# EFFECTS OF DIFFERENT FIRING PROFILES ON LAYER CHARACTERISTICS AND PASSIVATION PROPERTIES OF INDUSTRIAL ETP DEPOSITED SILICON NITRIDE FILMS

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ABSTRACT: OTB Netherlands has developed a tool ($DEP_X$) for the high-throughput processing of a silicon nitride antireflection coating (ARC) deposited by means of remote plasma enhanced chemical vapour deposition (RPECVD). The amorphous hydrogenated silicon nitride ($a$-$SiN_x$:H) films are deposited at a high rate (>1 nm/s) by industrially developed expanding thermal plasma (ETP) sources with $SiH_4$ and $NH_3$ as the precursor gasses. The effect of a thermal anneal on the layer characteristics of silicon nitride films with a different stoichiometry has been studied as well as the influence of the "firing" temperature on the amount of bulk passivation obtained on multicrystalline silicon solar cells. It was found that there are large differences in thermal stability in terms of refractive index, hydrogen loss, and N/Si ratio for films with a different stoichiometry. A correlation could be made between film density, thermal stability, hydrogen distribution, and the ability to obtain good bulk passivation. The passivation capability of these ETP deposited silicon nitride layers can compete with optimised low-rate deposited silicon nitride films deposited by microwave plasma's.
Keywords: PECVD, Silicon-Nitride, Passivation

## 1 INTRODUCTION

Silicon nitride films deposited by an Expanding Thermal Plasma (ETP) source from $SiH_4$ and $NH_3$ as precursor gasses have since recently found their way into industry. OTB Netherlands has industrialized the ETP concept an implemented it on an inline production tool ($DEP_X$) which is capable of processing 960 wafers per hour [1]. The Plasma Enhanced Chemical Vapour Deposition (PECVD) of these films from multiple ETP sources provides an excellent homogeneity regarding refractive index ($n$) and layer thickness. The technique had already proven to be capable of providing passivating silicon nitride layers [2] and these films have been further optimised. ETP deposited silicon nitride can now compete with low-rate deposited silicon nitride layers from the more conventional microwave plasma's. This optimisation is partially performed by studying the annealing behaviour of silicon nitride layers with a different stoichiometry and also their passivation capabilities at different firing temperatures. The findings of this study will be discussed in the next sections.

## 2 EXPERIMENTAL

Silicon nitride films with a different stoichiometry, obtained by varying the $NH_3/SiH_4$ ratio, were deposited on both monocrystalline silicon substrates and multicrystalline silicon solar cells at a deposition temperature of 350°C. Depositions were performed from three ETP sources which maintained an Ar-$NH_3$-$SiH_4$ plasma at ~3500 W. The films deposited on the monocrystalline silicon substrates were after the deposition exposed to a thermal anneal at temperatures ranging from 500 to 950°C in a standard conveyer belt firing furnace at ECN Solar Energy. The silicon nitride layers with different stoichiometry were deposited on multiple monocrystalline silicon substrates, so each anneal setting started with an as-deposited layer. The solar cells were further processed and fired at different temperatures in the same furnace. Before and after the thermal anneal the silicon nitride films were analysed with Fourier Transform Infrared Spectroscopy (FTIR) and spectroscopic ellipsometry (SE). The Tauc-Lorentz formalism and Bruggeman approximation were used to fit the SE data. Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection (ERD) were used to confirm the relationships found by Claassen *et al.* [3] that correlate FTIR and ellipsometry data with the Si/N ratio and also a new relation was found that links the film density with the refractive index and Si-N absorbance [4]. These relations were then used together with the parameters found by Landford and Rand [5] for the Si-H and N-H bond density to analyse the silicon nitride layers before and after annealing.

## 3 RESULTS

### 3.1 Optical properties

Figure 1 displays the results for the refractive index before and after the thermal anneal for the three different Si/N ratio films that were used.

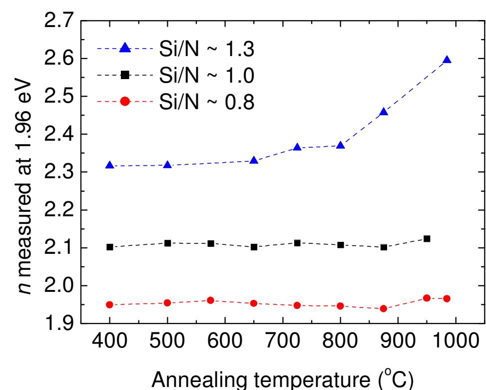



**Figure 1:** Refractive index as a function of annealing temperature for silicon nitride films with a different stoichiometry.

It shows that the refractive index increases with higher annealing temperatures for higher Si/N ratio films and that it remains stable for films that have a Si/N ratio closer to the stoichiometric ratio of $Si_3N_4$. This thermal stability for lower Si/N ratio films can be also seen from figure 2 which shows the results for the extinction coefficient ($k$) and layer thickness. The thickness of the different silicon nitride layers has been normalised to one for better comparison.

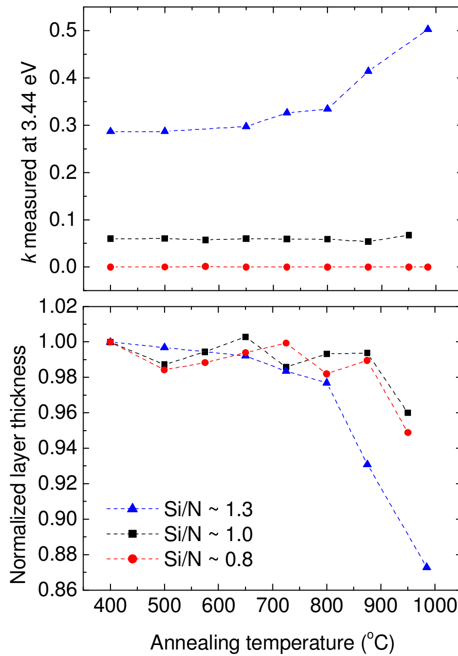



**Figure 2:** Extinction coefficient and normalised layer thickness as a function of annealing temperature for silicon nitride films with a different stoichiometry.

The higher Si/N ratio films show an also increasing $k$ at higher annealing temperatures, however, the extinction coefficient of the near stoichiometric silicon nitride layer remains stable at zero. Densification of the higher Si/N ratio film seems to start already at 500°C and shows a large increase at 800°C, whereas the layer thickness of the lower Si/N ratio films remains constant until 875°C.

3.2 Optical properties combined with FTIR

The Si/N ratio and an estimate for the film density have been determined from the relations obtained by comparing FTIR and ellipsometry with RBS and ERD, and are displayed in figure 3. It shows that lower Si/N ratio films (closer to stoichiometric ratio) have a higher film density and that the density increases as a function of annealing temperature for all three Si/N ratio's used. The Si/N ratio increases as well when raising the annealing temperature for higher Si/N ratio films, however, remains constant for the near stoichiometric silicon nitride layer.

The result for the bonded hydrogen is shown in figure 4 along with the wavenumber of the Si-H band which is the position of the maximum of the Si-H absorbance peak. The bonded hydrogen is determined by adding the N-H and Si-H bond densities which are calculated from the N-H and Si-H absorbances.

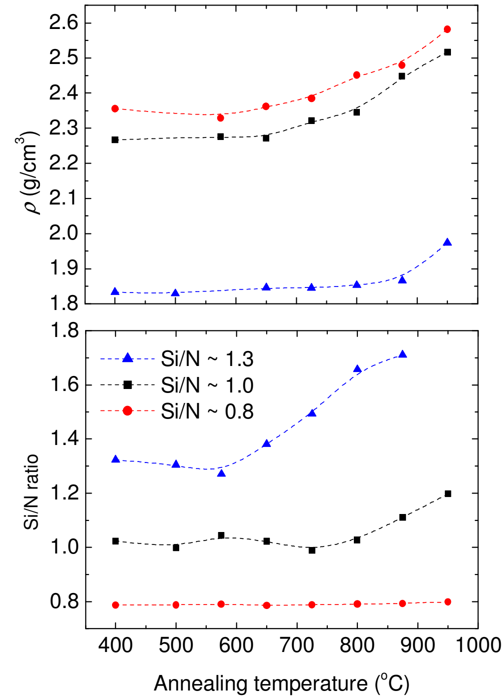



**Figure 3:** Film density and Si/N ratio as a function of annealing temperature for silicon nitride films with a different stoichiometry.

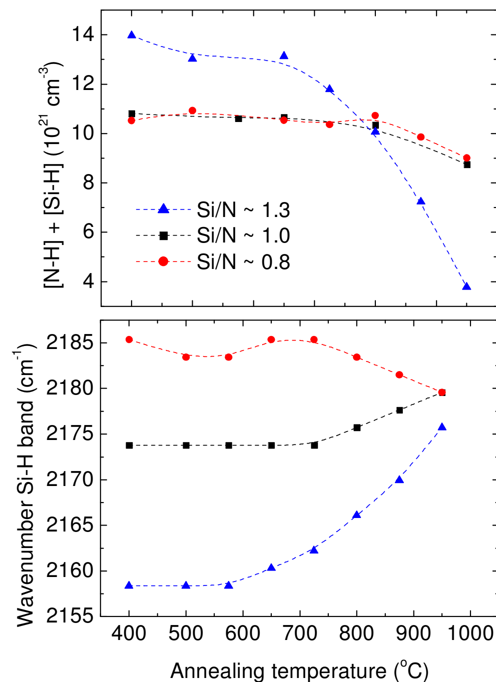



**Figure 4:** Hydrogen bond density and the position of the maximum Si-H absorbance as a function of annealing temperature for silicon nitride films with a different stoichiometry.

The hydrogen bond density is largest for the highest

Si/N ratio film which also releases its hydrogen at lower annealing temperatures and with the largest amount. The lower Si/N ratio films seem to retain their hydrogen until ~875°C and then release a moderate amount.

The wavenumber of the Si-H band for the different silicon nitride films shows an interesting behaviour. It is determined by the silicon nitride bond configuration, shifting from lower to higher wavenumbers when changing the configuration from silicon rich to nitrogen rich according to Bustarret *et al*. [6]. As can be seen from figure 4 all three Si/N ratio films shift to the same wavenumber (~2180 $cm^{-1}$) which corresponds with the configuration where hydrogen is equally divided between silicon and nitrogen atoms. This seems to be the configuration that has the highest thermal stability.

### 3.3 Solar cell results

The same silicon nitride layers were also used for solar cell processing. Each Si/N ratio film was deposited on 15 multicrystalline silicon solar cells and these cells were divided in three groups of five cells which were fired at different firing temperatures. The results for the short circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$) are displayed in figure 5 with each data point being an average of the five solar cells. The different firing temperatures that are used are the standard ECN Solar firing profile (centre data points), a 15°C higher temperature (right), and a 25°C lower firing temperature (left).

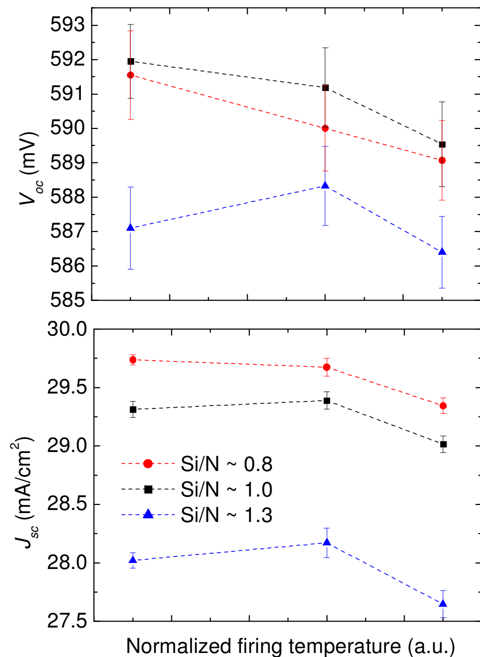
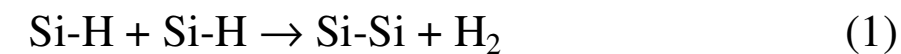



**Figure 5:** Open circuit voltage and short circuit density averaged over five solar cells coated with silicon nitride layers with a different stoichiometry fired at different temperatures.

The highest $V_{oc}$ is obtained by the silicon nitride film with a Si/N ratio of 1.0, however, the highest $J_{sc}$ is obtained by the near stoichiometric film. The highest Si/N ratio film shows lower values for the output parameters because of too much light absorption in the silicon nitride layer. It also appears that layers with a different stoichiometry have a different optimum firing profile. The lower Si/N ratio films seem to perform better at a lower firing temperature, while the highest Si/N ratio film shows the highest output parameters at the standard firing profile.

## 4 DISCUSSION

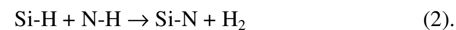
The increase in $n$ and $k$ as a function of annealing temperature is partially caused by the densification of the films which is shown by the reduction in layer thickness in figure 2. The dramatic increase for the highest Si/N ratio film can also be partially caused by silicon bond clustering according to the reaction



$$\text{Si-H} + \text{Si-H} \rightarrow \text{Si-Si} + H_2 \quad (1)$$

which is supported by the large decrease in Si-H bonds which mostly determined the bonded hydrogen content for the highest Si/N ratio film in figure 4. The fact that this film shows the highest degree of densification is related to the fact that it has the lowest film density and can thus be more compressed. Densification is probably caused by the loss of hydrogen atoms and the excluding of voids in the film by cross-linking, which also leads to the observed density increase. This cross-linking can cause film reconstruction which can also lead to the change in Si/N ratio as a function of annealing temperature shown in figure 3, if $NH_3$ is formed and escapes into the ambient. Hydrogen release in the form of $H_2$ or $NH_3$ during annealing has already been reported by for example Smith *et al*. [7].

The occurrence of film reconstruction is also evident from the shifting of the Si-H wavenumber shown in figure 4. The interesting fact that each film seems to reconstruct to a composition that corresponds with a wavenumber of ~2180 $cm^{-1}$ is a clear indication that films with an equal distribution of hydrogen have the highest thermal stability. These films have also a high mass density and show the highest solar cell output parameters according to figure 5. It appears then that the best passivating layers release their hydrogen according to



$$\text{Si-H} + \text{N-H} \rightarrow \text{Si-N} + H_2 \quad (2).$$

This might be attributed to the fact that in this way a strong Si-N bond will be formed which decreases the chance of leaving dangling Si or N bonds behind in the film. This might be sooner the case if hydrogen is released according to reaction (1) or via N-H bonds, leaving weak Si-Si and even weaker N-N bonds behind. Voids might then be created while a dense silicon nitride is necessary to retain the hydrogen and direct it into the multicrystalline wafer. Certainly the amount of hydrogen in a silicon nitride film is not important for its passivation capability. This can be seen from figure 4 which shows that the highest Si/N ratio film contains the most hydrogen, releases it at the lowest annealing temperatures and in the largest quantities, but has the lowest solar cell output parameters. This is, however, also caused by absorption of light in the layer because of the high $k$.

Still, the amount of hydrogen needed to fully passivate a multicrystalline silicon wafer is around three orders of magnitude lower than the amount of hydrogen that is released during a high temperature anneal. Polycrystalline silicon has a dangling bond density of ~$10^{18}$ $cm^{-3}$ [8], while the decrease in hydrogen bond density in a silicon nitride film after firing amounts to ~$10^{21}$ $cm^{-1}$. So it is not important how much hydrogen the silicon nitride layer contains but it matters how it is retained in the film and directed into the silicon.

## 5 FURTHER OPTIMISATION

The results of this firing study were used for further optimisation of ETP deposited silicon nitride layers by studying the growth of these layers, focussing on depositing films with an equal distribution of hydrogen and enhancing film density. Promising silicon nitride films were deposited on solar cells to investigate their passivation capability. Reverse scenario solar cells for which the silicon nitride deposition is performed after the firing were also processed and the $V_{oc}\times I_{sc}$ gain compared with the reverse scenario cells is displayed in figure 6.

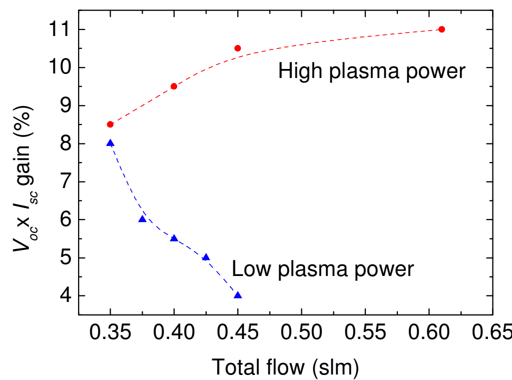



**Figure 6:** $V_{oc}\times I_{sc}$ gain compared with reverse scenario deposited silicon solar cells as a function of total flow for a high and a low plasma power.

It can be seen that total flow and plasma power are important growth parameters for ETP deposited silicon nitride. Furthermore, it is shown that a relatively high gain in $V_{oc}\times I_{sc}$ of 11% is reached for films which indeed had the highest film density and a Si-H wavenumber at ~2180 $cm^{-1}$. These optimised silicon nitride layers are deposited at ~7 nm/s. High-rate ETP deposited silicon nitride films are now at the level where they can compete with low-rate microwave deposited silicon nitride layers regarding multicrystalline silicon solar cell passivation.

## 6 CONCLUSIONS

It has been shown that ETP deposited silicon nitride films deposited at ~7 nm/s can provide excellent passivation of multicrystalline silicon solar cells. Results of a thermal anneal study have revealed that the amount of hydrogen in a silicon nitride layer is not important to obtain a high degree of passivation. More relevant is the way hydrogen is bonded, released, and directed into the substrate. This is best accomplished by high mass density silicon nitride layers which can retain hydrogen instead of releasing it into the ambient and also have a high thermal stability. This is related with an equal distribution of hydrogen between Si and N atoms, whereby hydrogen is released according to reaction (2), minimising voids by leaving a strong Si-N bond behind and no dangling Si or N bonds. Efficiencies >15% have already been obtained on multicrystalline silicon solar cells by these optimised ETP deposited silicon nitride layers [1].

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