BULK HYDROGENATION IN MC-SI BY PECVD SIN_X DEPOSITION ONLY

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ABSTRACT: Recent publications have studied the bulk hydrogenation of mc-Si by PECVD SiN_x deposition after a high temperature firing step. Our investigation focuses on the effect of bulk hydrogenation in mc-Si via PECVD SiN_x deposition at low temperatures without a subsequent firing step. Tests were performed on p-type String Ribbon wafers, p-type EFG Ribbon wafers and n-type and p-type wafers from mc-Si ingots. Adjacent and neighbouring wafers respectively are used to compare bulk lifetimes after single and double sided SiN_x deposition on wafers as grown and after P-gettering. Bulk lifetime was measured spatially resolved with µ-PCD. Surface passivation was done with an iodine-ethanol solution. The bulk hydrogenation effect is detectable for PECVD SiN_x deposition only, without additional firing step, but varies for different mc-Si materials. The effect is stronger in H-sensitive materials, however, a general statement for all mc-Si materials is difficult.
Keywords: Bulk hydrogenation, PECVD-SiN, mc-Si

1 INTRODUCTION

PECVD SiN_x is often used as surface passivation layer on both sides of wafer samples for bulk lifetime measurements. Mostly it is not considered that during the SiN_x deposition procedure at temperatures above 400° C and deposition times of about 20 min bulk hydrogenation possibly takes place and thereby bulk lifetimes could get enhanced. The aim of this investigation is to clarify the effect of SiN_x deposition on the bulk hydrogenation of different mc-Si materials and if possible to find an optimised surface passivation scheme suited for lifetime measurements of mc-Si.

The PECVD SiN_x was deposited in a centrotherm furnace (direct plasma, low frequency) at standard temperature (450° C). The minority charge carrier lifetimes of the samples were mapped spatially resolved using the method of microwave detected photoconductance decay (µ-PCD). Before each µ-PCD measurement the samples were chemically cleaned and their surfaces were passivated with an iodine-ethanol solution. The iodine-ethanol (I/E) solution has no effect on the bulk of the material, because there is no thermal treatment of the wafer for this surface passivation method. Measurements were also made after a 100 Ω/sq $POCl_3$ diffusion as on ribbon material bulk hydrogenation is more effective after a gettering step [1,2].

From our investigations we expect a gain of understanding of the bulk hydrogenation mechanism in mc-Si. Furthermore, the results of our study show which surface passivation scheme is adequate for spatially resolved lifetime measurements of the considered material. Hence the study is helpful for a correct measurement of lifetimes of mc-Si.

2 DESIGN OF EXPERIMENT

We investigated four different mc-Si materials: p-type String Ribbon Si, p-type EFG (Etch-defined film-fed grown) Ribbon Si, p-type and n-type material from mc-Si ingots. The material was sawn into 5x5 cm^2 wafers as this size is easy to handle during cleaning and I/E surface passivation steps. Doping, resistivity and wafer thickness of the four materials is shown in Table I. Tests were performed on three wafers (A, B and C) of each material. For being able to compare bulk lifetimes we used wafers adjacent in pulling direction in the case of ribbon materials. In the case of the ingot materials we used neighbouring wafers from the center part of the ingots.

Table I: Doping, resistivity and wafer thickness of the four investigated mc-Si materials

Material	Doping	Resistivity [Ωcm]	Thickness [µm]
String Ribbon	Boron, p-type	2 - 4	300
EFG Ribbon	Boron, p-type	2 - 4	300
n-type mc ingot	Antimony (Sb)	0.8 – 0.9	270
p-type mc ingot	Boron (B)	1 - 2	270

As shown in Fig. 1 on ribbon wafers bulk lifetimes can be compared within the same grains on adjacent wafers. The processing sequence for the three wafers A, B and C is shown in Fig. 2.

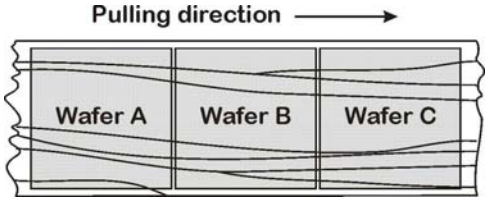

Figure 1: Schematic of a ribbon wafer. Lifetimes of the same grains on adjacent wafers are comparable.

At the beginning about 15 µm were removed on each side of the wafers by an acidic etching step. Subsequently all wafers were chemically cleaned. The defect etching was followed by a 100 Ω/sq $POCl_3$ diffusion of wafer C. After $POCl_3$ diffusion the emitter of wafer C was etched off in a CP6 solution (about 30 µm). Then wafer B and C were chemically cleaned, passivated with an I/E-solution and measured by µ-PCD. In the next step followed the PECVD SiN_x deposition. In order to get information on the difference between the effect of

single sided and double sided SiN_x deposition on the bulk hydrogenation, wafer A received a SiN_x layer only on the frontside, wafers B and C on front and backside. We used a PECVD furnace from company centrotherm with direct plasma.

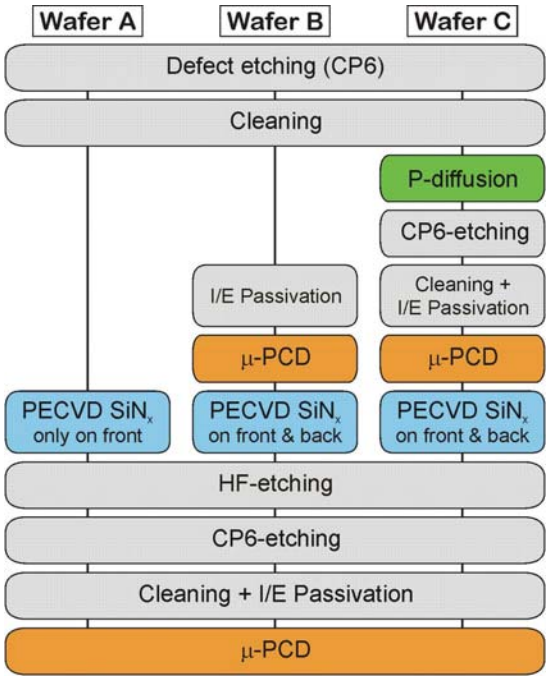

Figure 2: Processing sequence of wafers A, B and C of each investigated mc-Si material.

The deposition took place at standard temperature of 450° C and a plasma generator frequency of 40 kHz. The refractive index of the resulting SiN_x layer is between 2.0 and 2.1, measured at 600 nm. Then the wafers were etched in HF (10%) in order to remove the SiN_x layer and subsequently about 5 µm silicon per wafer side were etched in a CP6 solution. After cleaning and I/E surface passivation the lifetimes of wafer A, B and C were measured by µ-PCD.

3 RESULTS

3.1 String Ribbon material

Fig. 3 shows the bulk lifetime mappings of wafer A and B as grown and after single and double sided SiN_x deposition, respectively. It is clearly visible that the grains within already good lifetime regions turn out even better both after single and double sided SiN_x deposition. The shown colour code is the same for all String Ribbon lifetime maps. Purple is in the order of magnitude 0.1 µs, blue 1 µs, green 10 µs and red 100 µs. As a first step wafer C underwent a 100 Ω/sq $POCl_3$ diffusion. The improvement of good and poor lifetime areas after P-gettering compared to the adjacent as grown wafer can be seen in Fig. 4. The double sided SiN_x deposition after $POCl_3$ diffusion resulted in a further enhancement of good lifetime regions of wafer C (see Fig. 5). Poor areas became partly worse. This was also observed on wafer A and B after single and double sided SiN_x deposition without P-gettering in Fig. 3.

The arrangement of the lifetime maps of wafers A, B and C in the figures of the remaining three materials is the same as in the shown String Ribbon figures.

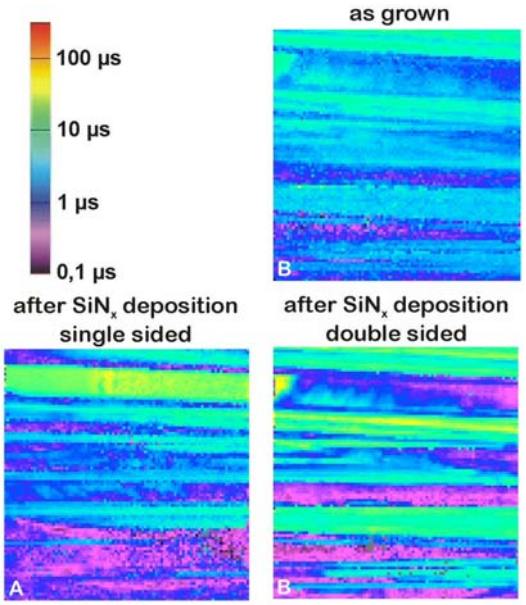

Figure 3: SR material: lifetime maps of wafer B as grown (top) and after double sided SiN_x deposition (bottom right). Wafer A after single sided SiN_x deposition (bottom left).

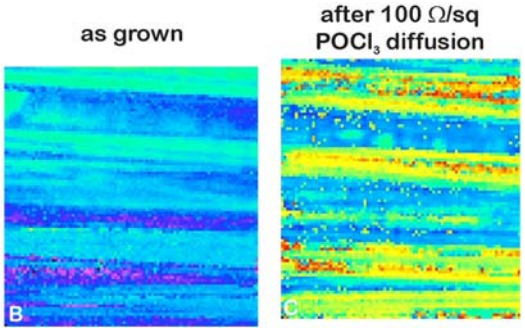

Figure 4: SR material: wafer B as grown (left). Improvement of adjacent wafer C after P-gettering (right).

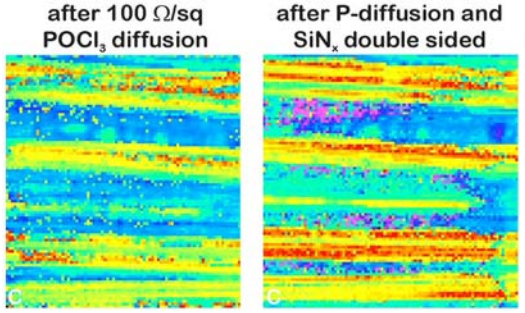

Figure 5: SR material: further improvement of wafer C after double sided SiN_x deposition (right).

3.2 EFG Ribbon material

The colour code for all EFG lifetime maps is equal to the colour code of the String Ribbon maps. On EFG material the single and double sided SiN_x deposition on as grown wafers led to a successive degradation of regions with good lifetimes as can be seen in Fig. 6.

However, poor regions became better. Fig. 7 shows the enhancement of wafer C via P-gettering. The double sided SiN_x deposition after $POCl_3$ diffusion only resulted in a slight improvement of lifetimes (Fig. 8). Again rather poor areas turned out better.

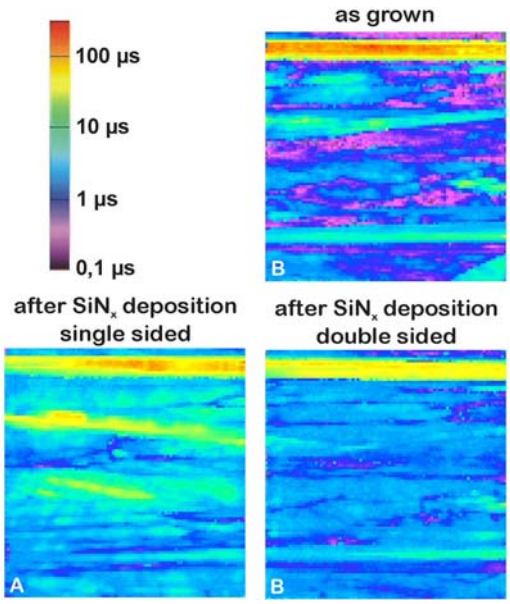

Figure 6: EFG material: lifetime maps of wafer B as grown (top) and after double sided SiN_x deposition (bottom right). Wafer A after single sided SiN_x deposition (bottom left).

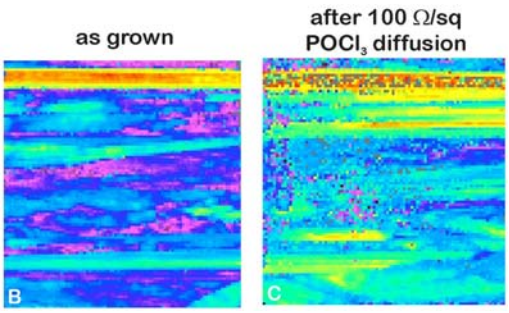

Figure 7: EFG material: wafer B as grown (left). Improvement of adjacent wafer C after P-gettering (right).

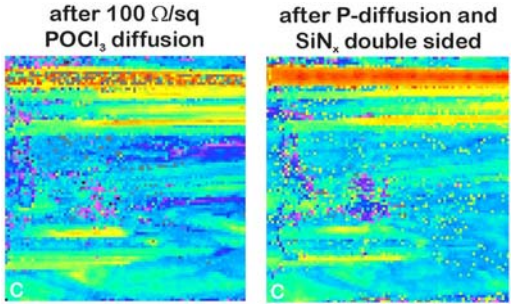

Figure 8: EFG material: slight improvement of wafer C after double sided SiN_x deposition (right).

3.3 N-type mc-Si material

The colour code for the lifetime maps of the n-type material is linear and reaches from 0 µs for purple up to 375 µs for red. From Fig. 9 is clearly visible that most of the good lifetime areas of the as grown wafer became much better after single and double sided SiN_x deposition. Fig. 10 shows the lifetime enhancement of the n-type material after $POCl_3$ diffusion. The subsequent double sided SiN_x deposition resulted in an explicit improvement of nearly all lifetime areas as can be seen in Fig. 11.

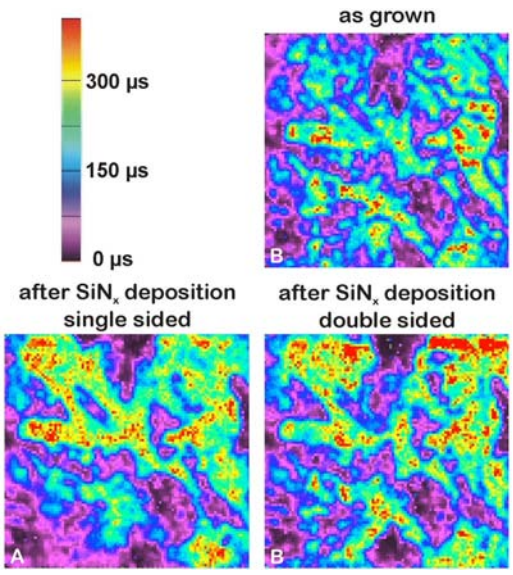

Figure 9: N-type mc material: lifetime maps of wafer B as grown (top) and after double sided SiN_x deposition (bottom right). Wafer A after single sided SiN_x deposition (bottom left).

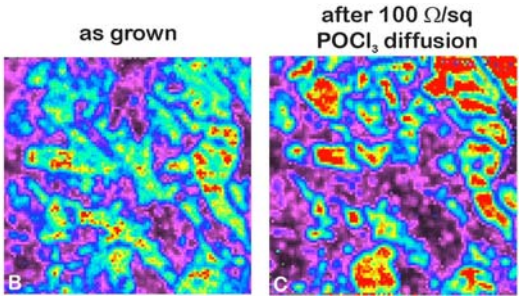

Figure 10: N-type mc material: wafer B as grown (left). Improvement of wafer C after P-gettering (right).

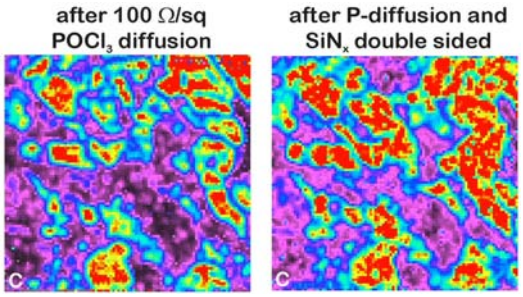

Figure 11: N-type mc material: further improvement of wafer C after double sided SiN_x deposition (right).

3.4 P-type mc-Si material

For the lifetime maps of the p-type mc wafers a linear colour code from 0 µs (purple) to 300 µs (red) was used. On this material the single sided SiN_x deposition on an as grown wafer led to a slight degradation of good lifetime regions. After the double sided SiN_x deposition on an as grown wafer some good areas became slightly

better, but also others became worse (see Fig. 12). Fig. 13 shows the improvement of good lifetime regions after P-gettering of wafer C as expected. However, the following double sided SiN_x deposition did not result in a similar clear improvement as on n-type material. Again some good regions turned out slightly better but others degraded. So on the p-type mc material a clear trend as on the n-type material was not visible. This could be due to the fact that excellent p-type material was investigated. The as grown wafers taken from the core of the ingot already had mean lifetime values of about 110 µs. On p-type mc material of poorer quality the effect of bulk hydrogenation during SiN_x deposition could have been stronger.

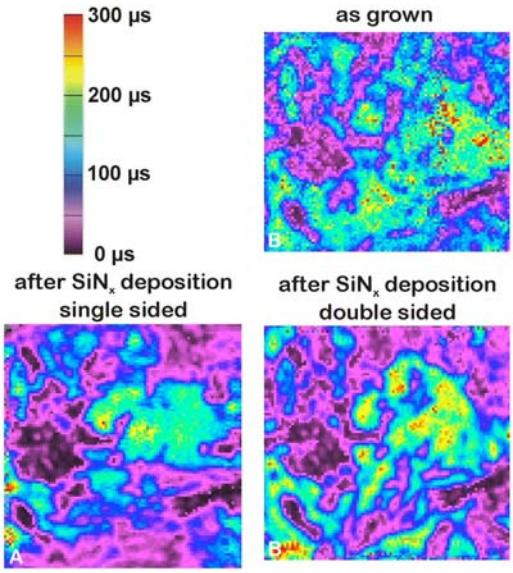

Figure 12: P-type mc material: lifetime maps of wafer B as grown (top) and after double sided SiN_x deposition (bottom right). Wafer A after single sided SiN_x deposition (bottom left).

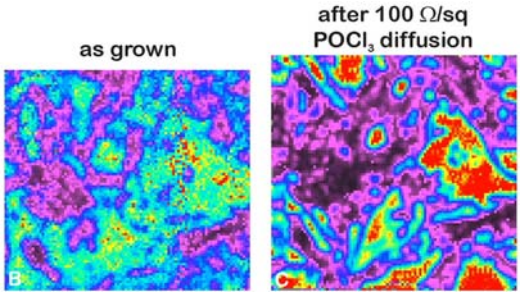

Figure 13: P-type mc material: wafer B as grown (left). Improvement of wafer C after P-gettering (right).

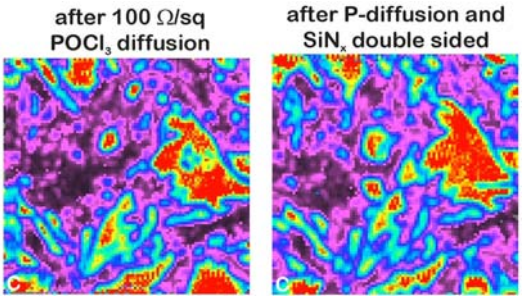

Figure 14: P-type mc material: little improvement of wafer C after double sided SiN_x deposition (right).

4 SUMMARY

Bulk hydrogenation in mc-Si takes place during PECVD SiN_x deposition at 450° C, without additional firing step. We observe this effect after single as well as double sided SiN_x deposition. A stronger hydrogenation effect is visible after P-gettering, especially for String Ribbon and n-type mc-Si. We found that the bulk hydrogenation varies for different mc-Si materials. The effect is stronger in H-sensitive materials like String Ribbon. On EFG Ribbon material the effect is only slightly visible and in comparison to String Ribbon good lifetime areas degraded and on the other hand poor regions became better. The different behaviour could be due to the varying C-content in the ribbon materials (EFG has a higher C-content compared to String Ribbon). On n-type mc ingot material a pronounced hydrogenation effect during SiN_x deposition is visible. This could not be observed for p-type mc ingot material. No definite trend is visible on this material, perhaps due to the already excellent quality of the investigated wafers.

A general statement for all mc-Si materials turns out to be difficult. However, it can be stated that if SiN_x is used for surface passivation one has to be careful with the interpretation of the measured lifetimes.

In former studies H-passivation during PECVD SiN_x deposition was also observed on Ribbon growth on substrate (RGS) silicon [3]. During the SiN_x deposition procedure the wafers reach temperatures above 400° C for about 20 min. It is not yet clear whether the hydrogen detected in the bulk originates directly from the plasma or from the SiN_x layer. More detailed investigations will be carried out in the future in order to get a better understanding of the hydrogenation mechanism in mc-Si during PECVD SiN_x deposition.

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6 REFERENCES

[1] P. Geiger et al., Solar Energy Materials & Solar Cells 85 (2005) 559-572
[2] B. Raabe et al., 21st EU PVSEC, Dresden 2006, 1490-1492
[3] G. Hahn et al., Prog. Photovolt. Res. Appl. 6, 163-167 (1998)