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INVESTIGATION OF BLISTERING OF SPUTTERED SILICON NITRIDE ANTI-REFLECTION LAYER

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In the course of a trend to use material with low quality for silicon solar cells there is a growing demand for good bulk passivation. An important parameter for the bulk passivation of multi crystalline solar cells is the hydrogen rate of the SiN:H anti-reflection layer. The hydrogen in this layer diffuses during the SiN;H deposition as well as during the contact formation process in the bulk and passivates impurities and defects. One advantage of the sputter technology compared to other deposition systems is the possibility to vary the amount of hydrogen easily. At high hydrogen concentrations in the SiN:H anti-reflection layer blistering occurs. Researches have shown that the cell performance increases with higher hydrogen concentrations, the only limiting factor being the occurring of blistering. In this work we present results for understanding the blistering effect and techniques to shift the blister boundary.

1 Introduction

For the production of a solar cell the hydrogen rate in the SiN:H anti-reflection layer is an important parameter. Several experiments [2,3] show the dependence of the cell performance of the hydrogen rate. The limiting factor of the hydrogen rate is the occurrence of blistering in the silicon nitride layer which affects the optical properties of the layer in a negative way. To the authors knowledge this is the first research of the effect of blistering for solar cells produced by an inline sputtering system. The investigations have shown that the amount of hydrogen in the SiN layer before blistering occurs depends on the roughness of the surface, PSG (phosphorus silicate glass) etching, pretreatments, emitter formation and the material used.

2 Experimental setup

The experiments where carried out on a ATON sputter coater manufactured [1,2,3] by Applied Materials. The system provides the possibility of dynamic coating. Instead of silane as the silicon source SiN-sputtering uses a target of pure silicon on which argon ions are accelerated by the TWIN MAG low frequency system. By adding nitrogen and ammonia gases to the process atmosphere the refraction index and the hydrogen content of the layer can be varied over a wide range. Another advance of sputtering is the possibility to define the hydrogen [3] ratio of the layer in a wide range, as shown in Fig. 1.

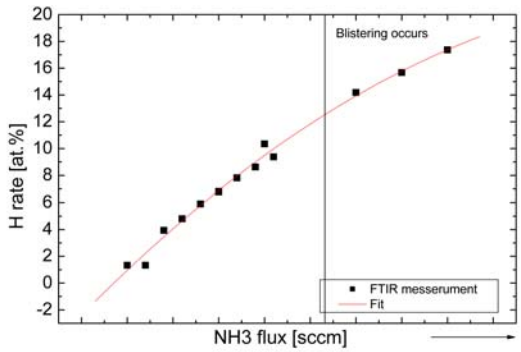

Figure 1: H concentration in the SiN:H layer versus the NH_3 flux measured with FTIR.

A nearly proportional dependence of the hydrogen rate and the NH_3 flux has been found. For sputtered SIN:H layer the H concentration can be chosen in a range of 1-20 at.%. A change in the density could not be found.
For investigation of blistering test were carried out. For blister tests the wafer gets a standard solar cell process by means of damage etching or texturing a $POCl_3$ tube diffusion and a PSG etching. After deposition of the SiN:H layer the wafer is fired at standard conditions in a fast firing furnace. For the analysis the wafer is optically analysed. The appearance of blistering is identified with the bare eye by a haze of the wafer (blister boundery). The appearance and density of bubbles can be studied using a standard microscope. The correlation of blistering with many different factors has been studied including wafer surface morphology, surface doping, drying after PSG etching, hydrogen content of the SiN:H and the firing temperature.

3 Influence of the emitter

The dependence of the bister boundary on an emitter is shown in Fig.2. The emitter influences the growth of the native oxide film strongly.
A higher defect density at the surface caused by the emitter enables a quicker oxidation [5]. This delivers the first evidence that the native oxide film influences the blister boundary.

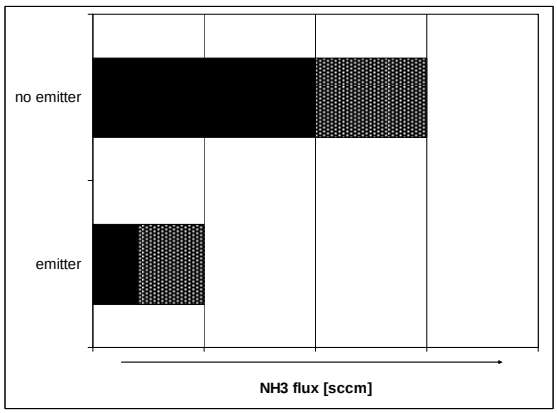

Figure 2: Blister boundary depending on flow of ammonia of mc 156mm^2 wafer with and without an emitter. The black bar indicated the boundary for isolated blistering (isolated blistering), the gray bar shows the boundary for strong blistering (sprong haze of the wafer).

4 Drying method after PSG etching

Fig 3 shows microscope images of blistering. On the left hand a homogeneous distribution of the blistering is visible. This wafer shows a hydrophobic behaviour after PSG etching. It is dryed in hot water and after this with hot air (PSG process 1). On the right hand side the wafer is dried in nitrogen atmosphere (PSG process). The wafer on the right in Fig. 3 shows an allocation of the blistering only at the grain boundaries. At the grain boundaries a higher density of crystal defect delivers more germ for the formation of blistering. The wafer shows a hygroscopic behaviour.

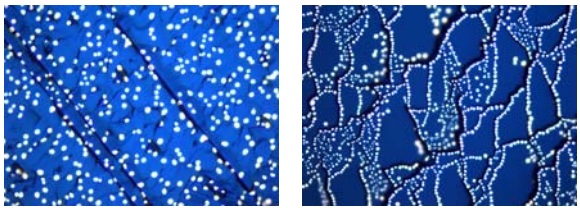

Figure 3: Microscope images extract (magnification of 50) of damage etched mc 125 mm^2 wafers after firing. The left sample is produced with PSG process 1, the right sample is done by PSG process 2.

The different arrangement of the blisters is caused by the drying method. The drying of the wafer after the PSG etching influences the structure and thickness of the native oxide grown on the surface. [6] reported that the oxidation of silicium at air can be described by a layer by layer growth. The Si atoms at a cleaned wafer surface are terminated by hydrogen. The Si-H bonds at the surface cause a hydrophobic behaviour. For the oxidation of Si in ultrapure water, [6] reported that the Si atoms of the native oxide surface are terminated by oxygen atoms or hydroxide groups. The Si-H groups exist at the oxide- Si interface. Such a surface is hygroscopic.
In Fig 4 the dependence of the blister boundary of different surface roughness (texture/bright etched) and PSG etching is shown. The PSG etching processes varied especially in the drying step. PSG process 1 has a hot water and air drying, PSG process 2 dried in a nitrogen atmosphere.

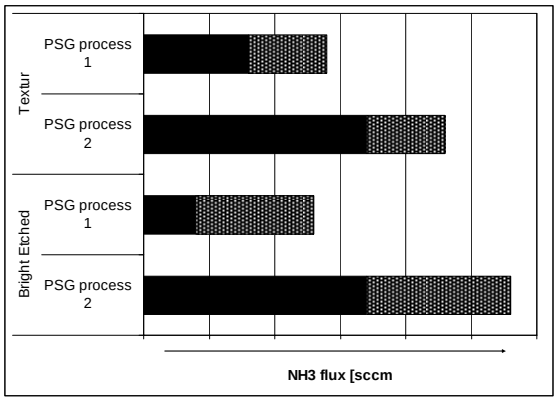

Figure 4: Blister boundary depending on the flow of ammonia of mc- wafer (size 156mm^2) different wet chemical surface treatments and PSG etches. The black bar indicated the boundary for isolated blistering. The gray bar shows the boundary for strong blistering.

The blister boundary increases by drying in a nitrogen atmosphere (process 2). This can be caused by a different thickness and structure of the native oxide layers. The benefit of the blister boundary depends on the roughness of the surface. The structure of the textured surface could act as seed for blistering. As mentioned before raised hydrogen content should cause an enhancement of the bulk passivation and therefore enhance the cell parameters of multi-crystalline silicon.
For this approach solar cells were produced with variation of the drying process and different emitters. To point out the enhancement of the bulk passivation IQE measurements were performed (Fig. 5).

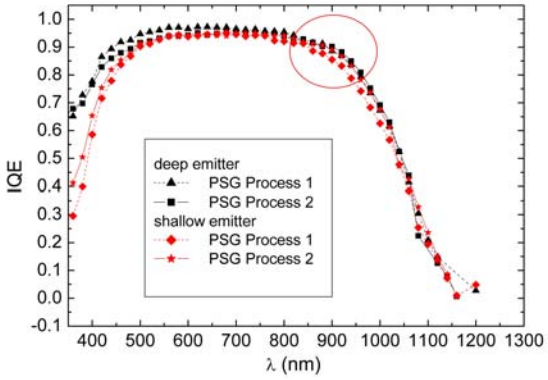

Figure 5: IQE measurement of cells from neighboring mc-Si wafers (size 125 mm^2) on the same grain with different emitters and drying processes.

Interpreting the IQE measurment, one can see that there are differences at low wavelengths caused by the emitter. The used emitters varied especially in the depth and in the phosphorus concentration at the surface. The shallow emitter has a higher surface phosphorus concentration. This increased phosphorus concentration leads to an enhanced passivation at the surface affecting the IQE values at low wavelengths. The variations at high wavelengths are explained by a different quality of bulk passivation.

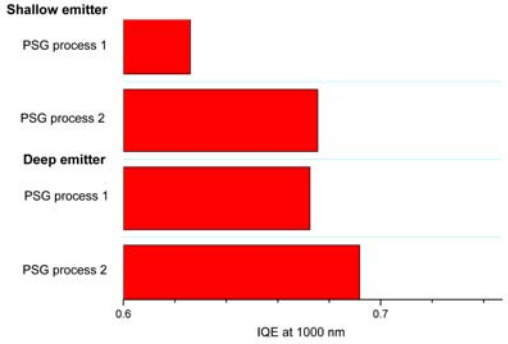

Figure 6: IQE values at 1000 nm for cells from neighboring mc-Si wafers (size 156 mm^2) on the same grain with different emitters and drying processes are shown.

A benefit of the IQE values at 1000 nm is caused by increased H concentration in the SiN:H layers. Especially the effect for samples with a shallower emitter is strong.

An interface between SiN:H and Si bulk enables an improved diffusion of hydrogen from the SiN-layer in the bulk. A thicker native oxide acts as a diffusion barrier for the hydrogen. With an optimized drying step it is possible to reduce the thickness of the native oxide. In Fig 7 the open gate voltage as a criterion for bulk pasivation for different emitter and PSG processes is shown.

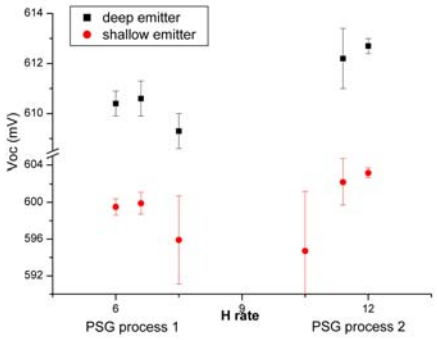

Figure 7: The open gate voltage of mc 125 mm^2 cells with different emitters and drying methods.

With an optimized drying process the blister boundaries can be shifted to increased H concentrations in the SiN:H layer. A benefit of 3 mV is obtained by an optimized drying process (Fig.7). This results from a better bulk passivation by the diffused hydrogen [4]. The benefit in the V_{oc} is independent on the used emitter. This shows the great potential of an optimized drying process. Also a trend to better V_{oc} values at higher H rates is visible.
The precise mechanisms how the native oxide influences the blistering is unknown yet. A connection with the different structures of the native oxid grown in air or water probably exists.

5 Pretreatment

Another possibility to change the attributes of the native oxide offers a pretreatment by an ammonia plasma.

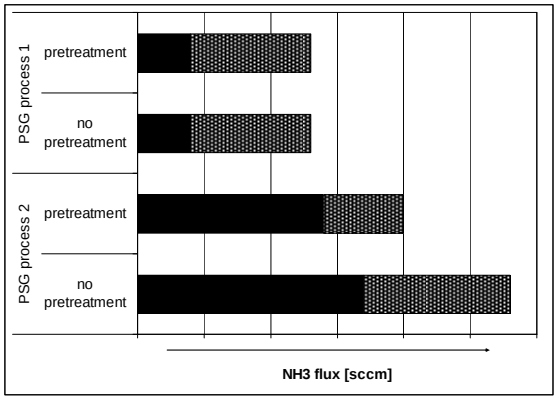

Figure 8: Blister boundary depending on flow of ammonia of mc 156mm^2 Si-wafer using different drying methods and pretreatments. The black bar indicated the boundary for isolated blistering, the gray bar show the boundary for strong blistering.

In [7] it was reported that an ammonia plasma in a PECVD (Plasma-Enhanced Chemical Vapor Deposition) system cleaned the interface of a wafer. The plasma is ignited inside the normal sputter process chamber only with ammonia as process gas. Due to the missing argon, nearly no deposition takes place. It should generate mainly an ion bombardment on the wafer.
The use of a pretreatment shows no significant effect on the blister boundary, rather it reduces the blister boundary (shown in Fig.8). However, in case of higher magnification of the blistering (Fig.9) a clear distinction is observable.

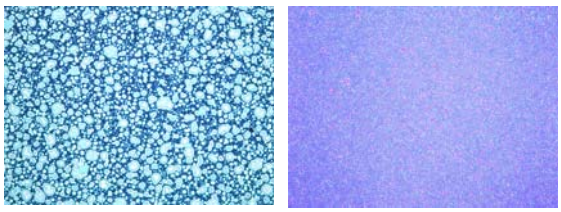

Figure 9: Microscope images (magnification of 50) of mc Si wafers (size 156 mm^2) with a very high hydrogen concentration after deposition without (left) and with (right) pretreatments.

Without a pretreatment (Fig. 9 left) the blisters are huge. With a plasma cleaning (Fig. 9 right) the blisters get smaller but the density remains constant. The pretreatment affects the adhesion of the SiN:H layer. Although the blister bondary is not affected by a pretreatment, a clear enhancement of the passivation can be observed. The variations of the J01 valeaus are a good rate for the passivations of the solar cell.

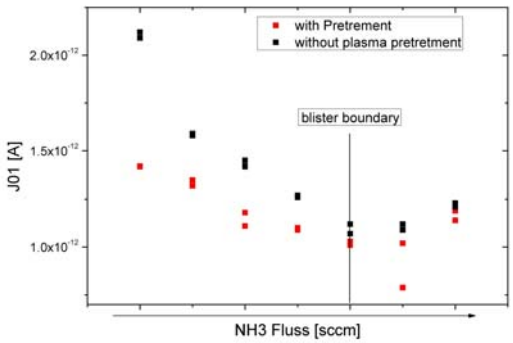

Figure 10: J01 valaues for neighboring mc 156 mm^2 cells with different hydrogen content and pretreatments are shown.

Higher hydrogen content tends to result in lower J01 valeaus which indiced a better passivation until the blister boundary (Fig. 10) is reached. The pretreatment gives a benefit for the J01 values for all hydrogen contents. The improvement by a preplasma could be caused by improved diffusion of the hydrogen diffusion to the bulk. The mechanism how the pretreatment improves the diffusion is unknown. A likely explanation is an etching or a change of the structure of the native oxide by the pretreatment. This could improve the diffusion through the native oxide. Another machanismen could be an implanting of hydrode in the silicon surface.

6 Conclusion

A dependence between the structure and thickness of the native oxide layer and blister boundary could be shown. The dependence of the blister boundary and the existence of an emitter is an evidence for this.
With an improved drying method after PSG etching in a nitrogen atmosphere the blister boundary could be shifted to higher hydrogen content. A changed distribution of the blistering can be observed. This is again visible in the open gate voltage and J01 valeaus. A benefit in the open gate voltage of 3 mV is obtained. A possible explanation is the account of a modified structure of native oxides through different drying processes.
The application of a preplasma causes no change of the blister boundary. The size of the bubbles is reduced by the pretreatment, the density remains constant. This might be a sign, that the pretreatment affects the adhesion of the SiN:H layer. It could be shown by J01 measurement that the pretreatment clearly improves the passivation quality. This effect is not yet understood completely.

7 Acknowledgements

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8 Reference

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