BULK HYDROGENATION IN MC-SI BY PECVD SIN_X DEPOSITION USING DIRECT AND REMOTE PLASMA

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ABSTRACT: Our investigation focuses on the effect of bulk hydrogenation in mc-Si via PECVD SiN_x deposition at low temperatures, so without a subsequent firing step. In a recent publication we have shown that bulk lifetime improvement in mc-Si takes place during PECVD SiN_x deposition at 450°C in a PECVD furnace with direct plasma and low plasma generator frequency. In this work we study the bulk hydrogenation of mc-Si during SiN_x deposition in different PECVD systems with direct and remote plasma. Tests were performed on p-type and n-type wafers from mc-Si ingots, p-type String Ribbon wafers and p-type EFG ribbon wafers. Neighbouring and adjacent 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 provided with an iodine-ethanol solution. Significant bulk lifetime improvement in mc-Si takes place during SiN_x deposition at low temperatures in PECVD systems with direct and remote plasma, without additional firing step. The effect varies for different mc-Si 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 between 350 and 450°C and deposition times of about 5 to 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.

In a recent publication we have studied the bulk hydrogenation of mc-Si by PECVD SiN_x deposition using a centrotherm furnace with direct plasma and low plasma generator frequency [1]. We have shown that bulk hydrogenation in mc-Si takes place during PECVD SiN_x deposition at 450°C. In this work the SiN_x was deposited in two different PECVD systems: a STS furnace with direct plasma and high plasma generator frequency and a R&R MW PECVD system with remote plasma. 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 [2,3].

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

For each PECVD system investigations on four different mc-Si materials were carried out: p-type and n-type material from mc-Si ingots, p-type String Ribbon Si and p-type EFG (Etch-defined film-fed growth) ribbon Si. 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.

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

Material	Doping	Resistivity [Ωcm]	Thickness [µm]
p-type mc ingot	Boron (B)	1 - 2	240
n-type mc ingot	Antimony (Sb)	0.8 – 0.9	270
String Ribbon	Boron (B)	2 - 4	210
EFG Ribbon	Boron (B)	2 - 4	270

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. 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. 1. At the beginning about 15 µm were removed on each side of the wafers by an acidic etching step (CP6). 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. As the next step PECVD SiN_x deposition was carried out. In order to get information on the difference between the effect of single sided and double sided SiN_x deposition on bulk hydrogenation, wafer A received a SiN_x layer only on the front side, wafers B and C on front and backside.

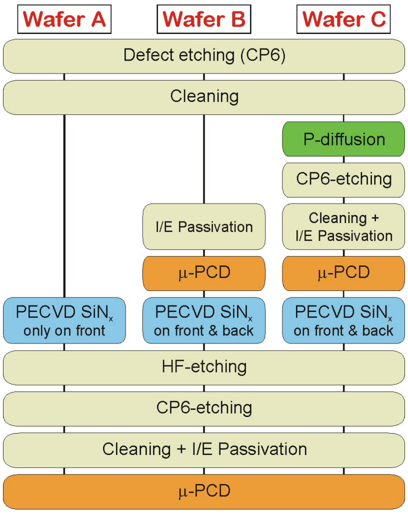

Figure 1: Processing sequence of wafers A, B, and C of each investigated mc-Si material.

The deposition in both PECVD systems took place at standard temperature between 350 and 400°C. But deposition time varied for both systems: about 9 min in the STS system, about 2 min in the R&R system (for single sided deposition). The STS furnace with direct plasma operates with a plasma generator frequency of 13.56 MHz. The refractive index of the resulting SiN_x layer is about 2.7. The source of the R&R MW PECVD system is a remote, linear microwave plasma source, operating at 2.45 GHz. The refractive index of the resulting SiN_x layer is about 2.1. After the SiN_x deposition 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 SiN_x DEPOSITION IN STS PECVD SYSTEM WITH DIRECT PLASMA

3.1 p-type mc-Si material

Fig. 2 shows the bulk lifetime mappings of wafer A and B as grown and after single and double sided SiN_x deposition, respectively, and accordingly wafer C after $POCl_3$ diffusion and after double sided SiN_x deposition. The shown colour code is the same for all five lifetime maps and reaches from 30 µs (dark blue) up to 200 µs (red). It is clearly visible that nearly all lifetime areas of the as grown wafer became much better after single and double sided SiN_x deposition in the STS system. After single sided SiN_x deposition wafer A shows even slightly better lifetimes than wafer B after double sided deposition. Lifetime enhancement of the p-type material after $POCl_3$ diffusion can be observed on wafer C, as expected. The subsequent double sided SiN_x deposition resulted in an explicit improvement of good lifetime areas.

The arrangement of the lifetime maps of wafers A, B, and C in the following figures is the same as in Fig. 2.

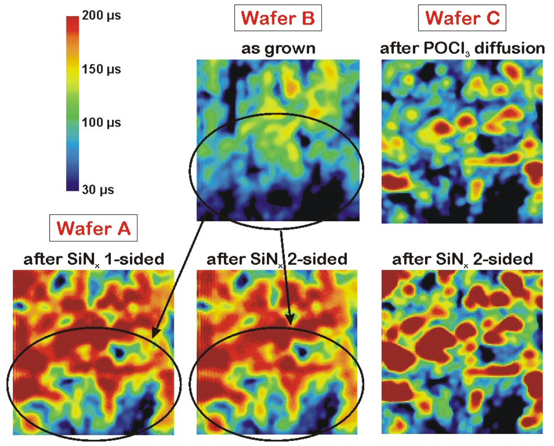

Figure 2: p-type mc- material: lifetime maps of wafer B as grown and after double sided SiN_x deposition in STS system (center). Wafer A after single sided SiN_x deposition (left). Wafer C after $POCl_3$ diffusion and after double sided SiN_x deposition (right).

3.2 n-type mc-Si material

For the lifetime maps of the n-type mc wafers a linear colour code from 40 µs (dark blue) to 350 µs (red) was used. On this material the single and double sided SiN_x deposition on as grown wafers led to a successive improvement of regions with good lifetimes as can be seen in Fig. 3. The double sided SiN_x deposition after $POCl_3$ diffusion also resulted in a clear improvement of lifetimes.

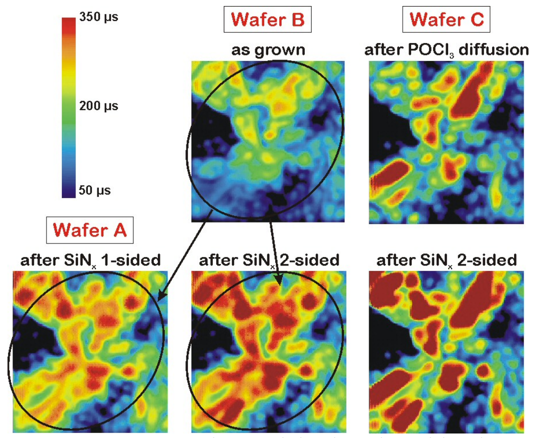

Figure 3: n-type mc-Si material: SiN_x deposition in STS system. Arrangement of lifetime maps according to Fig. 2.

3.3 String Ribbon material

For the lifetime maps of String Ribbon (SR) wafers a logarithmic colour code was used. Dark blue is in the order of magnitude 1 µs, green 10 µs and red 200 µs. On SR material the single and double sided SiN_x deposition on as grown wafers only led to a slight enhancement of regions with good lifetimes (see Fig. 4). Poor areas remained unchanged. The lifetime enhancement of wafer C via P-gettering is clearly visible. After double sided SiN_x deposition again a slight improvement of good areas can be observed.

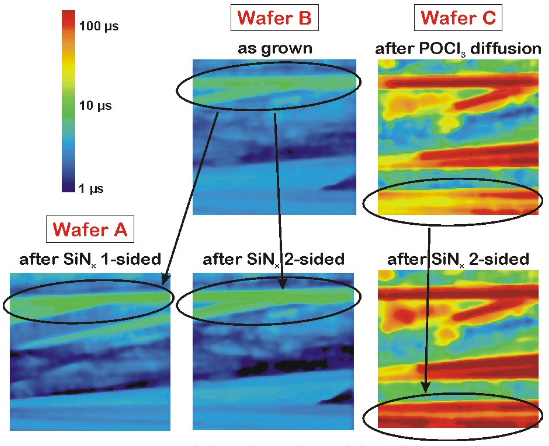

Figure 4: SR material: SiN_x deposition in STS system. Arrangement of lifetime maps according to Fig. 2.

3.4 EFG Ribbon material

The logarithmic colour code for EFG material reaches from 1 µs (dark blue) to 100 µs (red). On this material the single and double sided SiN_x deposition on as grown wafers resulted in an enhancement of good and poor regions as can be seen in Fig. 5. The double sided SiN_x deposition after $POCl_3$ diffusion also led to improved lifetimes in all areas.

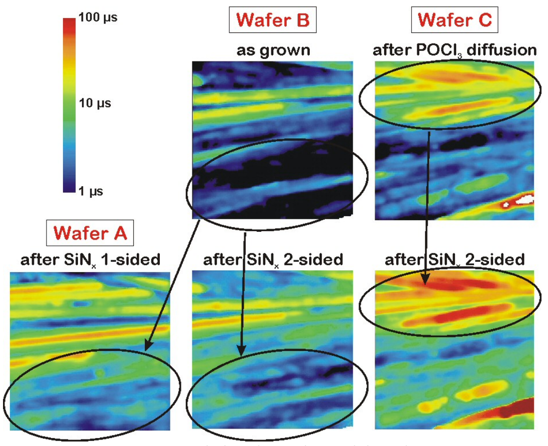

Figure 5: EFG material: SiN_x deposition in STS system. Arrangement of lifetime maps according to Fig. 2.

4 SiN_x DEPOSITION IN R&R MW PECVD SYSTEM WITH REMOTE PLASMA

4.1 p-type mc-Si material

From Fig. 6 it is clearly visible that single and double sided SiN_x deposition on p-type mc material in the R&R system led to a significant improvement of lifetimes, for the as grown wafers A and B as well as for the P-gettered wafer C. However, wafer A shows after single sided SiN_x deposition even better lifetimes than wafer B after double sided deposition.

4.2 n-type mc-Si material

Single and double sided SiN_x deposition on as grown wafers in the R&R system resulted in a successive improvement of areas with good lifetimes (Fig. 7). SiN_x deposition after $POCl_3$ diffusion also resulted in a significant improvement of lifetimes.

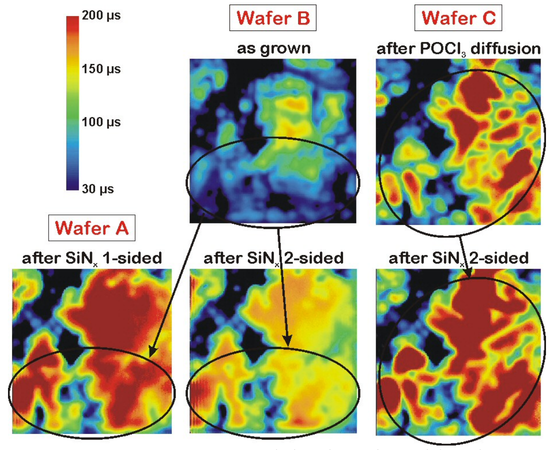

Figure 6: p-type mc- material: SiN_x deposition in R&R system. Arrangement of lifetime maps according to Fig. 2.

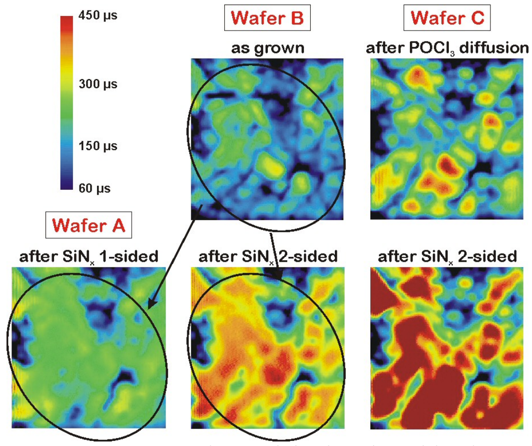

Figure 7: n-type mc-Si material: SiN_x deposition in R&R system. Arrangement of lifetime maps according to Fig. 2.

4.3 String Ribbon material

Single and double sided SiN_x deposition on SR material in the R&R system had the same effect as SiN_x deposition on this material in the STS furnace: only good lifetime areas become slightly better (see Fig. 8 and Fig. 4).

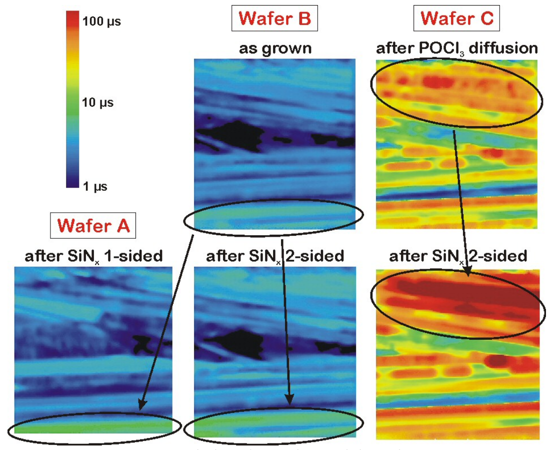

Figure 8: SR material: SiN_x deposition in R&R system. Arrangement of lifetime maps according to Fig. 2.

4.4 EFG Ribbon material

On this material predominantly regions with poorer lifetimes get enhanced after single and double sided SiN_x deposition. The effect is the same on as grown wafers A and B as on P-gettered wafer C (see Fig. 9).

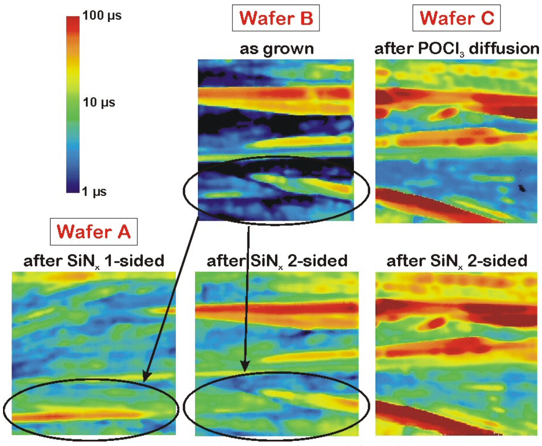

Figure 9: EFG material: SiN_x deposition in R&R system. Arrangement of lifetime maps according to Fig. 2.

5 DISCUSSION

The improved material quality after PECVD SiN_x deposition of the various mc wafer materials under investigation could be caused by two effects. The easiest explanation is the passivation of bulk defects by hydrogen during SiN_x deposition. The temperature range of 350 – 450°C is high enough to enable significant diffusion of atomic hydrogen through at least part of the wafer even within different deposition times (5 – 20 min). Although this is currently the best explanation of the obtained results, the fact that SR and EFG material (which are normally known to react quite similarly in hydrogenation experiments, see e.g. [2]) react differently in this investigation leaves room for other explanations. E.g. a pure temperature effect can not be ruled out at the moment. More experiments in this direction are necessary to further investigate this phenomenon. One of the future experiments will therefore be a direct comparison of neighbouring (or adjacent) wafers, with both wafers submitted to the same thermal load but only one wafer submitted to the plasma-enhanced deposition.

The fact that bulk lifetimes can change significantly after PECVD SiN_x deposition without additional firing step has consequences for the selection of surface passivation schemes for lifetime measurements. If bulk lifetimes of (multicrystalline) Si materials should not be affected by the way the surfaces are passivated, PECVD SiN_x does not seem to be the best choice for surface passivation. In this case methods that do not involve elevated temperatures above 300°C and/or hydrogen containing layers or ambients should be chosen. One alternative is e.g. the use of an iodine-ethanol solution at room temperature, although the correct wafer cleaning and handling before immersion in the passivating solution is critical. Another disadvantage using this method is the limited stability of the surface passivation with time.

6 SUMMARY

Significant bulk lifetime improvement in mc-Si takes place during PECVD SiN_x deposition at low temperatures (350 – 450°C) in PECVD systems with direct and remote plasma, without additional firing step. We observe this effect after single as well as double sided SiN_x deposition. The results of this investigation are in line with the results of a recent publication, where the same investigation was carried out in a centrotherm PECVD furnace with direct plasma and low plasma generator frequency [1]. We found that the bulk lifetime improvement varies for different mc-Si materials. On p-type and n-type mc ingot material a pronounced lifetime improving effect during SiN_x deposition is visible. On String Ribbon and EFG material the lifetime improving effect is also clearly visible. But on SR material only areas with good lifetimes improved after SiN_x deposition in both PECVD systems. On EFG material mainly poor regions improved in the R&R system, while lifetime was improved in all areas in the STS system.

A general statement for all investigated PECVD systems and 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 as bulk material quality might have changed.

In former studies material improving effects during PECVD SiN_x deposition were also observed on Ribbon Growth on Substrate (RGS) silicon [4]. During the SiN_x deposition procedure the wafers reach temperatures between 350 and 450°C for about 10 to 20 min. The easiest explanation for the origin of the improved lifetime is a passivation of bulk defects by atomic hydrogen during SiN_x deposition. It is not yet clear whether the hydrogen detected in the bulk might originate directly from the plasma or from the SiN_x layer.

An alternative to the use of PECVD SiN_x as surface passivation method is immersion of the wafer into an iodine-ethanol solution. In this way bulk lifetimes are not affected, but the correct application of this method of passivation requires skilful handling of the wafers.

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