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IMPACT OF AMMONIA PRETREATMENT OF THE SILICON SURFACE PRIOR TO THE DEPOSITION OF SILICON NITRIDE LAYER BY PECVD

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ABSTRACT: PECVD Hydrogenated silicon nitride is widely used for Silicon solar cell as antireflection coating and passivation layer. This kind of layer exhibits a high hydrogen content, which is likely to diffuse during thermal step, leading to a chemical change of within the layer and at the interface. Thus a problem of adherence of silicon nitride, called blistering, may occur after rapid thermal anneal. NH_3 or N_2 plasma pretreatment has been here applied before deposition step for standard and Si-rich silicon nitride. Both treatments have successfully prevented surface to blister. In term of passivation, this pretreatment degrades the surface velocity recombination after deposition, but high life-times are recovered after anneal, particularly for NH_3. The treatment is efficient starting from 30s. Ammonia plasma cleans the surface of the silicon by removing carbon, but not does N_2. No nitridation of the surface is observed due to this pretreatment, and the native silicon oxide is not removed.
Keywords: PECVD, Silicon-Nitride, Passivation.

1 INTRODUCTION

Hydrogenated silicon nitride (SiN_x:H abbreviated SiN in the following) deposited by PECVD is widely used for anti-reflection coating (ARC) and passivation layer for silicon solar cells. Numerous advantages come from the high hydrogen content of this type of layer, leading to volume and surface passivation during the firing step. However, a problem of adherence of the layer sometimes occurs after the contact-firing step, depending on the composition of the layer and on the surface quality. This phenomenon has been described as “blistering” [1], and consists in the formation of small spots, typically 5-20 µm in size, at the Si/SiN interface (Figure 1). Such degradation can have a detrimental effect on the surface velocity recombination, but also on the optical properties of the ARC.

Different research teams have search for a remedy to cure this problem [1,2]; most of them were using RF plasma for deposition (13.56 MHz). The solution seems to consist in a plasma pretreatment applied before SiN deposition. We have investigated different treatments to prevent the blistering, on our low frequency PECVD system (440 kHz). They have consisted on various kinds of plasma pretreatment, N_2 or NH_3-based, immediately prior to the deposition of the Silicon nitride layer. Several plasma parameters have been tested, for two types of SiN layers. The influence of such treatments is evaluated on the angle of the blistering limitation, and on the angle of the surface passivation degradation. SIMS analysis are also carried out to evaluate the surface cleaning process during pretreatment.

2 EXPERIMENTS

Study has been mainly conducted on 2” FZ P-Type 5 Ω.cm silicon wafers, with both surfaces mirror-polished. Multicrystalline Silicon wafers, NaOH textured, have been added to each run, to verify the impact of the treatment on this kind of surface. Two different kinds of layers have been deposited:

- Standard SiN layer (abbreviated SiNs in the following), with a refractive index close to 2, used for anti-reflection coating,
- Silicon-rich nitride (SiNr) with a refractive index close to 3, good for surface passivation purpose after deposition.

The refractive indexes and thicknesses have been verified by spectroscopic ellipsometrie measurements, using HORIBA Jobin-Yvon UVISEL apparatus. According to our process, half of the wafers have been cleaned before deposition following a standard CARO process. The other wafers have undergone a simple HF-dip prior to the deposition to remove the native oxide.

Silicon nitride layers are deposited with a low frequency (440 kHz) PECVD system from SEMCO Engineering, with a vertical configuration, described elsewhere [7]. Precursor gases are pure Silane (SiH_4) and Ammonia (NH_3). Pressure is 1500 mTorr, deposition temperature is set to 370°C. The average plasma power density is 50 mW/cm^2. After deposition samples are annealed in a lamp furnace at 800°C for few seconds in air, to simulate the contact firing step of PV cell.

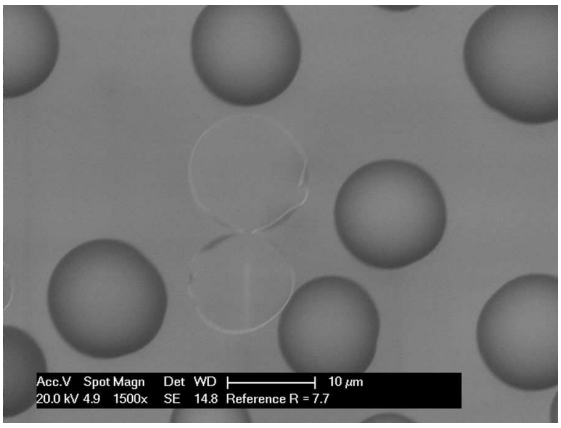

Figure 1: Blistering spots on a mono-Si surface. Two “bubbles” have cracked, pealing off the SiN layer and revealing the Si surface.

We have chosen to use plasma pretreatment before deposition. It consists in N_2 or NH_3 plasma, applied di-

rectly prior to the SiN deposition. The plasma power and the temperature during the pretreatment step are the same than during the deposition process. Minimum plasma duration is 30 s. The impact on the blistering effect has been studied by optical and secondary electron microscopy (SEM). Changes in the surface passivation due to the pretreatment have been determined by measuring the effective minority carriers lifetime by QSSPCD method [3], on samples with both sides identical. Due to the quality of the FZ silicon wafers, bulk lifetimes are high (about 5 ms) and identical for every wafer, thus effective lifetime measurements are relevant to the surface recombination velocities. SIMS analysis have also been carried out to chemically study the Si/SiN interface for various treatments: carbon, oxygen, nitrogen and hydrogen profiles have been qualitatively determined.

3 BLISTERING LIMITATION

Blistering occurs after rapid thermal anneal for mono (Figure 1) and multicrystalline silicon (Figure 2) when no pretreatment is applied. Small bulbs, 5 to 10 µm in diameter, develop on the surface and sometimes crack. In the worst cases, this phenomenon can cause the SiN layer to peal off. This effect appears to be stronger on Si-rich than on N-rich SiN. This is in agreement with the literature [6, 7]: Si-rich SiNr contains higher Si–H bonds, which breaks at lower temperature than N–H bond. SiNr is thus more inclined to deteriorate during RTA. During thermal anneal, molecular hydrogen can come from the dissociation of Si–H and N–H bond, and lead to a reorganization of the surface (Si–Si or Si–N). This leads to an increase in the film stress, and consequently to cracks and blisters [4,5].

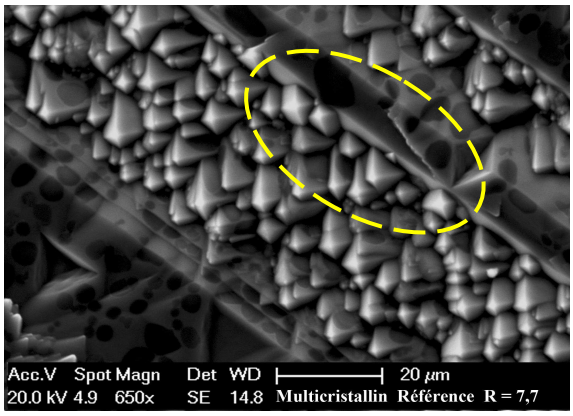

Figure 2: Blistering spots on a textured mc-Si surface.

According to Table 1, N_2 and NH_3 plasma treatments have been applied and appear to be efficient enough to suppress the blistering effect. In very few cases, small blistering occurs on SiNs, especially on localized surface defects. As reported by Dekkers et al. [6], small defects can lead the surface to blister. Blistering is in fact more noticeable on textured mc-Si surface than on monocrystalline silicon (Figure 2) We must note that CARO cleaning process does not lead to any difference on the point of view of blistering.

Table 1: Blistering quantification by optical and electronic micrographs, depending on the pretreatment (duration 30 s.)

	SiNs	SiNr
NH_3	unnoticeable	minimal
N_2	unnoticeable	minimal

To determine the correct process, we have taken into consideration the impact of the pretreatment on the effective minority carrier lifetime.

4 IMPACT OF THE PRETREATMENT ON THE SURFACE PASSIVATION

After deposition, the surface passivation is more effective for Si-rich than for standard silicon nitride, as reported elsewhere [7] and seen with reference samples. This is usually attributed to a general tendency to form more Si–H chemical bond at the interface and within the layer than for standard silicon nitride (N-rich).

4.1 Influence of the nature of the pretreatment

The pretreatment plasma leads to a degradation of the effective minority carrier lifetime, as reported on Figure 3. The degradation caused by the plasma is predominant over the nature of the silicon nitride deposited. N_2 plasma leads to a major degradation of the surface than NH_3 plasma (which is not relevant for SiNs). We do not see significant impact of the CARO cleaning on effective lifetime for pre-treated wafers.

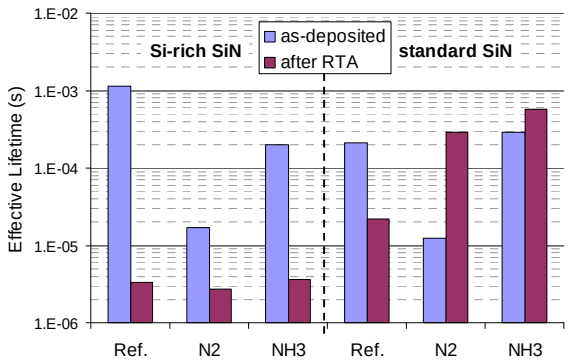

Figure 3: Effective lifetime for different pretreatments (30 s) before and after RTA (given at 7.10^{14} cm^{-3} injection rate). *Ref* stands for simple layer with no pretreatment.

After RTA, lifetimes drop down for Si-rich SiN. This can be generally attributed to the weakness of Si–H bond, compared to Si–N. This explained also why this type of nitride is more inclined to blister. The degradation of the layer is the key phenomenon in that case, thus lifetime does not depend on the pretreatment.

For standard SiNs there is a recovering of the potential damage of the surface due to the pretreatment. The healing is strongly effective for N_2 process. This could be due to a damaged zone at the interface, cause by the N_2 plasma, which acts as a hydrogen storage during deposition, and releases it during RTA [8]. However the lifetimes reach higher values with NH_3 plasma. This is probably due to an increase in the hydrogen concentra-

tion on the surface of the wafer, comparing to N_2 pretreatment.

4.2 Influence of the duration of the pretreatment

The duration of the NH_3 plasma pretreatment seems to have no significant impact on the effective lifetimes, as shown on Figure 4. After deposition, a small auto-curing effect is noticeable with this kind of plasma: lifetime increases with pretreatment duration. This could be attributed to hydrogen injection at the interface during this step.

For standard SiN, the better results are obtained after RTA for 30 s of pretreatment, and a longer treatment tends to degrade lifetime values. In every cases the lifetime is at least one order of magnitude lower after RTA for SiNr comparing to SiNs.

The NH_3 pretreatment seems thus to be more adequate in term of limitation of the surface degradation. However low surface recombination velocities can be screened on standard PV cell by the highly-doped emitter (45-60 Ωsq.).

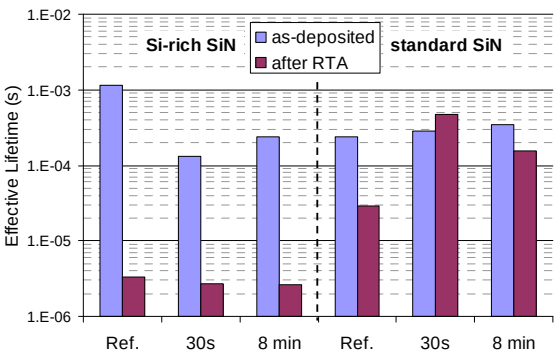

Figure 4: Effective lifetime for NH_3 pretreatment before and after RTA, depending on the plasma duration. *Ref* stands for simple layer with no pretreatment.

5 SURFACE ANALYSIS BY SIMS

Since blistering can be enhanced by small defect on the silicon surface, we have to evaluate the surface cleanliness. This can be evaluated by quantifying the carbon concentration at the Si/SiN interface, by SIMS analysis. Figure 5 shows that the carbon content is higher for N_2 pretreatment. This phenomena is not visible with NH_3, which leads to the cleanest surface. Since every gases used in the process are of ultrapure quality, the increase in C concentration can either come from the impact of N_2 plasma on graphite electrodes, or can demonstrate a less effective cleaning effect of the surface. Since the C content is the same within the SiN layers whatever the pretreatment is, it is very likely than NH_3 plasma is more effective to clean the surface than N_2. This general trend is similar for SiNr layers. The reaction of the NH_3 plasma with the surface leads to the removal of organic impurities, more efficiently than a CARO cleaning.

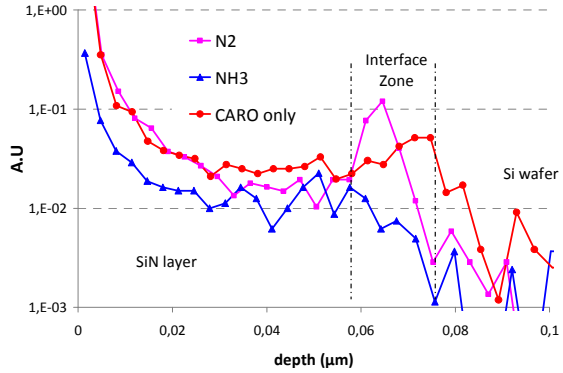

Figure 5: Comparison before RTA of carbon SIMS profiles between N_2 or NH_3 pretreatment (30 s) and simple CARO clean, for SiNs layers (layers thicknesses may slightly vary from one sample to another).

A low quality oxide on the surface of silicon, such as native oxide, has been reported to increase the blistering effect [6]. The oxygen profiles given on Figure 6 seem to indicate that the native oxide present at the SiN/Si interface is not removed during the pretreatment. The oxygen level increases in this zone and does not depend on the treatment (plasma or simple CARO). Thus a 30 s pretreatment is not efficient enough to remove the native oxide, but leads to the limitation of blistering.

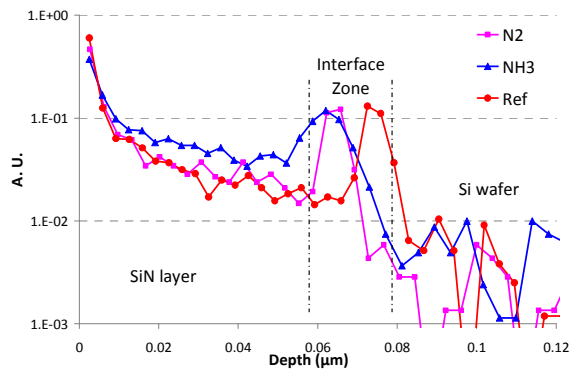

Figure 6: Comparison after deposition of Oxygen SIMS profiles between N_2 or NH_3 pretreatment (30 s) and simple CARO clean, for SiNs layers (layers thicknesses may slightly vary from one sample to another).

We have also made analysis on the Hydrogen level. There is no significant difference at the SiN/Si interface, whatever the treatment is. It seems that NH_3 does not lead to any increase in H concentration at the boundary, after deposition.

The pretreatment of the surface by NH_3 or N_2 plasma has been reported to create a nitridation of the surface, i.e an incorporation of nitrogen in a few nanometers within the silicon surface [9]. In our case the SIMS profiles for N indicate that there is no significant incorporation of nitrogen within the silicon (Figure 7), at least for a 30 s plasma. A small increase of N is however visible for the Silicon-rich layers, whatever the nature of the pretreatment is (NH_3 or N_2).

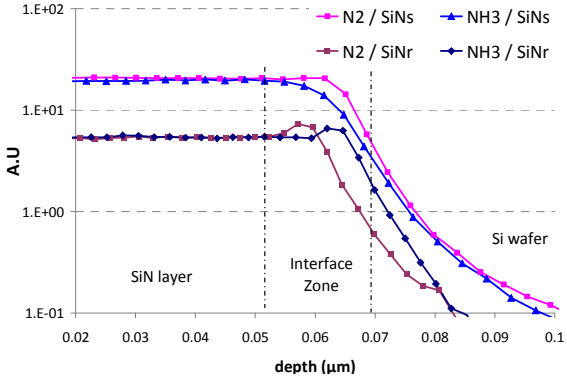

Figure 7: Comparison before RTA of Nitrogen SIMS profiles between N_2 or NH_3 pretreatment (30 s), for SiNs and SiNr layers (layers thicknesses may slightly vary from one sample to another).

6 CONCLUSION

NH_3 or N_2 plasma pretreatment appears to be a relevant solution to prevent the surface from blistering after rapid thermal anneal, with standard or silicon-rich SiN. The treatment leads to a degradation of the surface velocity recombination after deposition. The major degradation comes with N_2 pretreatment. It is however fully cured after firing for standard SiN with NH_3 plasma. Further more the cleaning of the surface, quantified by the Carbon concentration, is more effective with NH_3 than for N_2. However the treatment does not seem to remove the native silicon oxide at the SiN/Si interface, and does not lead to the nitridation of the interface.

7 REFERENCES

[1] Hauser A., Spiegel M., Fath P. et al. Sol. Energy Mat. and Solar Cells 75 (2003), pp. 357–362.
[2] J. Nigo *et al.* Proc. of 21st European PVSEC, Dresden (2006), pp. 934–937.
[3] R.A. Sinton and A. Cuevas. Ap. Phys. Let. 69 (1996), pp. 2510–2512.
[4] M. P. Hughey and R. F. Cook. Thin Solid Films 460 (2004), 7–16.
[5] N. Jehanathan. PhD Thesis, Univ. Western Australia (2007).
[6] H. Dekkers *et al.* Proc. of 3rd World Conf. on PV conversion (2003), pp. 1143–1146
[7] J.-F. Lelièvre. PhD thesis, INSA-Lyon (2007).
[8] B. Sopori, Y. Zhang *et al.* Proc. of 31st IEEE PVSC, (2005), pp. 1039-1042.
[9] A. Masuda *et al.* App. Surface Science 113/114 (1997), pp. 610–613.