SILICON FOIL FABRICATION AT FRAUNHOFER ISE

Marion Drießen, Nena Milenkovic, Andreas Lösel, Jan Benick, Stefan Janz, Stefan Reber
Fraunhofer Institute for Solar Energy Systems
Heidenhofstraße 2, D-79110 Freiburg, Germany
Phone: +49 761 4588 5259, fax: +49 761 4588 9250
E-mail: marion.driessen@ise.fraunhofer.de

ABSTRACT: Cost reduction is still a major goal in photovoltaic development. Silicon foils offer the possibility to reduce silicon consumption and with this production costs while maintaining a high efficiency potential. In this work silicon foils are fabricated by implementation of a release layer in a silicon substrate, reorganization of this layer and epitaxial thickening prior to detachment. For the formation of the release layer two approaches are investigated, hydrogen implantation and electrochemical etching of porous silicon. Hydrogen implanted layers reorganize during heat treatment to layers with low amounts of small pores or with blisters depending on the implantation dose. The overall amount of pores can be increased by applying several implantation processes. With the more often applied electrochemically etched porous silicon as release layer the defect density in the foil deposited in a lab-type CVD reactor could be reduced to $(6 \pm 2) \times 10^3$ cm^{-2} by optimization of the reorganization process. Effective carrier lifetimes up to 56 µs are measured. Additionally, 5 x 5 cm^2 foils deposited in a continuous CVD reactor are presented.
Keywords: CVD Based Deposition, Epitaxy, High Deposition Rate, Hydrogen Implantation, Porous Silicon

1 INTRODUCTION

Silicon foil fabrication using lift-off technologies is well established for microelectronics. Some processes are already successfully transferred to photovoltaic (PV) applications. However, mostly microelectronic equipment is used. The most frequently investigated process sequence for PV applications is based on a porous silicon release layer that is electrochemically etched into a silicon substrate. During treatment at high temperatures the porous layer reorganizes forming the release layer. Subsequently an epitaxial silicon layer is deposited on the porous layer forming the final silicon foil [1, 2, 3]. A second approach is based on a release layer formed by hydrogen implantation. Typically the so called Smart-Cut process is applied, where the final foil is part of the original silicon substrate in which hydrogen is implanted directly into a depth corresponding to the desired silicon foil thickness [4, 5]. After heat treatment with temperatures up to 600 °C the silicon foil is detached.

In this work two process sequences for silicon foil fabrication are investigated. One is the porous silicon approach. Here mainly the influence of different reorganization processes on the structure of the porous silicon layer and the quality of the resulting silicon foil are investigated. The reorganization and epitaxial deposition processes are mainly carried out in a lab-type atmospheric pressure chemical vapor deposition (CVD) reactor [6] that is designed for the development of processes that can be transferred to the high-throughput inline reactors ConCVD and ProConCVD built at Fraunhofer ISE [7, 8]. First results of foils deposited in the ConCVD reactor are additionally shown.

The second process sequence regarded in this paper is based on hydrogen implantation. Instead of direct detachment of silicon foils after deep implantation with high acceleration voltages (few MeV) [5] a two-step approach similar to the porous silicon route is aspired. First a shallow hydrogen rich layer is implanted with comparatively low acceleration energies (up to 40 keV) into a silicon substrate. Then the silicon layer for the final silicon foil is deposited on top of the substrate prior to detachment. The main challenge of this approach seems to be the high temperature required for epitaxial deposition (around 1200 °C) as typically only temperatures up to 600 °C are applied prior to detachment [4]. Therefore the evolution of the implanted region with temperature is regarded in this paper. Additionally, samples with up to three hydrogen layers implanted with different acceleration voltages are investigated to improve detachment properties.

2 EXPERIMENTAL PROCEDURE

2.1 Release layer by hydrogen implantation

For this approach samples with one, two and three hydrogen rich layers were investigated. All samples were implanted with hydrogen in a Varian VIIsta HC. For the samples with a single hydrogen layer 1 Ωcm, n-type, chemical polished FZ wafers were used. Implantation parameters were adopted from the Smart-Cut process [4], so implantation doses between 3×10^{16} cm^{-2} and 10×10^{16} cm^{-2} were applied. The acceleration voltage was set to 40 kV to obtain a depth of the release layer of 450 – 500 nm. For the experiments with two and three hydrogen layers chemical mechanical polished substrates were used as the lower surface roughness allows for a better characterization of damages induced during implantation and reorganization. The two layer samples were implanted with acceleration voltages of 10 kV and 40 kV, with a dose of 3×10^{16} cm^{-2} and 5×10^{16} cm^{-2} per layer and different implantation orders. The samples with three layers were implanted with 3×10^{16} cm^{-2} hydrogen ions per layer. Two samples with different distances between the layers were fabricated by applying the acceleration voltages 40 kV, 23 kV and 10 kV in one and 40 kV, 33 kV and 27 kV in the other.

After implantation some samples of each type were treated in hydrogen atmosphere at temperatures between 600 and 1200 °C for 2 min as epitaxial deposition is usually performed at 1100 – 1200 °C in our CVD reactors.

2.2 Release layer by electrochemical etching

For the experiments with reorganization of and epitaxial deposition on porous silicon Cz wafers with electrochemically etched porous silicon double layers were supplied by IMS. Between porous silicon etching and reorganization of the porous silicon layers the samples were stored for more than 300 days in clean room atmosphere. Some samples were HF dipped prior to reorganization to remove the native oxide. Reorganization and epitaxial deposition were carried out in chemical vapor deposition reactors built at Fraunhofer ISE [6, 7].

Most processes are conducted in a lab-type CVD reactor [6]. Here a variation of the reorganization process in hydrogen atmosphere with temperatures between 800 °C and 1150 °C and times between 5 min and 30 min is investigated. For epitaxial deposition of the foils the standard process at 1150 °C with trichlorosilane in hydrogen is used. Ca. 40 µm thick layers were deposited in 47 min with a boron concentration of 8×10^{16} cm^{-3}.

Additional experiments were performed in the continuous working CVD reactor ConCVD [7], but in stationary mode. The porous silicon layers were reorganized for 15 min at 1100 °C in a H_2/Ar atmosphere prior to epitaxial deposition with a standard process (1100 °C, silicon tetrachloride in H_2 with a ratio of 1 / 70, 100 min, boron concentration of 5×10^{16} cm^{-3}).

Defect densities were evaluated with an optical microscope after using a Secco solution [9] for defect decoration. For lifetime measurements foils were mechanically detached after laser scribing. The porous silicon layers were removed with CP71. The resulting foils were passivated with 20 nm thick Al_2O_3 layers deposited by atomic layer deposition (ALD) on both sides followed by an annealing step at 425 °C for 25 min. Measurements were performed using a microwave photoconductive decay (MWPCD) measurement setup.

3 RELEASE LAYER BY HYDROGEN IMPLANTATION

3.1 Samples with one hydrogen rich layer

First samples with one implantation process with an acceleration voltage of 40 kV resulting in a depth of hydrogen ion penetration of 450 – 500 nm are regarded. Mainly the influence of the implantation dose on the behavior of the hydrogen rich layer during heat treatment is investigated. It is reported that for each acceleration voltage a threshold dose exists above which blistering occurs in annealed (typically up to 600 °C) hydrogen implanted samples [10]. For 40 kV this threshold dose lies between 4×10^{16} cm^{-2} and 5×10^{16} cm^{-2}.

On the surfaces of samples implanted for this work no blistering is visible for hydrogen ion doses up to 5×10^{16} cm^{-2} prior to heat treatment (left two pictures in upper row in Figure 1). Samples implanted with 10×10^{16} cm^{-2} show lifted and partly peeled off blisters already after implantation (right picture in upper row in Figure 1). After heat treatment the dose at which blistering occurs decreases with increasing temperature. Treatment at 600 °C for 2 min leads to lots of visible blisters on samples implanted with 5×10^{16} cm^{-2} and very few on samples implanted with 4×10^{16} cm^{-2}. After treatment at 1200 °C only the sample with 3×10^{16} cm^{-2} implantation dose shows no blisters while all other samples exhibit lots of partly peeled off areas (bottom

row in Figure 1). With increased annealing temperature the threshold dose for the occurrence of blistering seems to decrease.

Dose	3×10^{16} cm^{-2}	4×10^{16} cm^{-2}	10×10^{16} cm^{-2}
After implantation			
Treated at 1200 °C	30 µm		
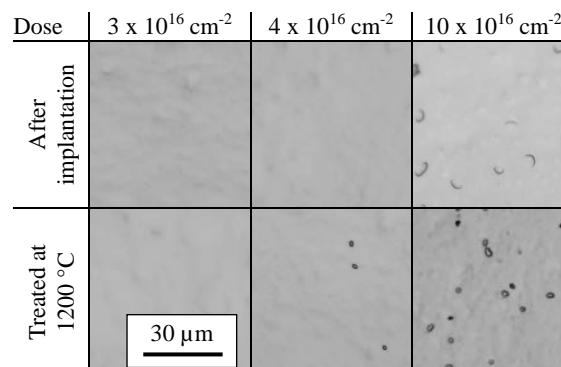
Figure 1: Microscope images of surfaces of ion implanted samples (40 kV) with different doses, after implantation (top row) and after heat treatment in hydrogen atmosphere at silicon deposition temperature (bottom row).

Besides the formation of blisters visible on the surface the shape of the hydrogen rich plane varies with temperature. Up to 800 °C a region with micro cracks persists, at 1000 °C the hydrogen implanted plane reorganizes to a region with small pores and a surrounding silicon crystal with apparently low damage as can be seen on defect etched cross sections in scanning electron microscope (SEM) images in Figure 2. However, all samples exhibit no sufficient density of pores to enable lift-off of a grown silicon layer.

	Implanted	Treated at 600 °C	Treated at 1200 °C
Broken			
Defect etched			1 µm
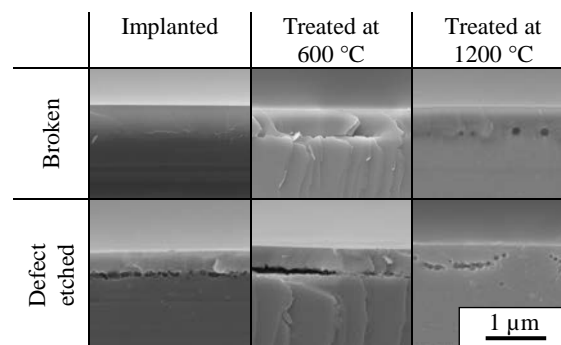
Figure 2: SEM images of samples implanted with 4×10^{16} cm^{-2} hydrogen ions, partly heat treated and defect etched in a Secco solution [9].

It can be concluded that for the regarded silicon foil fabrication approach (shallow hydrogen implantation and epitaxial deposition prior to detachment), that requires temperatures around 1200 °C, a maximum hydrogen dose of 3×10^{16} cm^{-2} is tolerable. Higher doses lead to blistering. However, the pore density formed at 1200 °C with this dose is too low to enable detachment.

3.2 Samples with several hydrogen rich layers

To increase the overall amount of pores a second layer of hydrogen atoms was implanted in a reduced depth (ca. 150 nm for 10 kV acceleration voltage) resulting in samples with two separate layers with micro cracks after heat treatment at 600 °C (see Figure 3). The pores after heat treatment at 1200 °C are mainly located in the same two layers, in which hydrogen is initially implanted. However, some pores also move in the region

between. Still the density of pores is too low to enable lift-off. Nevertheless, the amount of hydrogen that can be implanted without leading to blistering after heat treatment and with this the overall amount of pores can be increased by applying a second implantation process. For example two layers each implanted with 3×10^{16} cm^{-2} exhibit only very few blisters even after heat treatment at 1200 °C, whereas the sample implanted with one layer with 5×10^{16} cm^{-2} shows lots of blisters. One additional parameter to be varied is the order of the implantations. Implantation of the first layer with 10 kV and the second with 40 kV leads to lower damage, amount of pores and blisters and roughness of the resulting surface after heat treatment between 400 and 1200 °C than samples with layers implanted in the reversed order.
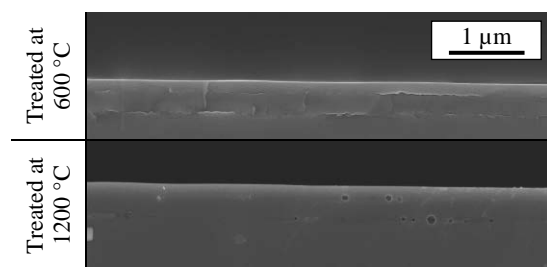
Figure 3: SEM images of cross sections of samples implanted with two layers with a dose of 3×10^{16} cm^{-2} each, first layer implanted with 40 kV, second with 10 kV. The samples were treated at different temperatures.

For the samples with three hydrogen layers a further increase of the amount of overall implanted hydrogen without leading to blistering is aimed for. However, both samples with different distances between the hydrogen rich layers show lots of blisters in the whole temperature region between 600 °C and 1200 °C. The blisters in the sample with larger distances between the hydrogen rich layers (acceleration voltages of 10 kV, 23 kV and 40 kV corresponding to implantation depths around 150 nm, 310 nm and 470 nm) are significantly smaller than the blisters in the sample with minor distances between the layers (27 kV, 33 kV and 40 kV aiming for depths around 370 nm, 420 nm and 470 nm). The density of blisters, however, is similar.

The formed layers are different in both samples. In the sample with larger distances between the layers the initial implanted layers are visible even after heat treatment at 1200 °C. The two upper layers in this sample show significantly more microstructure and pores after treatment at temperatures up to 800 °C and above 1000 °C, respectively. The reason might be hydrogen diffusion from the deeper layer to the upper ones through the crystal that is defective to some extent. The three implanted layers in the samples with the targeted 50 nm distances between the layers are hardly visible after implantation. Heat treatment between 600 °C and 1200 °C leads to a reduction to one layer with microstructures or pores depending on the temperature. The pore density could not be increased with this process compared to the sample with one hydrogen layer and a dose of 10×10^{16} cm^{-2}.

In conclusion with hydrogen implantation and reorganization at epitaxial deposition temperatures layers with single pores can be obtained. However, the pore density is too low to enable detachment of an epitaxially

grown layer when keeping the implantation dose below the threshold for blistering. This threshold dose can be increased by implanting several layers of hydrogen in different depths but only to a small extent. Up to now no sufficient pore density could be obtained with this process. The question if this process is suited for silicon foil fabrication still remains open and challenging for future experiments. Possibly a wider variation of implanted layers, distances between those layers and implantation doses might lead to a reliable release layer.

4 RELEASE LAYER MADE BY ANODIC ETCHING

4.1 Reorganization temperature

The temperature at which a significant reorganization starts depends on the process parameters, especially on the oxygen background as the native oxide on the walls of the etched porous structure has to be removed first. Knowledge of the starting temperature for reorganization in the specific reactor is useful for further process development, like varying temperature ramps or holding times in special temperature ranges. Therefore the reorganization temperature was varied between 800 °C and 1000 °C keeping the reorganization time constant at 30 min. For this examination aged samples with a high amount of native oxide are chosen. SEM images of the reorganized samples are shown in Figure 4. For comparison a sample reorganized at the standard deposition temperature (1150 °C) for the same time is additionally depicted. All porous silicon layers treated at lower temperatures apparently reorganized to some degree (upper row) as an as-etched sample exhibits much smaller structures that could not be resolved. However, structures are still significantly smaller than in the sample reorganized at 1150 °C, especially in the bottom layer of high porosity. Additionally, an examination of the porous silicon layer close to the surface is interesting. Up to 950 °C open structures and a rough surface are visible, after treatment at 1000 °C the surface is smooth and a ca. 12 nm thick closed silicon layer has formed. Therefore, a reorganization process with a temperature or ramp variation in this range might influence the resulting porous silicon layer and with this the quality of the silicon foil and the detachment properties. This is e.g. shown in [11] for a process with a reduced temperature ramp.
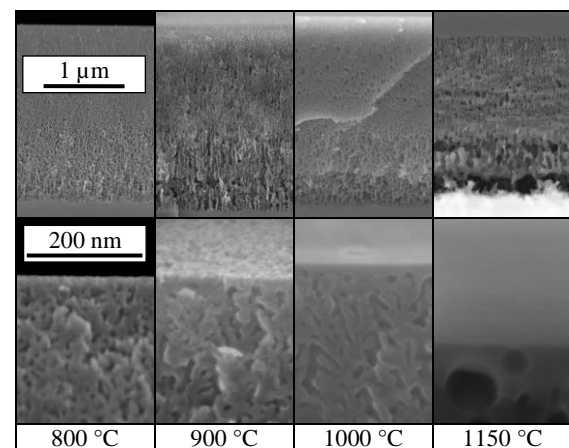
Figure 4: SEM pictures of cross sections of samples reorganized at different temperatures for 30 min.
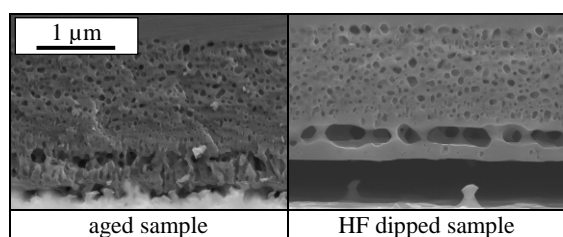
The influence of a reorganization process with a plateau at reduced temperature on the crystal quality was investigated using the standard deposition process. In Figure 5 defect densities (stacking fault density SFD and etch pit density EPD) of samples pretreated at reduced temperatures up to 900 °C in hydrogen atmosphere are depicted. Despite the different appearance of the reorganized samples at these lower temperatures no influence on the defect density is visible. The reason probably is an ongoing reorganization during heating to and epitaxial deposition at 1150 °C that was investigated with SEM images of these samples. A plateau at 1000 °C is assumed to have a negative effect on the reorganization as silicon dioxide might be incorporated in the porous silicon layer that is not removed during further heat treatment due to the already closed surface and prevents a proper reorganization as argued in [11]. To confirm this assumption this process has to be caught up.
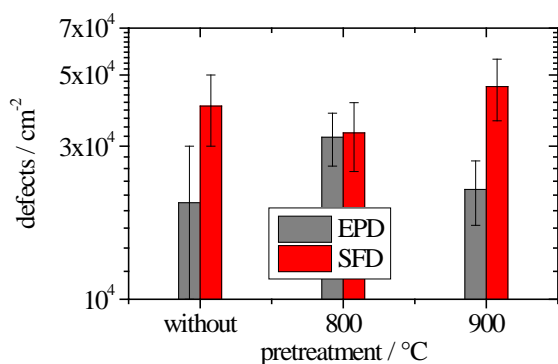
Figure 5: Defect densities of samples pretreated in hydrogen atmosphere at different temperatures for 30 min before epitaxial growth.

4.2 Oxidized and non-oxidized porous silicon

Reorganization is enhanced significantly as soon as the native oxide within the porous silicon layer is removed. It is reported that the degree of oxidation within porous silicon layers increases even after several months, e.g. [12]. This might affect mainly the deeper regions as top regions should be oxidized much faster. If the surface of the porous silicon layer is closed before the oxide in the deeper regions is removed, the reorganization process is prevented. During our typical reorganization process (1150 °C, 30 min, temperature ramps of 100 °C/min) this seems to be the case as a comparison between an aged sample and an equal sample that is HF dipped before reorganization to remove the native oxide indicate (see Figure 6). The degree of reorganization is much higher and accordingly the structure sizes much larger in the deeper highly porous layer of the additionally HF dipped sample.

Figure 6: SEM images of cross sections of reorganized and epitaxially deposited samples with and without HF dip prior to the process.

The degree of reorganization influences the detachment behavior of the silicon foils. The enhanced reorganization of the samples treated in HF prior to reorganization to remove the native oxide leads to a significantly improved detachment behavior. All laser scribed 4 x 4 cm^2 foils could be detached from the HF treated samples. The oxidized samples, however, could only be detached partially.

4.3 Influence of reorganization time and HF dip on crystal quality

Besides the temperature the duration is an important parameter for the reorganization process. In Table I defect densities of epitaxially grown layers deposited on porous silicon layers reorganized at 1150 °C are shown. In addition to the temperature the influence of an HF dip prior to reorganization is denoted. With rising reorganization time from 5 to 30 min a decrease in SFD by one order of magnitude is visible. However, the SFD in the best samples is still two orders of magnitude higher than in references without porous silicon. EPDs indicating threading dislocations could not be reliably evaluated on samples reorganized for 5 min due to the high amount of stacking faults. The EPD of samples reorganized for 30 min corresponds to the EPD of the reference. Therefore, the main crystallographic defect that is influenced by the porous silicon layer seems to be the density of stacking faults. This has to be further reduced within future experiments by adaptions of the reorganization process and possibly the porous silicon etching process. Regarding the defect density no difference can be observed comparing oxidized and HF dipped samples.

Beside the crystal quality the lifetime of minority carriers is measured. In Table I effective carrier lifetimes measured by microwave photoconductance decay (MWPCD) are stated. The values are averages of 50 measurement points. High errors originate from inhomogeneous effective surface recombination velocities due to partly highly doped regions on one side. As indicated by the crystal quality an increased reorganization time leads to an enhancement of the lifetime. In contrast to the defect density an additional slight increase in lifetime is observed for the HF dipped and 30 min reorganized sample. Whether this increase is influenced by the improved detachment behavior mentioned in section 3.2 or not is not clear until now.

Table I: EPD, SFD and effective carrier lifetime τ_{eff} of epitaxially grown layers deposited on oxidized and HF dipped porous silicon layers reorganized at 1150 °C for different times. Reference refers to a layer deposited on a Cz wafer without porous silicon.

Reorganization	EPD / cm^{-2}	SFD / cm^{-2}	τ_{eff} / µs
reference	$(7 \pm 8)\cdot10^3$	< 10	-
5 min, oxidized	not meas.	$(4 \pm 2)\cdot10^4$	9 ± 2
5 min, HF dipped	not meas.	not meas.	7 ± 2
30 min, oxidized	$(2 \pm 1)\cdot10^3$	$(5 \pm 1)\cdot10^3$	16 ± 7
30 min, HF dipped	$(6 \pm 5)\cdot10^3$	$(6 \pm 2)\cdot10^3$	22 ± 5

The best process (HF dipped samples reorganized for 30 min) was repeated with an improved process without highly doped regions. In Figure 7 a lifetime mapping on the corresponding 4 x 4 cm^2 foil is depicted. Locally lifetimes up to 56 µs are measured. Still inhomogeneities

are visible that are attributed to the porous silicon removal process prior to passivation. The mean value of this mapping is 48 ± 4 µs. This corresponds to a diffusion length of > 280 µm which is already more than five times the thickness of the silicon foils.
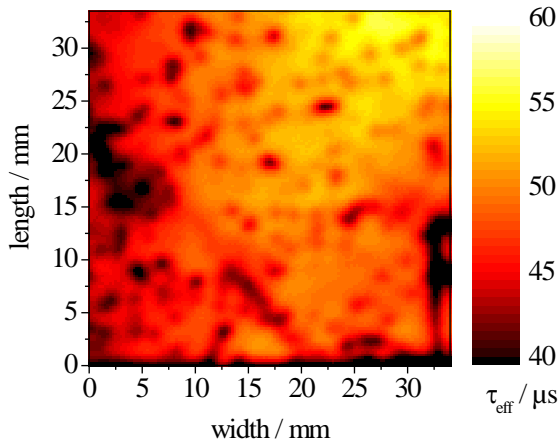
Figure 7: MWPCD mapping of the effective carrier lifetime of a passivated 40 µm thick silicon foil.

4.4 Silicon foil deposited in continuous CVD reactor

With continuous CVD reactors like the ConCVD the throughput of reorganization and epitaxial deposition processes can significantly be increased. After the process described in section 2.2 the porous silicon layer shows a different structure compared to samples deposited in the lab-type reactor shown in previous sections (see Figure 7). Besides a different pore diameter distribution all pore surfaces exhibit microstructures instead of smooth walls. Reason and consequence of this effect is not clear up to now. Further characterization of these silicon foils has to be conducted.
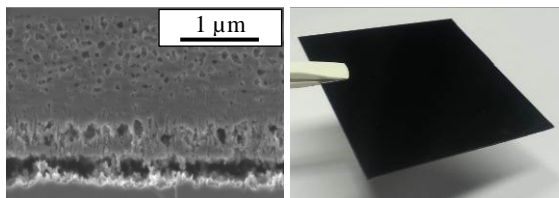
Figure 8: Left: SEM image of the porous silicon layer after reorganization and epitaxial deposition; Right: picture of a 5 x 5 cm^2 detached silicon foil deposited in the ConCVD reactor.

Nevertheless, the reorganized bottom highly porous layer enabled a successful detachment of several 5 x 5 cm^2 silicon foils (right picture in Figure 8). Unfortunately some issues occurred both during porous silicon removal and during ALD deposition of the passivation layer leading probably to an increased surface recombination velocity. The measured effective carrier lifetimes on these samples up to 6 µs can therefore only be regarded as a lower limit for the real bulk lifetimes in the grown layers. Still this is a promising result for future experiments with optimized reorganization and deposition processes as well as an optimized post treatment.

6 SUMMARY

In this paper results for two approaches for silicon foil fabrication are presented. Both are based on the implementation of a release layer close to the surface of a silicon substrate and epitaxial growth with APCVD of the final silicon foil.

In one approach hydrogen implantation is used for release layer formation. After heat treatment up to 800 °C micro cracks are dominating. At higher temperatures pores are formed while the surrounding regions exhibit a reduced damage. Using one hydrogen implanted layer, the density of pores is too low to enable detachment or blistering occurs depending on the implantation dose. The amount of hydrogen, which can be implanted without leading to blisters, can be increased by implanting more than one layer. But up to now the overall amount of pores is too low for successful detachment. However, our investigations in this field are still in a preliminary phase. With further variation of number of layers, acceleration voltages, dose and reorganization process a successful implementation of a release layer might still be possible.

With electrochemically etched porous silicon a successful fabrication of silicon foils is already possible. Significant reorganization starts between 950 °C and 1000 °C. Temperature plateaus up to 900 °C prior to epitaxial deposition don not influence the crystal quality. The main crystal defects in the foils are stacking faults. By implementing an HF dip prior to reorganization and increasing the reorganization time the stacking fault density obtained in a lab-type CVD reactor could be reduced to (6 ± 2) x 10^3 cm^{-2}. Locally effective carrier lifetimes up to 56 µs could be reached corresponding to a diffusion length of more than five times the foil thickness. However, these lifetimes are still limited by surface and bulk effects like metal contamination and internal stress. Additionally, 5 x 5 cm^2 silicon foils fabricated in a continuous CVD reactor could be successfully detached and effective carrier lifetimes up to 6 µs were measured. In future experiments reorganization processes and post treatments like porous silicon removal have to be further optimized.

ACKNOWLEDGEMENTS

REFERENCES

[1] Petermann, J.H., et al., Progress in Photovoltaics: Research and Applications 20(1) (2012) 1.
[2] Radhakrishnan, H.S., et al., IEEE Journal of Photovoltaics 4(1) (2014) 70.
[3] D.M. Powell et al., Appl. Phys. Lett. 103 (2013) 263902.
[4] B. Aspar et al., Microelectronic Engineering 36 (1997) 233.
[5] F. Henley et al., Proceedings of the 26th European Photovoltaic Solar Energy Conference (2011) 971.

[6] S. Reber et al., Proceedings of the 19th European Photovoltaic Solar Energy Conference (2004) 471.

[7] M. Keller et al., J. Nanosci. Nanotechnol. 11(9), (2011) 8024.

[8] S. Reber et al., Proceedings of the 27th European Photovoltaic Solar Energy Conference, Frankfurt, p. 2 Germany (2012)

[9] F. Secco D'Aragona, J. electrochem. Soc. 119 (1972) 948.

[10] B. Terreault, Phys. Stat. Sol. (a) 204(7) (2007) 2129.

[11] N. Milenkovic et al., presented at the 4th SiliconPV conference (2014).

[12] L.T. Canham, Appl. Phys. Lett. 57 (1990) 1046.