicon nitride in current manufactured solar cells is threefold: as an antireflection coating and as a vehicle for the passivation of both the surface and bulk of the solar cells, hence further enhancing the electronic properties of the cell material and increasing its efficiency.

As an antireflection coating, it is of primary importance that the optical properties i.e., refractive index n and thickness d, are optimized (n = 2.1 and d between 80 – 100 nm depending on the surface topography). The rule of thumb for the refraction index is that it should be high enough to reduce losses at encapsulation level and low enough to reduce absorption in the layer itself, allowing for the maximum amount of photons to be available for conversion into useful electrical power.

As an instrument for passivation of the cell, it has been shown in the past that in order to maximize the gain in the conversion process, i.e., optimize surface and bulk passivation, structural properties of the layers need to be optimized, i.e., Si-N bond densities [1,2]. In this paper we will review this optimization and consider also other structural properties of the SiN_x layer, such as the Si-H peak position and the total hydrogen concentration.

In most industrial solar cell lines the optimisation of the SiNx layer, for instance deposited by large PECVD systems, is still done empirically, using completely processed solar cells [3]. Since the results of our approach give us insight in the dependency of the optical and structural properties on both the deposition parameters and on the cell efficiency, they will enable us to do simpler and faster optimisations, directly on the deposited SiN_x layer. By measuring n, k and the bond densities on these samples (i.e. a SiN_x layer deposited directly on a cleaned Cz or FZ wafer), and taking into account the thickness and homogeneity of the layer, process optimization can be done without having to process complete solar cells.

Furthermore, from the analysis of the relation between n and the Si-N bond density at different deposition parameters, we will gain more scientific knowledge about the underlying chemistry and density of the layers.

2 EXPERIMENT

a-$Si_xN_yH_z$ layers are deposited with an industrial Roth & Rau SINA-L MW PECVD reactor.

To investigate the influence of process parameters on the structural properties of the layer, we deposited a-$Si_xN_yH_z$ layers while varying the deposition pressure, SiH_4 and NH_3 flow rate ratios, total flow and temperature.

The layers were deposited on double polished Cz grown silicon wafers for FTIR and ellipsometer measurements from which the Si-N, N-H and Si-H bond densities and the optical parameters n and k were determined.

Furthermore the same silicon nitride layers were deposited on sets of matched multi-crystalline silicon solar cells to evaluate their passivation and anti-reflection properties.

In previous publications ([4]) it was shown that the V_{oc} and J_{sc} of solar cells have maximum values around Si-N bond densities of $1.3*10^{23}$ cm^{-3}. These maximum efficiency layers also had a refraction index of 2.1.

However, in these experiments, while changing the Si-N bond density over quite a wide range; mainly by tuning the NH_3/SiH_4 gas flow ratio R and the deposition pressure P, the different SiN_x:H layers also obtained different refraction indices.

Basically, the trend was that n decreases while the Si-N bond density increases, although there was quite some spread in data (see figure 1, old data).

Since a refraction index around the value of 2.1 is optimal for the anti reflection, in the latest experiments the deposition parameters were changed in such a way to keep n constant, while varying the Si-N bond density.

The thought behind this experiment is that by maintaining the refractive index constant, the optical loss or gain due to changes in the optical matching will be decoupled from the changes in J_{sc} and V_{oc} due to structural changes in the layer.

Si-N bond densities ranging from $1.0*10^{23}$ cm^{-3} to $1.5*10^{23}$ cm^{-3} were reached by changing the deposition temperature *T*, total gas flow *Q*, and deposition pressure *P*. At the same time, the refraction was kept constant at a value of 2.08 +/- 0.02 by adjusting the gas flow ratio *R* at each point.

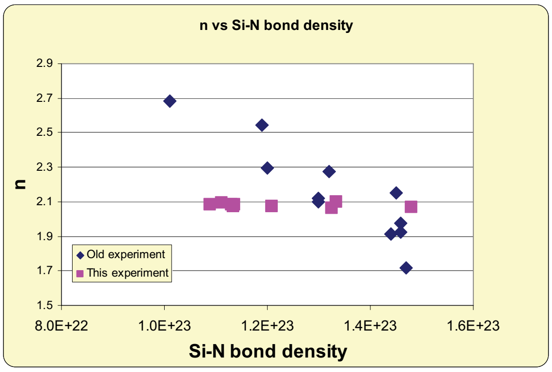

Figure 1: different refraction indices were reached while changing the Si-N bond density in an old experiment, while in this new experiment the refraction index was kept constant at n = 2.1

3 RESULTS AND DISCUSSIONS

3.1 FTIR Results

The structural properties of the silicon nitride layers, the Si-N, Si-H and N-H bond densities and Si-H peak position, were measured with a Perkin Elmer Fourier Transform Infrared spectrometer. In previous experiments it was shown that the Si-N bond density is a measure of the mass density, while the Si-H and N-H bond densities give the percentage of hydrogen present in the $Si_xN_yH_z$ layer. [5]

The temperature and total gas flow were found to have the larges influence on these properties: As can be seen in figure 2, increasing either T or Q decreased the Si-N bond density of the layer.

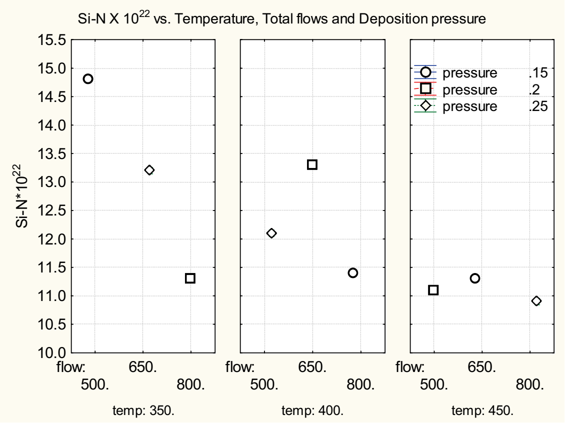

Figure 2. Si-N bond density vs. Temperature, Total flow and deposition pressure

The Si-H and N-H bond densities were mainly influenced by the temperature *T*, although also *Q* plays a role. Both decreased while increasing T, indicating a decrease in amount of hydrogen present in SiN_x:H layers deposited at higher temperatures as it can be seen in figure 3 and 4

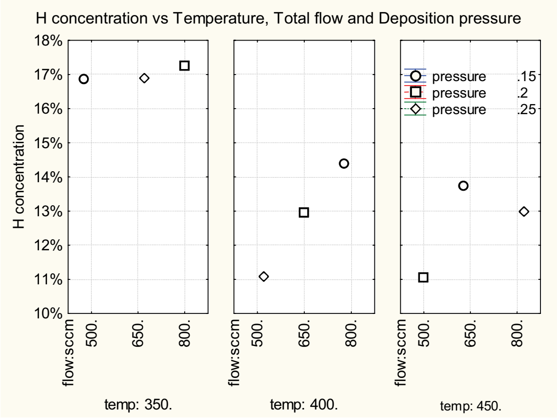

Figure 3 . H concentration vs, Temperature, Total flow and deposition pressure

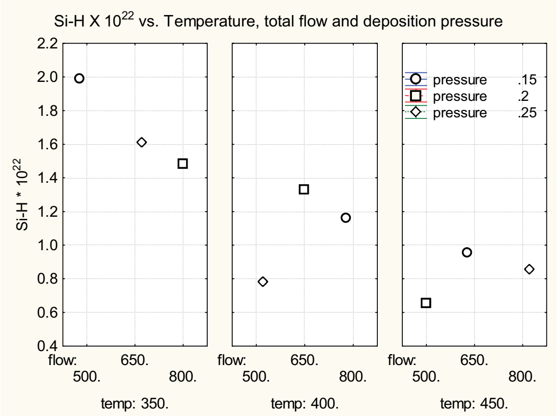

Figure 4 . Si-H bond density vs, Temperature, Total flow and deposition pressure

3.2 Si-H peak position

The Si-H peak position, while decreasing with increasing Q was found to increase with T (see figure 5).

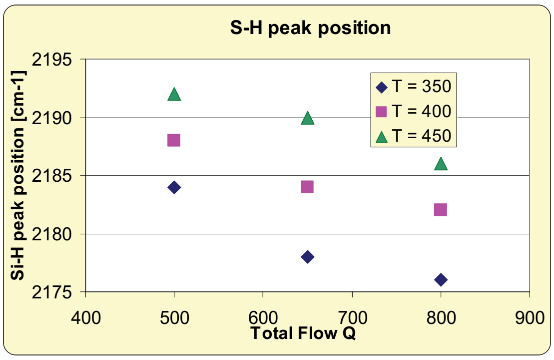

Figure 5: Si-H peak position as a function of T and Q

The Si-H peak position around 2170 cm^{-1} is a measure for the N- or Si- back bonding of the Si-H bond, or for the Si-H/N-H ratio. High resonance frequencies indicate the presence of more nitrogen, while lower resonance frequencies indicate that there is more silicon present in the SiNx:H layer.

According to Giorgis [6,7] resonances at several frequencies indicate the presence of the following structures in silicon nitride: 2100 :- H-Si-NSi_2 2140: H-Si-SiN_2, H-Si-HNSi. 2170: H-Si-HN_2, 2220: H-Si-N_3.

In previous publications the relation between Si-N bond density and Si-H peak position was shown for layers deposited with different refraction indices [1. With increasing Si-N bond density, the Si-H peak position also increased. (see figure 6, old experiment) This was explained by the fact that in a denser silicon nitride, there is more nitrogen present: A higher amount of nitrogen means both an increase in Si-N bond density over Si-Si and Si-H bonds *and* an increase in Si-H peak position [1].

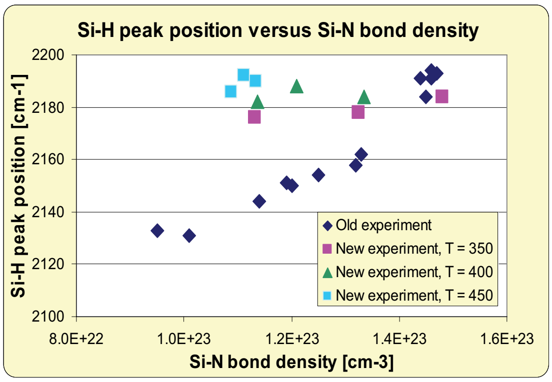

Figure 6: Si-H peak position as a function of the Si-N bond density of several different layers from different experiments

However, in our new experiment presented in this paper, different relations were found, as can also be seen from figure 6. Even at low Si-N bond densities the Si-H-back bonds seem to be mainly formed by nitrogen, since the peak position remains above 2170 cm^{-1}. This implies that the N/Si ratio is more or less fixed over the whole range of Si-N bond densities. This assumption is supported by the fact that the refractive index is constant over the whole range (see figure 1), while n was found dependent on the N-H/Si-H ratio in previous experiments (figure 7).

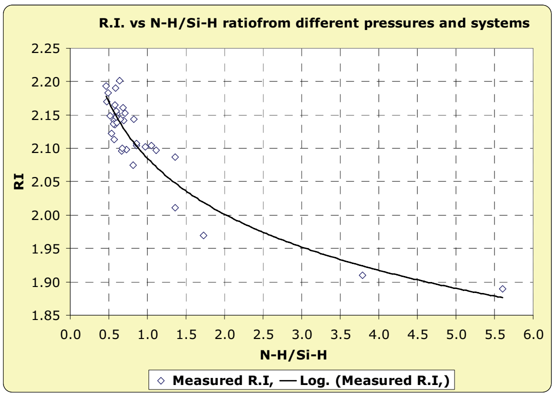

Figure 7. Refractive index vs NH/Si-H ratio for different deposition pressures, temperatures and systems

high T the Si-H peak position increases up to almost 2200 cm^{-1}.At these resonance frequencies (going from 2170 ($H\text{-}Si\text{-}HN_2$) to 2220 ($H\text{-}Si\text{-}N_3$) the difference is mainly caused by a decrease in hydrogen. The hydrogen concentrations shown in figure 8, where they are plotted against the Si-H peak positions, confirm this to a certain degree.

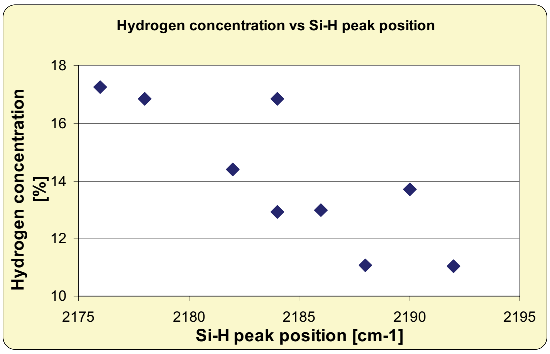

Figure 8: H concentration versus the Si-H peak position.

Increasing the temperature decreases the amount of hydrogen that is incorporated into the SiN_x:H layers, regardless of the Si-N bond density, or density of the layer. This could be due to a higher recombination of hydrogen radicals in the plasma itself due to higher energies available.

3.3 Cell results

In earlier publications, maximum bulk and surface passivation was found at Si-N bond densities around $1.3*10^{23}$ cm^{-3}, regardless of the wafer quality and of the type of SiNx:H [1,4] .

In these earlier experiments, the passivating SiNx:H layers were deposited with a small pilot SiNA MW PECVD system, and the refractive index was not kept constant.

In figure 9, the IV results from our new experiment are shown. Again, we see a clear maximum in cell results ($J_{sc}*V_{oc}$) for Si-N bond densities ~ 1.3*1023 cm-3. Since all SiNx:H layers have a constant refractive index of n = 2.08 +/- 0.02, the difference in cell results cannot depend on a difference in light coupling of the layers.

This means that it is solely an effect of bulk and surface passivation.

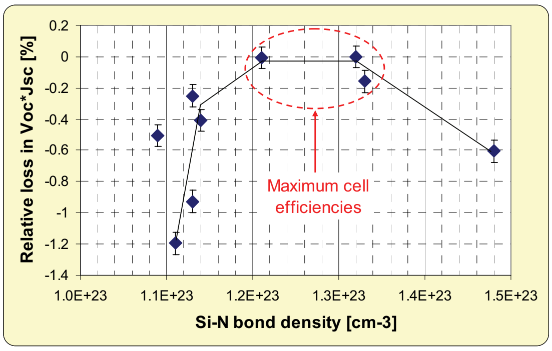

Figure 9: Maximum passivation between 1.2 and $1.3*10^{23}$ cm^{-3} for all wafers, regardless of their quality

In previous publications it was already shown that not the amount of hydrogen, but the Si-N bond density should be taken as a measure for the amount of bulk passivation.

The recent results confirm these findings as shown in the graph below (figure 10). The two best performing layers have different hydrogen concentrations, (11 % and 17 %), and no dependence of $J_{sc}*V_{oc}$ on the hydrogen concentration is found. The only common factor between the two best performing layers is that both have a Si-N bond density between 1.2 and 1.3 10^{23} cm^{-3}.

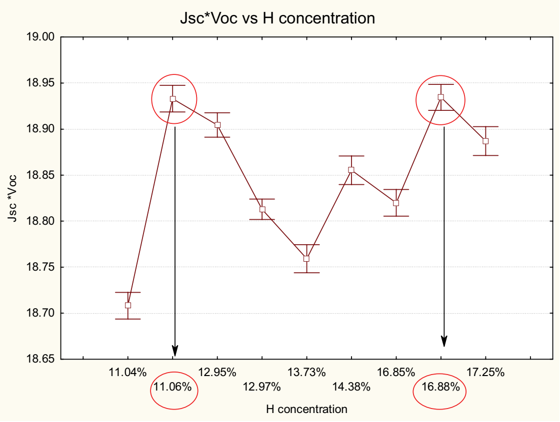

*Figure 10. J_{sc}*V_{oc} vs. Hydrogen concentration on the a-$Si_xN_yH_z$ layer*

The results from this investigation support our earlier findings that the Si-N bond density is a good measure for the maximum passivation of SiN_x:H layers, even if the refraction coefficient is already at the optimum value.

An example of how to optimise the machine parameters in order to obtain the correct Si-N bond density is shown below as a desirability profile graph in figure 11.

In this case desirability profile values are set to 1 for $13*10^{22}$ and zero as it diverts from it.

It is important to keep in mind that although the trends found in this work are of general nature, these desirability results are specific to the system in question and experimental runs such as these are recommended for every system in order to realise its full potential.

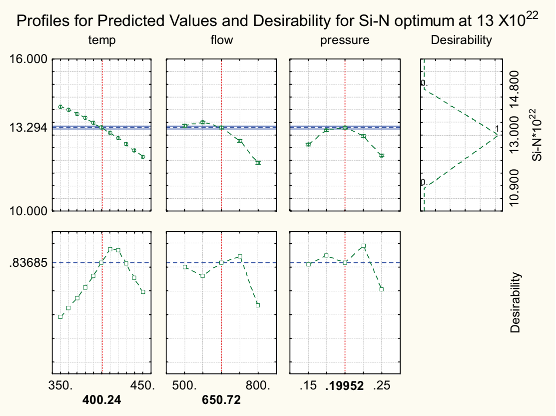

Figure 11 Desirability profiles for Si-N bond density

4 CONCLUSIONS

- Si-N bond density can be varied to a large extent even though refractive index is kept constant.
- Even for a fixed refractive index, in this case kept at 2.08 +/- 0.02, the optimization of Si-N bond density to within $1.2\text{-}1.3*10^{23}$ bond/cm^3 range will provide the best passivation for the cells.
- The hydrogen concentration on the *a-SixNyHz* layer is not a measure of layers ability to passivate the solar cells.
- General guidelines on how to optimize R MW PECVD reactors.
  - Create a uniform layer in thickness and refractive index
  - Make the layer thick enough to cover all surface irregularities
  - Optimise refractive index for maximum optical performance
  - Optimise Si-N bond density to be between 1.2 and $1.3*10^{23}$ bonds/cm^3.

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