SIN:H ANTI-REFLECTION COATINGS FOR C-SI SOLAR CELLS BY LARGE SCALE INLINE SPUTTERING

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ABSTRACT: This paper presents the investigation into the use of the sputtering technology for deposition of passivating SiN_x:H anti-reflection layers on multi-crystalline silicon solar cells. The experiments were carried out on a large area inline sputtering system - manufactured by APPLIED FILMS – that features a Twin-Magnetron mid frequency cathode system which provides excellent uniformity of thickness and high deposition rates. By adding ammonia to the process gases the hydrogen content of the sputtered layers could easily be varied over a wide range leading to cell efficiencies of 15,3% on multi-crystalline silicon solar cells. By IQE and FTIR analysis the sputtered layers were compared to PECVD-reference SiN_x:H layers showing equal surface passivation and excellent bulk passivation properties of sputtered SiN_x:H anti-reflection coatings.
Keywords: sputtering, silicon nitride, multi-crystalline

1 INTRODUCTION

Currently most anti-reflection (AR) coatings for multi crystalline solar cells are hydrogen containing silicon nitride (SiN_x:H) layers deposited by plasma enhanced chemical vapor deposition (PECVD). The advantage of SiN_x:H -layers over other AR-coatings like titanium dioxide is the ability of good surface and bulk passivation [1,2]. Besides of these benefits the technique of PECVD deposition has several drawbacks. Mainly the use of explosive gas and short service cycles, but also appearing problems in achieving uniform coating thickness on large scale inline coaters result in growing interest in different deposition techniques. As sputtering of various material on large area substrates features high throughput, good uniformity and long service cycles [3,4] it is a promising method for SiN-coatings on solar cells [5,6].

2 INLINE SPUTTER COATER "ATON"

All experiments were carried out on a prototype system of the ATON sputter series - built by APPLIED FILMS and set up at the Fraunhofer ISE demonstration laboratory - which, in contrast to the true inline system has only one load area (Figure 1). Up to 16 wafers are placed on a carrier – see Figure 2 - with a coating area of 50 cm width and 60 cm length and are heated up to 200 – 400°C under vacuum.

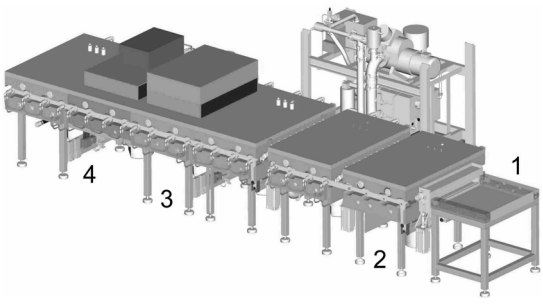

Figure 1: Scheme of the sputter coater manufactured by APPLIED FILMS. 1) load area (carrier not drawn) for up to 16 wafers. 2) vacuum load lock. 3) TWIN-MAG cathode. 4) HF cathode.

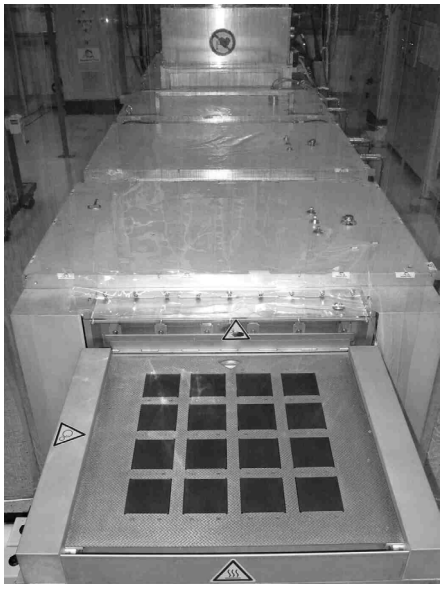

Figure 2: Photo of the carrier on the load area of the SiN sputter coater set up at the Fraunhofer ISE in June 2003.

The system then provides the possibility of dynamic coating either in a RF discharge or with a dual magnetron (TWIN-MAG®) system. Instead of the highly explosive silane as the PECVD-Si source both sputter systems feature solid silicon targets. In the case of the TWIN-MAG-system two boron doped targets are alternately sputtered using a mid frequency power supply under argon atmosphere. By adding reactive gases like nitrogen, hydrogen or ammonia to the sputter gas the index of refraction and the hydrogen content of the SiN_x:H layer can easily be varied. The advantage of TWIN-MAG-sputtering over other SiN_x:H coating technologies, e.g. PECVD is the possibility of scaling up the coating area up to widths of over 3 m. Optimization of the size and the shape of the cathode aperture leads independently of the size of the coating area to good uniformity of layer-thickness. After the first optimization of the cathode aperture the layers deposited with TWIN-MAG were showing a maximum deviation of +/- 2 % over the total coating area; as can be seen in Figure 3.

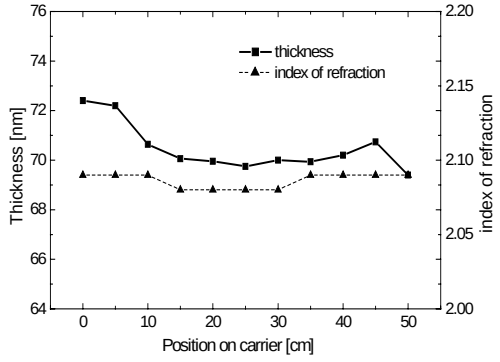

Figure 3: Uniformity of thickness and index of refraction of AR-SiN:H-layers deposited with a TW IN-MAG-system over the width of 50 cm. The uniformity was measured after the first optimization of the cathode aperture.

With subsequent optimization of the aperture the homogeneity should further increase. In addition to the good layer uniformity the TW IN-MAG system features high dynamic deposition rates of about 40 nm*m/min, allowing the design of a high throughput sputter system.

3 DEPOSITION OF SILICON NITRIDE ON MULTI CRYSTALLINE SOLAR CELLS

Boron doped Baysix mc-si wafer from the middle of an ingot, with a thickness of 330 µm +/- 15 µm, a size of 100x100 mm and a resistivity in the range of 0.5 Ωcm to 2.0 Ωcm have been used for all experiments. To make a comparison between the different experimental variations, neighboring wa fers were taken. The processing of all wafer has started with a saw damage removal in a KOH-acid followed by a surface cleaning sequence. A standard $POCl_3$ emitter diffusion in a quartz tube lead to a resistivity of 40 ohm/sqr. The wafers were then coated either in the ATON coater or as references in a high frequency direct PECVD system (Multiplex STS) [7]. After a standard front and back side screen printing process, the contact formation was performed by a firing through process. Beside the contact formation this RTF-process enables hydrogen passivation of the bulk material. The whole proces s sequence is close to an industrial solar cell process sequence.

3.1 Influence of sputter plasma on emitter damage

Given the fact that sputtering plasmas contain ions with energies up to 200 eV, it was unclear if there is damage of the surface and the e mitter. Dark I-V measurement of solar cells can be used to determine the parameters of the diode law, especially the saturation current density caused by recombination in the depletion region, called I_{02}. For this reason we investigated the influence of different Rapid-Thermal-Firing (RTF) peak temperatures and ammonia flux on I_{02} of mc solar cells with a sputtered SiN_x:H-AR layer. As can be seen in Figure 4 low I_{02} values of about $2*10^{-8}$ A/cm^2 are reached for small firing peak temperatures and increasing ammoniaflow.

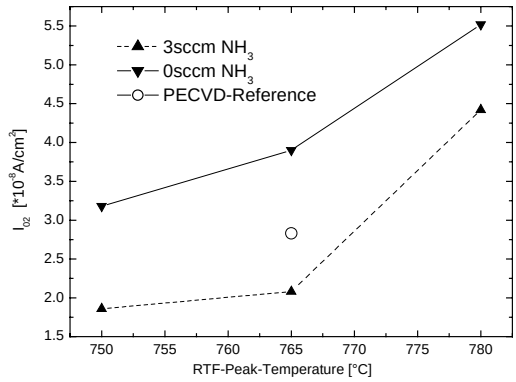

Figure 4: Influence of Rapid-Thermal-Firing (RTF) peak temperature and ammonia flow rate on I_{02} of mc solar cells. The low values of I_{02} - for 3sccm NH3 and low RTF peak tem perature - com pared to P ECVD implies [8], that there is no significant em itter damage due to high energy ions.

Higher values of I_{02} with increas ing firing peak temperature and zero ammonia flow are caused by a deep penetration of the front side grid, as reported by Huljic [8]. Because damage of the em itter through high energy ions out of the sputter plasma would lead to high values of I_{02} independently of Rapid-Thermal-Firing (RTF) peak temperature and ammonia flux we therefore conclude that there is no em itter damage due to high energy ions. These results are cons istent with sim ulations of the surface damage caused by the impact of energetic ions on silicon [9].

3.2 Solar cell results

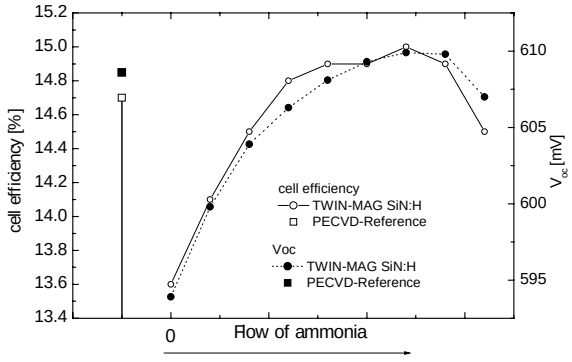

Figure 5: Influence of different ammonia flow rates on cell efficiency and open gate voltage V_{oc} for mc solar cells with TW IN-MAG-sputtered SiN_x:H AR coating on neighboring wafers. Also shown is the reference value of a solar cell with PECVD SiN AR coating.

Figure 5 is showing the influence of an increasing ammonia flow on the efficiency and the open circuit voltage of mc-solar cells w ith AR coatings by TWIN-MAG sputtering. Starting from SiN_x:H layers deposited without adding ammonia or hy drogen - resulting in hydrogen free SiN_x - the cell efficiency increases with increasing ammonia flow

Table I: Comparison between parameters of multicristalline solar cells coated with sputtered and PECVD-AR-SiN:H. The cells were processed from neighboring wafers.

Coating system	V_{oc} [mV]	J_{sc} [mA/cm^2]	FF [%]	efficiency [%]
PECVD	609	30,23	80	14,7
TWIN-MAG	611	30,7	80	15

from 13,6 % to a maximum of 15 %. Further enlargement of the flow results in a generation of hydrogen cavities – called blistering – in the SiN_x:H layer leading to a deterioration of the optical properties. In table I the solar cell results for the best sputter process and the P ECVD reference proces s are summarized, highlighting the excellent quality of TWIN-MAG sputter anti reflection coatings on mc-solar cells.

4 FTIR AND IQE ANALYSIS

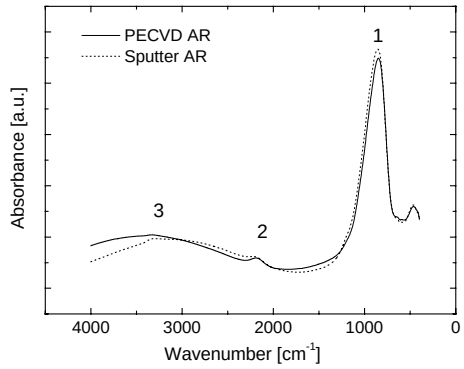

Figure 6: FTIR spectra of sputter– and PECVD-AR coatings. Both coatings have a com parable thickness. The identifiable peaks are belonging to following bonds: 1) Si-N bond; 2) Si-H bond; 3) N-H bond

For better understanding of the general properties of sputtered AR coatings SiN_x:H layers deposited by TWIN-MAG sputtering were investigated by FTIR measurements.

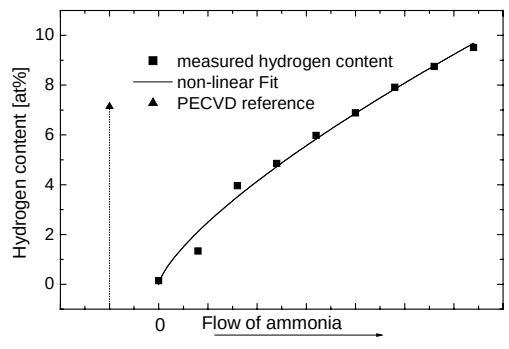

Figure 7 Influence of ammonia flow on hydrogen content of TWIN-MAG sputtered SiN_x:H-layers. The hydrogen content was calculated from the sum of the peak area of the Si-H and N-H bond.

As shown in Figure 6 the bond densities – calculated from the peak areas and the thicknes s – can be seen as nearly equal. Calculating the sum of the bond densities of the Si-H and the N-H bond one can estimate the amount of hydrogen existent in the SiN_x:H layer.
Figure 7 clearly shows that with increasing flow of ammonia there is an alm ost linear increas e in hy drogen content.

4.1 Spectral response

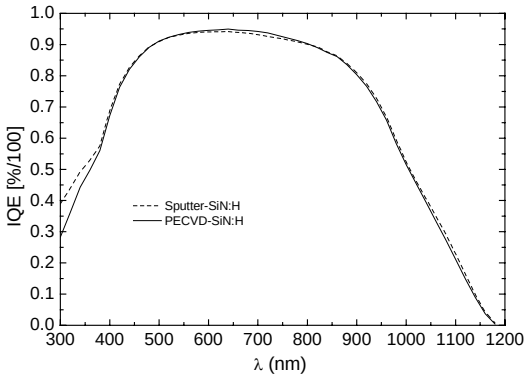

Figure 8: Spectral response of mc solar cells with TWIN-MAG sputtered SiN:H AR coating. Also shown is the spectral response of a solar cell with a PECVD processed SiN:H layer.

The spectral response (IQE) of solar cells in the short wavelength region gives information about passivation of the front side and the em itter. The region between 700-1100 nm is mainly influenced by the carrier lifetime in the bulk. The com parison between the bes t solar cells with TWIN-MAG SiN_x:H and the PECVD reference in Figure 8 clearly shows that surface passivation as well as bulk passivation ability of sputtered and PECVD processed SiN_x:H are on a par. The differences in cell efficiency between sputter and P ECVD processed solar cells - s ummarized in table I - are caused by worse optical qualities of the PECVD layer, due to higher absorption and bad homogeneity of thickness.

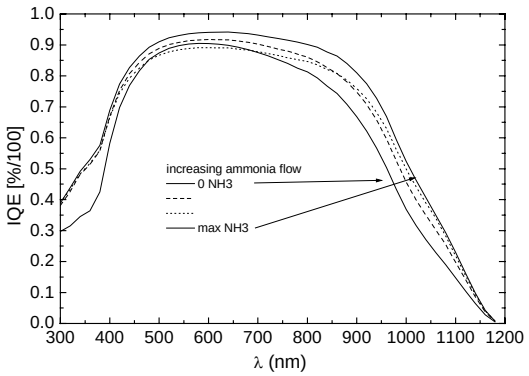

Figure 9: Spectral response of mc solar cells from neighboring wafers with TWIN-MAG sputtered SiN_x:H AR coating. Shown is the influence of increas ing ammonia flow on a grain with s mall charge carrier lifetime.

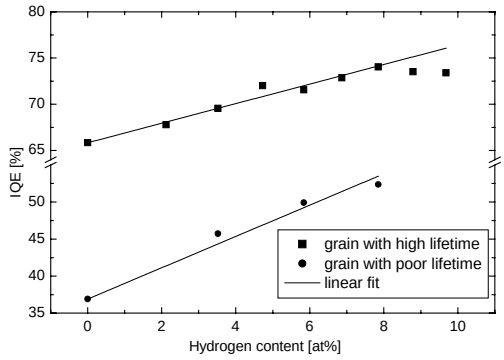

Figure 10: Spectral response at 1000 nm of mc solar cells with TWIN-MAG sputtered SiN:H AR coating. Shown is the influence of increasing hydrogen content of the SiN_x:H layer on grains with different charge carrier lifetimes.

Analyzing the variation of ammonia flow from Figure 5 with IQE in Figure 9 shows a slight increase for short wavelengths. The strong increase of IQE in the long wavelength region is ascribed to the enhanced passivation of bulk defects by indiffusion of hydrogen. This effect is visualized in Figure 10. Presenting only the IQE values at the wavelength of 1000 nm one can observe a linear increase in IQE with increas ing hydrogen content of the SiN_x:H layer. The gradient of IQE improvement is bigger for grains with poor charge carrier lifetime.
As the above m entioned blistering is a lim iting factor in increasing the hydrogen content of SiN_x:H AR layers research on sputter processes focused on avoiding blistering in SiN_x:H layers with high hydrogen content.

4.2 Further development of sputter SiN:H layers

Further variation of sputter process parameters focusing on high hydrogen content of the SiN_x:H layer resulted in solar cell parameters shown in table II. The cell efficiency of 15,3 % clearly demonstrates the excellent quality of sputtered SiN_x:H layers for the use on multi-crystalline solar cells.

Table II: Best results of parameters of multi-crystalline solar cells coated with sputtered AR SiN_x:H reached so far. The solar cells were trea ted with the near industrial process sequence described in chapter 3.

Coating system	V_{oc} [mV]	J_{sc} [mA/cm^2]	FF [%]	efficiency [%]
TWIN-MAG	614	31,3	79,5	15,3

5 CONCLUSION

A large scale inline coater m anufactured by Applied Films was used to deposit SiN_x:H antireflection coatings with varying hydrogen content on multi-crystalline silicon solar cells by reactive TW IN-MAG sputtering. The TWIN-MAG system features an error in thickness of under 2 % over the total coating area and deposition rates of about 40 nm*m/min - for one TWIN-MAG assembly - leading to a throughput of up to 1800 solar cell wafers per hour, with two cathodes and a assumed coating width of 850 mm.

By variation of ammonia flow a strong increase in cell efficiency was observed. FTIR measurements showed that this variation of ammonia flow is leading to a linear increas e of the hy drogen content of the SiN_x:H layers. By analyzing the spect ral response of cells with increasing hydrogen content of the SiN_x:H AR layer a linear increase in IQE in the long wavelength region could be seen. Furthermore no difference between sputter SiN_x:H and PECVD SiN_x:H was found by IQE and FTIR measurements. Corresponding to an improved passivation of bulk defects with increasing hy drogen content - and therefore advanced cell characteris tics - further development of sputter processes focused on SiN_x:H with high hydrogen content.

These advanced TW IN-MAG processes lead to cell efficiencies of 15,3 % on m ulti-crystalline solar cells. Combined with the results from the FTIR and IQE analysis this dem onstrates that sputtered SiN_x:H layers have at least the sam e qualities com pared to PECVD SiN_x:H for the use as anti reflection coatings on c-S i solar cells.

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