ON COMBINING SURFACE AND BULK PASSIVATION OF SiN_x:H LAYERS FOR mc-Si SOLAR CELLS

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ABSTRACT

A route, as followed by ECN, is described for development of SiN_x:H layers deposited by microwave (MW) PECVD, which are suited for surface and bulk passivation of mc-Si solar cells. First research was focussed on surface passivation and this resulted in the development of SiN layers that were Si-rich and where the hydrogen is mainly bonded to silicon atoms. A disadvantage of such Si-rich layers is their large absorption at shorter wavelengths, which make them unsuitable as front side AR coatings. Further, these layers appeared to be less suitable for bulk passivation. The next step therefore was the development of SiN layers for bulk passivation. For good bulk passivation of solar cells by means of a thermal anneal of the SiN layers, we found that SiN layers with high N-H bonding concentrations are required. Fine-tuning of the deposition conditions of these layers, finally resulted in the development of a SiN layer type which combines the three desired properties: low absorption (good anti-reflection coating), good surface passivation (S_{eff} on FZ wafers less than 50 cm/s) and good bulk passivation.

INTRODUCTION

Good SiN_x:H layers have to fulfil three requirements when applied in mc-Si solar cell manufacturing: act as a non-absorbing antireflection coating, provide surface passivation and induce bulk passivation of the silicon wafer. The latter effect can be accomplished by a thermal activation of the layer (e.g. during firing of a screen-printed metallisation) by which hydrogen diffuses from the SiN_x:H into the silicon wafer where it passivates crystal defects and impurities [1,2]. It has been found very difficult to combine all three aspects in one SiN_x:H layer. We have found that nitride layers dedicated to surface passivation require rather different deposition conditions than nitride layers which are good for bulk passivation [3]. Physical properties of nitride layers for surface passivation have been investigated to some extent [4] but the properties of nitride layers which are good for bulk passivation have not been investigated so far. In this paper we will compare the atomic structures of both types of layers in order to find a route for combining surface and bulk passivation in one nitride layer.

EXPERIMENTAL METHODS

The microwave PECVD system at ECN which has been used for depositions of the SiN_x:H layers has been described in detail in previous papers [1,3]. The system is capable of continuous processing of 150 wafers (10×10 cm^2) per hour and we have shown that the deposition process is robust when applied on industrial scale; i.e. when a large number of wafers is being processed [5]. With this MW plasma source we have developed an optimized SiN_x:H layer for surface passivation by systematically varying the deposition conditions: substrate temperature, pressure, MW power and SiH_4 and NH_3 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 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 plasma probe measurements and by Residual Gas Analysis (RGA) using a Prisma 200 mass spectrometer. Plasma probe measurements are performed with a linear plasma probe array with the following features: 16 probes at 50 mm distance; diameter of the plasma probes 6 mm (planar probe).

Surface passivation was established by growing identical SiN layers on front and rear side of FZ wafers and subsequent measurement of τ_{eff} by Quasi Steady State Photo Conductance (QSSPC) [6] and Modulated Free Carrier Absorption (MFCA). In another experiment we developed an optimized SiN layer for industrial mc-Si solar cell processing. Again we systematically varied deposition conditions for SiN layers used as front side AR coatings on cells with a 50 Ω/□ emitters. After SiN deposition the front and rear side metallization was screen printed. Subsequently the cells were fired in a belt furnace in order to obtain good ohmic contacts. Atomic structure of the layers was established by Elastic Recoil Detection (ERD) [7] and FTIR measurements.

RESULTS

Plasma properties

Microwave power and duty rate in first instance have been fine tuned to optimize the homogeneity of the deposition. Plasma probe measurements on a pure NH_3 plasma helped us to do this optimization in an efficient way. In Fig. 1 probe current densities as a function of the distance along the MW source are shown for various MW powers. These probe current densities, measured at -15 V at 50 mm from the source, are a direct measure of the plasma density and therefore also a direct measure of the deposition rate. The plasma density increases proportionally with the MW power but it can also be observed that for larger MW powers the skew of the density towards the walls (at 0 and 750 mm) increases. This skew is caused by recombination of positive ions at the walls. The larger the skew, the smaller the area for homogeneous depositions. Since we want to apply a deposition area with a width of 600 mm, (that is for x between 100 and 700 mm in fig. 1) we have limited the MW power to about 1200 W.

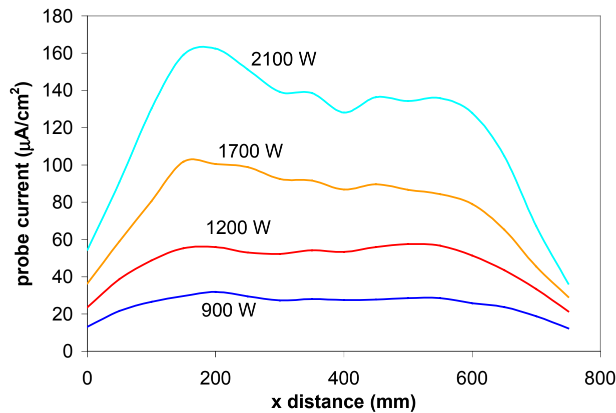

Figure 1: Plasma probe currents for various MW power densities.

From the probe current the electron temperature can be calculated. Despite the moderate electron temperatures (2-4 eV) in the plasma, the dissociation of the process gasses is very efficient. In Figure 2 a typical RGA spectrum as recorded during one deposition cycle is shown.

It can be observed that as soon as the MW power is switched on, the QMA signals of both NH_3 (at 16 and 17 a.m.u.) and SiH_4 (at 30 and 31 a.m.u.) decreases drastically. From these data we can deduce the depletion ratio's for both gasses yielding approximately 85-90% for NH_3 and 90-95% for SiH_4. The depletion ratio for SiH_4 and in particular for NH_3 are quite large in comparison to other PECVD systems, and permit a very efficient use of the process gasses.

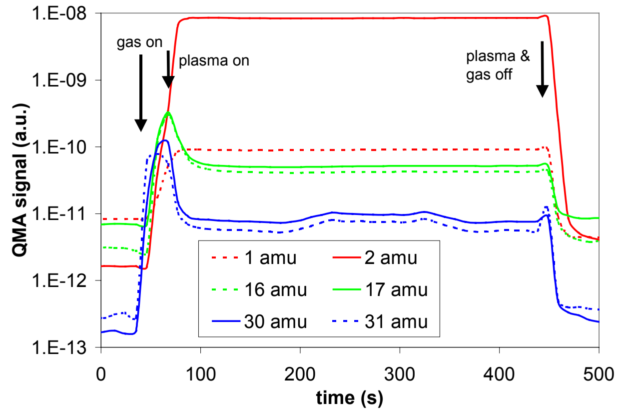

Figure 2: Residual gas analysis spectrum during one deposition.

Physical properties SiN$_x$

In Table I we present a survey of physical properties of four typical SiN_x:H layers as grown on mono-crystalline Cz-Si wafers. SiN-I was developed for surface passivation, yielding S_{eff} < 20 cm/s on p-type FZ wafers. SiN-I has a high refractive index and a high absorption at shorter wavelengths and is therefore not suited for solar cell processing. SiN-II was optimized for mc-Si solar cell efficiency with a processing scheme including a ‘firing through’ of the front side metallization [1]. The surface passivating properties of SiN-II are rather poor (S_{eff} is about 1000 cm/s on p-type FZ). SiN-III and SiN-IV, finally, are intermediate results of our optimization experiments. SiN-IV provides an excellent A.R. coating, but its surface and bulk passivation properties are poor. The properties of SiN-III, moderately passivating, are in between those of SiN-II and SiN-IV. Data presented in the table are those obtained before annealing (b.a.) and after annealing (a.a.) where the annealing simulates the ‘firing through’ step.

It can be observed that both SiN-I and SiN-II contain approximately the same amount of hydrogen, but that the bonding of the hydrogen is very different. For SiN-I, optimized for surface passivation, the hydrogen is predominantly bond to silicon atoms, whereas for SiN-II the bonding is more equally distributed over N and Si atoms with a small bias in favor of N atoms.

In fig. 3 the FTIR spectra for both SiN-I and SiN-II are shown. The position of the Si-H absorption peak at about 2200 cm^{-1} is slightly different for both types of SiN. For the SiN-II type the maximum is at a higher wavenumber, which is due to the higher amount of N atoms backbonded to Si atoms.

Table 1: survey of physical properties of four exemplary SiN layers. (b.a. means before annealing; a.a. means after annealing)

Layer	Passivation	n	ρ (g/cm^3)	N/Si	Si-H (10^{22} cm^{-3})	N-H (10^{22} cm^{-3})	Si-N (10^{22} cm^{-3})	NH/SiH
		ellipsometry	ERD	ERD	FTIR	FTIR	FTIR	FTIR
SiN-I b.a.	surface	2.30	2.25	0.91	1.19	0.27	3.53	0.23
SiN-I a.a.		2.28	2.26	0.88	1.17	0.10	3.54	0.09
SiN-II b.a.	good bulk	2.17	2.53	1.29	0.50	0.88	4.13	1.76
SiN-II a.a.		2.15	2.50	1.33	0.52	0.83	4.14	1.60
SiN-III b.a.	bulk	2.03	2.41	1.33	0.31	0.75	3.81	2.42
SiN-III a.a.		2.02	2.38	1.33	0.34	0.77	3.90	2.27
SiN-IV b.a	no	2.05	2.33	1.20	0.54	0.62	3.63	1.15
SiN-IV a.a.		2.05	2.32	1.19	0.52	0.58	3.70	1.12

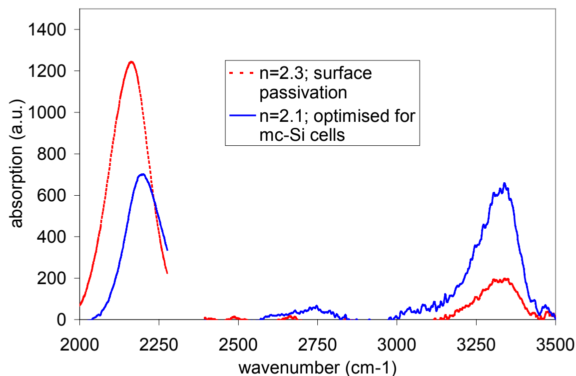

Figure 3: FTIR spectra for SiN-I and SiN-II.

Passivating properties

First we will present the internal quantum efficiency (IQE) of cells processed with SiN-I and SiN-II. In fig. 4, results of IQE on mc-Si cells with SiN-I and SiN-II layers are shown. It is observed that the SiN-I layer does not provide a good blue light response. At 400 nm the IQE for the cell with SiN_x-I is 30% lower than that of SiN_x-II. Somewhat less than 20% is due to the larger absorption in the SiN_x-I layer. The remaining part is probably caused by thermal degradation of the surface passivation during the firing of the metallization [4]. Further it is observed that the IQE at wavelengths longer than 800 nm is only slightly worse for SiN-I than for SiN-II. At 1000 nm the difference is less than 10%. This means that with SiN-I layer also significant bulk passivation can be obtained. On the other hand we have seen that SiN-II provides some surface passivation since the IQE at wavelengths below 500 nm is clearly higher than for unpassivated cells [1].

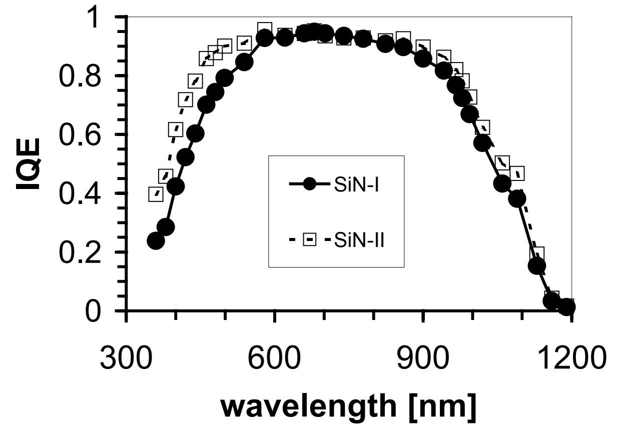

Figure 4: Internal Quantum Efficiencies of mc-Si solar cells with two different SiN AR coatings

SiN-II, SiN-III and SiN-IV have optical properties that are suited for solar cell processing (low absorption). Furthermore the composition is more or less similar. From Table I we can see that not only the bonding of the hydrogen determines the ability of passivation, but that also the total amount of hydrogen and the density of the layers are of importance. The relation with the density of the SiN layers has also been established by Hong et al. [8].

DISCUSSION

Surface passivation

In the SiN-I layers the NH/SiH ratio is much smaller than the N/Si ratio, which implies that the hydrogen is predominantly bonded to the silicon atoms. This probably explains the good surface passivation by SiN-I: in this layer, and at the SiN/Si interface there will be a very low fraction of the Si dangling bonds. This may occur at the expense of a higher number of unpassivated N dangling bonds but these defect centres do not play a role as recombination centres since their energy levels are positioned below and just above the valence band [9].

Bulk passivation

Although the composition of SiN_x-I and SiN_x-II are completely different, both layers result in bulk passivation. Both layers contain more or less the same amount of hydrogen before anneal (≈ 1.4E22 cm^{-3}) which is significantly more than in the non-passivating SiN-IV (1.1E22 cm^{-3}). During anneal the SiN-I film loses much more hydrogen than the SiN-II film (ΔH is about 1.9E21 cm^{-3} and 0.3E21 cm^{-3} respectively). The extra hydrogen loss of SiN-I does not lead to better bulk passivation, but the IQE at 1000 nm is somewhat more than 90% of that for cells with a SiN-II layer. For cells without passivation

the IQE at 1000 nm is less than 80% of that for cells with a SiN-II layers [1]. This implies that the bulk passivation by the SiN-I layer is moderate. A large part of the hydrogen from SiN-I is probably lost by out diffusion to air or by formation of molecular hydrogen in voids since this material is less dense than SiN-II. This effect is also found by Hong et al [8].

Combination of surface and bulk passivation

The ideal SiN_x:H layer for solar cell applications combines the best of three worlds: a) good anti-reflection, b) good surface passivation and c) good bulk passivation. Successful attempts have been undertaken to combine (a) and (b) by developing SiN_x:H layers with low refractive index and low absorption [10]. Bulk passivating capabilities of these layers is still an open question however. An alternative route would be to start with SiN-II (which combines (a) and (c)) and to optimize its surface passivating properties by taking care that at the Si/SiN interface all Si dangling bonds are passivated by hydrogen. At ECN we recently have been quite successful with this last approach. Further improvement of SiN_x-II resulted in a layer with good surface passivation (S_{eff} < 50 cm/s on p-type FZ). On completed solar cells this layer resulted in an extra increase of 5-10 mV in V_{oc} compared to cells with SiN-II layers. The efficiency of these cells processed using a very simple industrial type processing scheme (alkaline saw damage etch, belt furnace diffusion, SiN deposition, screenprinted metallization followed by co-firing) is about 15%. Detailed characterization of the solar cells and the improved SiN_x layers will be carried out in the near future. The thermal stability of the surface passivating properties needs to be investigated too.

CONCLUSIONS

Microwave PECVD appears to be an effective and efficient tool for deposition of SiN_x:H layers serving both as anti-reflection layers and as surface and bulk passivating layers. Good bulk passivation can be obtained by layers that combine a relatively high density and a large concentration of N-H bonds. Good surface passivation can be obtained by layers with a large Si/N ratio but we found that these layers do not produce optimal bulk passivation. A combination of bulk and surface passivation was obtained by optimization of the bulk passivating SiN. This resulted in the development of a SiN layer type which can increase the V_{oc} of mc-Si solar cells with more than 30 mV by bulk passivation, and which can provide an S_{eff} of less than 50 cm/s on FZ wafers.

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