CHARACTERIZATION OF IMPROVED HOT-WIRE DEPOSITED SILICON NITRIDE (SIN_X:H) ON MULTICRYSTALLINE SOLAR CELLS.

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We report on an investigation of SiN_x:H deposited by Hot-Wire Chemical Vapor Deposition (HW-CVD). To find the type of HWCVD SiN_x:H layer best suited for application in solar cells, various layers with different source-gas ratios were deposited on glass and c-Si wafers for optical characterization (R/T) and infrared absorption spectroscopy (FTIR). Also Elastic Recoil Detection (ERD) and Rutherford backscattering analysis (RBS) were conducted The N/Si ratio of the films varies between 0.3-1.4 and the Hydrogen concentration was between 8 - 12 at.-%. The SiN_x:H with best optical properties was used as antireflection coating on textured mc-Si solar cells from ECN. These cells reach efficiencies up to 15.7%, which is very close to the standard textured reference cell with a MW-PECVD SiN_x:H ARC and is the highest ever reported for HWCVD SiN_x:H. The V_{oc} is as high as 605 mV, the J_{sc} reaches a value of 34.9 mA/cm^2 and the IQE measurements in combination with the high V_{oc} values confirm the good bulk passivation. Investigation of a SiNx layer with similar deposition parameters shows that the N/Si-ratio of this material is 1.20 and that the material has a density of 2.9 g/cm^3, very high for a deposition method offering these high deposition rates. Structural analysis of an anneal series confirms the layers thermal stability because no changes in either the N/Si ratio or the density occur during heating. Investigation of the N-H and Si-H bond densities demonstrates that in the first 90 seconds of annealing there is a transfer of hydrogen from nitrogen-bonded sites to silicon-bonded sites, in addition to the expected out diffusion. Determination of the diffusion constant shows that the hydrogen diffusion to the mc-Si wafer is mainly N-H driven.

Keywords: Silicon-Nitride, Antireflection coating, Multicrystalline Solar Cells

1 INTRODUCTION

Silicon nitride is a widely used material with many technological applications, of which its use in multi-crystalline silicon (mc-Si) solar cells is one. In this study SiN_x:H is used as top layer where it simultaneously acts as an antireflection coating (ARC) and induces bulk and surface passivation of the mc-Si wafers. The SiN_x:H coating is able to act as a good ARC because of its high and tunable refractive index [1] and low extinction coefficient. Apart from these good optical properties, the passivating properties of the deposited SiN_x:H are at least as important. During a short anneal, needed to form a contact to the screen-printed silver metallization, hydrogen is released from the SiN_x:H layer and partly diffuses into the bulk of the mc-Si wafer. This hydrogen generates passivation of defects and impurities within the bulk, and defects on the surface of the wafer enabling an important enhancement of the cell performance.

The SiN_x:H layers discussed in this article are deposited with the new HWCVD technique, also known as Hot Filament (HF) CVD or Cat-CVD. With this simple method the source gasses are catalytically decomposed at the heated wires. A benefit of HWCVD is that no plasma is needed to decompose the source gasses preventing the substrate to be damaged by the ion-bombardment. In addition, it has been demonstrated that HWCVD can be scaled up to be compatible with large area deposition systems [2].

The goal of this paper is to show that with HWCVD SiN_x:H ARC just as good solar cell results can be accomplished as with other, conventional, deposition techniques, but with potentially higher throughput due to the high deposition rate and potentially lower costs.. Furthermore we have characterized the SiN_x:H layer used in the solar cells and have gained more insight in the layer behavior under annealing.

2 EXPERIMENTAL DETAILS

Various SiN_x:H layers were deposited on both Corning Glass 1737 and highly resistive mono-crystalline Si wafers using different flow-ratios and with different thicknesses. The deposition was made with a a four-filament Hot-wire (HW) reactor in an ultra high vacuum multi-chamber system (PASTA) [3]. As source gasses pure silane (SiH_4) and ammonia (NH_3) were used, which were catalytically decomposed at the 2100 °C tantalum filaments without using hydrogen dilution. The substrate was heated by radiation from the filaments only and reached a temperature of about 450 °C. During the deposition process no ions are created, which makes HWCVD a deposition method free of surface damage.

A shutter is situated between the sample and the wires to control the duration of the deposition and to let the substrates thermally equilibrate before the start of the deposition. For thickness uniformity of the layer a square showerhead gas inlet was used to create a uniform deposition area of 5x5 cm^2. The size of the uniform area is only limited by the size of the reactor chamber.

For characterization of the SiN_x:H layers properties Reflection/Transmission, Fourier Transform Infra Red Spectroscopy (FTIR), Rutherford Back Scattering (RBS), and Elastic Recoil Detection (ERD) were used. The Reflection/Transmission measurements were performed to determine the refractive index, extinction coefficient and layer thickness. RBS and ERD analysis were used to establish the composition of the layers and the total hydrogen concentration. For the N-H and Si-H bond density determination by FTIR, the ERD calibrated proportionality constants [4] for this material were used.

To investigate the behaviour of the applied SiN_x:H under firing of the contacts an anneal series was prepared. For this purpose one layer with a thickness of 260 nm was made under equal deposition conditions as the ARC on the solar cells. The sample was cut into 25 samples. Each sample was annealed for a different time, between 0 to 600 s. The annealing experiments were performed with a rapid thermal process (RTP) furnace at 800 °C.

To evaluate the passivating properties of the HW-CVD SiN_x:H with the best optical properties for application as an ARC, the material is deposited on mc-Si texture-etched solar-cells from ECN Solar Energy. After completion of the SiN_x:H depositions, the metallization at the front and backside was also applied at ECN using screen printing. For comparison and reference, solar cells with MW (microwave) PECVD SiN_x:H ARC were made from neighboring wafers in the ingot.

3 RESULTS

3.1 Film properties

First, samples were deposited using different NH_3/SiH_4 gas flow ratios in the range of 10-30. Their composition was established using ERD analysis and is plotted in Fig. 1 together with the deposition rate. The composition of Si-rich layers up to stoichiometry is highly sensitive to the flow ratio, whereas for higher flow ratios the composition alters only slowly from stochiometric to N-rich SiN_x:H. The deposition rate of the samples shows a non-linear dependence on the flow ratio whereby Si-rich layers do show higher deposition rates than N-rich samples. However, because the composition parameter N/Si-ratio is a physically more meaningful parameter for structural characterization than the gas flow ratio, in the rest of the paper we will correlate all features to this compositional parameter.

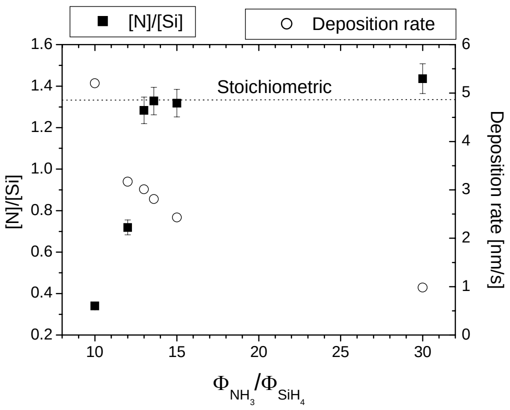

Figure 1: The composition and deposition rate of layers with different NH_3/SiH_4 gas flow ratios.

With the R/T measurements for each of the layers the refractive index and the extinction coefficient (k) was determined using our 'OPTICS' routine based on the Maxwell equations. From stochiometric to N-rich samples the k was almost zero were for Si-rich samples it rose quite sharply. The refractive index rose from 1.95 for N-rich samples to 2.5 for samples with a N/Si ratio of 0.3. All layers were annealed at 800 °C and none of them reveal blistering or any other major structural/mechanical changes as is confirmed by ERD and RBS measurements. This shows the thermal stability of the layers.

ERD analysis of the anneal series shows a constant N/Si ratio of 1.20 and a density of 2.9 g/cm^3. The initial hydrogen concentration of 11.5 at.-% decreases exponentially to just below 10 at.-% after 600 seconds of annealing, as can be seen in figure 2.

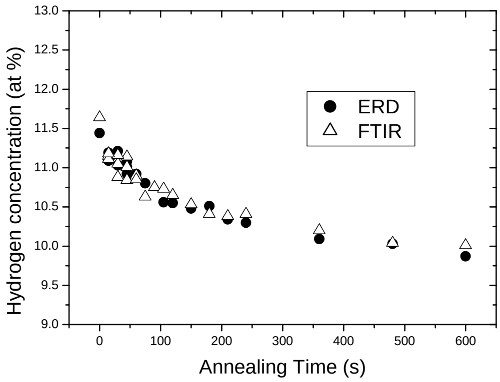

Figure 2: The hydrogen concentration of the SiN_x:H layer during annealing at 800 °C.

The FTIR measures the IR absorption caused by N-H and Si-H vibrational modes , which can be used to determine the respective bond densities of the annealed samples. These bond densities are shown in Fig. 2 during annealing there is the expected out-diffusion of hydrogen from the SiN_x:H layer and simultaneously a transfer of N-H to Si-H within the first 90 seconds of the annealing treatment.

3.2 Solar Cells

The best optical properties of HW-CVD SiN_x:H were obtained for slightly Si-rich material, at the cross-over between N-H and Si-H bond densities. This layer was deposited on a textured mc-Si solar cell from ECN. In Table 1 the open circuit voltage (V_{oc}), the short circuit current density (J_{sc}) and the fill factor (FF) are summarized together with the efficiency of the median and the best solar cell. All cells are initially deposited on a 10 cm x 10 cm wafer, which is afterwards laser-cut into 5.5 cm x 5.5 cm.

	Voc (mV)	Jsc (mA/cm^2)	FF	eff (%)
HWCVD median	595	33.8	0.750	15.3
MW RPECVD median	601	33.9	0.765	15.5
HW CVD best	**604**	**34.6**	**0.750**	**15.7**
MW RPECVD best	**606**	**34.3**	**0.774**	**16.1**

Table 1: An overview of the solar cell parameters for the cells with the HWCVD SiN_x:H ARC and for the reference cells.

The J_{sc} of the cells with the HWCVD deposited SiN_x:H is identical to that of the reference cells, whereas the V_{oc} is only slightly lower. The largest difference between the two groups of cells is found in the FF, where the values for the HWCVD SiN_x:H cells are roughly 0.02 lower than the reference cells. This difference is most likely caused by the fact that all other process parameters in cell processing were optimized for MWCVD SiN_x:H cells.

Besides the high V_{oc} values, also the Internal Quantum Efficiency (IQE) measurements illustrate good passivation properties for the cells with HW SiN_x:H as ARC. In Fig. 3 and Fig. 4 the IQE of the HW deposited SiN_x:H is plotted together with the IQE of the conventional MWCVD SiN_x:H. In the IQE measurements the blue response of the of the HWCVD SiN_x:H cells looks better when compared to the reference cells. Since the V_{oc} is similar for both types of cells and these IQE values are not corrected for absorption this is most likely a result of better transmission of the HWCVD SiN_x:H.

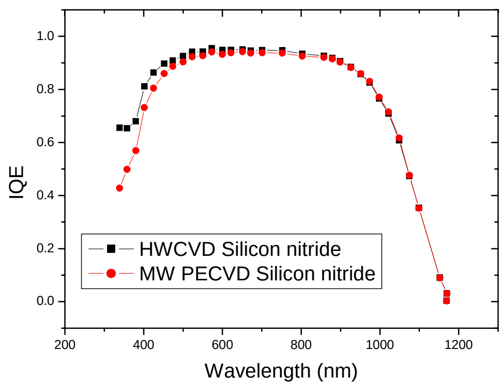

Figure 3: The IQE of a cell with HW-SiN_x:H ARC and a reference cell.

4 DISCUSSION

Earlier investigations [1,5] already confirmed that HWCVD SiN_x:H used as an ARC on a mc-Si cell instead of conventional PECVD SiN_x:H results in comparable performance. However this time it is demonstrated that HWCVD is also well applicable to textured solar cells and to our knowledge this is the highest efficiency ever published for mc-Si solar cells with HWCVD SiN_x:H as ARC. In all, the HW-CVD SiN_x:H layer presented in this paper performs significantly better than those reported earlier. It is anticipated that optimization of other cell processing procedures may lead to even better results for HW-CVD SiN_x:H leading to, among others, an increase in FF.

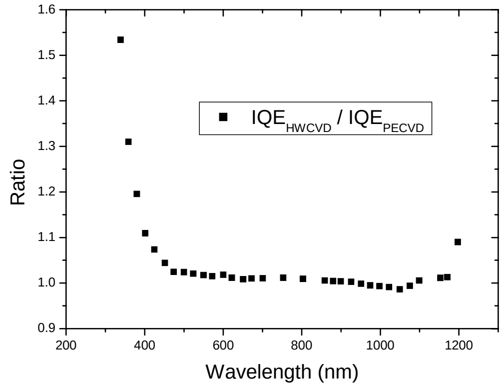

Figure 4: The IQE spectra of the HWCVD SiN_x:H cell relative to the reference cell. The blue response is clearly higher for the HWCVD SiN_x:H.

A closer look to HWCVD SiN_x:H material deposited with the same deposition parameters leads to some interesting observations. For instance, despite its high deposition rate this material has a very high density of 2.9 g/cm^3, whereas for comparable deposition rates with other techniques densities between 1.5 and 2.6 g/cm^3 are reported [6,7,8,9]. The layers are also thermally stable, whereas for plasma deposited layers it is known that a change in N/Si ratio can occur during annealing [10], which can make good control of the deposited layers difficult. These two differences might be caused by the improved dehydrogenation of the growth surface by the high flux of atomic H in the HWCVD reactor.

For passivation of the bulk of the wafer the diffusion of hydrogen from the SiN_x:H layer to the mc-Si wafer is an important aspect. The diffusion of H is monitored by measuring the N-H and Si-H bond densities for different annealing times. In Fig. 2 the hydrogen evolution is illustrated for N-H and Si-H bond densities. With these results the diffusion constants of both N-H and Si-H can be determined using Eqn. 1 [11].

$$C_H = C_{H,0} e^{\frac{-\pi^2 D_H t}{L^2}} \qquad (1)$$

For our HWCVD $SiN_{1.2}$:H material, the diffusion constants are 2.2*10^{15} cm^2/s and 1.3*10^{14} cm^2/s for Si-H and N-H respectively. Clearly the diffusion of N bonded hydrogen is mostly responsible for the hydrogen diffusion into the mc-Si wafer (and thereby for good hydrogen passivation of the dangling bonds). This is a the first quantified evidence of the observation by Holt *et al.* [3] that the N-H stretching mode decreased faster under annealing then the Si-H stretching mode. To eliminate any influence of the N-H to Si-H transfer process that takes place at short anneal times, only samples with annealing times longer than 100 seconds are used for diffusion constant determination.

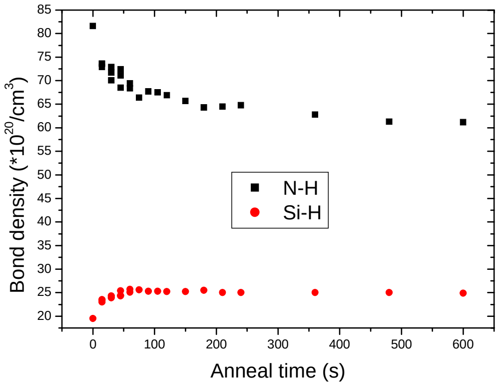

Figure 5: The relative absorption of the N-H and Si-H stretching mode as determined with FTIR. In the first 90 seconds there is a transfer of hydrogen from N-H to Si-H.

When using the FTIR spectra to study the Si-H and N-H bond densities the proportionality constants are of great importance and probably the largest source of errors. In this paper we made use of the ERD calibrated proportionality constants as determined for this type of SiN_x:H (x = 1.2) material [4]. It is noted that for the determination of the diffusion constants, these proportionality constants are of no influence because the *slope* of the logaritmic plot does not change when using different constants. Therefore, prior determinations of the diffusion constants are not influenced by possibly incorrect proportionality constants.

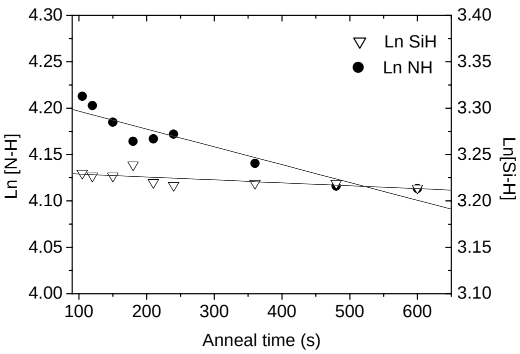

Figure 6: The logarithm of the N-H and Si-H bond density, the slopes of the line are proportional with the diffusion constant. To avoid any influence of the H transfer from N-H to Si-H only points at annealing times over 100 s are taken into account.

5 CONCLUSIONS

HWCVD SiN_x:H used as passivation layer and ARC on mc-Si wafers leads to solar cell results comparable to those obtained from reference cells on which conventional MWCVD SiN_x:H is used. The efficiency of solar cells with the HWCVD SiN_x:H reaches 15.7%, with a V_{oc} of 604 mV and a J_{sc} of 34.6 mA/cm^2. These parameters are all very close to those of reference cells. The FF of the cells is a little lower in comparison with the reference cells, which is probably caused by unoptimized cell processing. The IQE measurements of cells with HWCVD SiN_x:H in combination with the high V_{oc} clearly demonstrate good bulk passivation. The blue response of the IQE measurements of the HWCVD SiN_x:H cells also looks better when compared to the reference cells. Since the V_{oc} is similar for both types of cells this is most likely a result of lower absorption.

Investigation of a layer with deposition parameters identical to those used on the solar cells, show that the N/Si-ratio of this material is 1.20 and that the density is 2.9 g/cm^3, which is very high for a deposition technique with deposition rates of 5 nm/s. Annealing experiments prove that the layer is thermally stable and that no major structural changes occur in the Si-N network during heating at 800 °C. Determination of the diffusion constant from the N-H and Si-H bond densities learns that the hydrogen diffusion to the mc-Si wafer is mainly driven by the release from N-H bonds, from which it can be suggested that N-H bonds are most important for bulk passivation.

6 ACKNOWLEDGMENTS

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