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ScienceDirect

Energy Procedia 55 (2014) 552 – 558

Energy Procedia

4th International Conference on Silicon Photovoltaics, SiliconPV 2014

Reorganization of porous silicon: effect on epitaxial layer quality and detachment

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Abstract

Cost reduction is still a main goal in solar cell research and can be achieved by going towards thinner silicon bulk material. One way to avoid kerf loss and to reach thicknesses of less than 50 µm is a lift-off approach using porous silicon and epitaxial thickening for silicon foil fabrication. The porous layer structure requires a reorganization step that was varied in this work to optimize the detachment properties and the crystal quality of the epitaxial Si film. All processes were carried out in a quasi-inline Atmospheric Pressure Chemical Vapour Deposition (APCVD) reactor. Cross-sections were observed to see if the porous layer shows the desired structure. Stacking fault densities in epitaxial layers deposited on porous silicon layers significantly decrease with increasing reorganization time but are at least one order of magnitude higher than in epitaxial layers deposited on polished wafers. Microwave photoconductive decay (MWPCD) measurements and photo luminescence (PL) imaging were carried out to determine the effective carrier lifetimes of the detached foils and to correlate them with stacking faults and cracks. A detached 40 µm thin silicon foil with an averaged effective carrier lifetime of 22 µs is shown which corresponds to a diffusion length of over 200 µm. This investigation shows that silicon foils deposited in a quasi-inline APCVD reactor exhibit good detachment properties and a good crystal quality, which is both needed for high efficiency solar cell processing.

Peer-review under responsibility of the scientific committee of the SiliconPV 2014 conference

Keywords: porous silicon, epitaxy, reorganization, silicon foils, MWPCD

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Peer-review under responsibility of the scientific committee of the SiliconPV 2014 conference
doi:10.1016/j.egypro.2014.08.023

1. Introduction

Lift-off processes using the porous silicon technique and epitaxial thickening are well developed for microelectronics and have already been successfully transferred to photovoltaic (PV) applications [1, 2]. In this concept a low porosity layer on top of a high porosity layer which are both electrochemically etched in a silicon substrate are used. During a high temperature anneal the top region of the low porosity layer reorganizes to a closed surface which serves as a template for epitaxy. The high porosity layer forms at the same time a separation layer with large cavities which allow detachment of the epitaxially grown foil from the reusable substrate. Using this approach for solar cell manufacturing requires high-throughput porosification and epitaxy processes on large area substrates. Inline Atmospheric Pressure Chemical Vapour Deposition (APCVD) reactors with a high throughput are therefore essential for this concept [3].

The reorganization step that restructures the porous layer prior to epitaxy has a significant effect on the crystal quality of the epitaxial grown Si film and the detachment properties. A not sufficiently closed or smooth surface leads to defect growth in the epitaxial layer and detachment is only possible if an adequate separation layer has been formed. Reorganization can be influenced by the heating ramp, the duration of the reorganization process and the gaseous atmosphere [4]. The storage time of the samples after porosification leads as well to a different reorganization result and is therefore also investigated in the following experiments.

In this work all experiments were carried out using a lab-type quasi-inline APCVD reactor. The gained results can be transferred later on to processes carried out in high-throughput APCVD-reactors. The aim of this investigation was to reach good detachment properties and to enhance the crystal quality of the silicon foils by optimizing the post-porosification processes prior to epitaxy. The following chapter gives a short overview of the sample preparation. The reorganized porous structures were observed using a scanning electron microscope (SEM). To determine the crystal quality of the deposited epitaxial layers the defect densities and effective carrier lifetimes were measured on samples processed with different reorganization parameters.

2. Sample preparation

The porosified 6 inch p-type Cz substrates with a specified resistivity of 10-20 mΩcm were supplied by IMS (Institut für Mikroelektronik Stuttgart). They exhibit a low porosity layer on top of two high porosity layers with slightly different porosities and an approximately 1 cm wide rim without porous layer. The samples were quartered before processing to fit in the sample holders of the lab-type CVD reactor. All processed samples were featuring the same porosification and were processed after over 300 days of aging in clean room atmosphere. To study whether an oxide is responsible for aging some of the porosified substrates were etched for 5 min in 50 % $HF_{(aq)}$, then rinsed in DI water and dried under a flow box prior to reorganization and epitaxy.

Table 1. Parameters for the different reorganization processes.

Process	process temperature [°C]	ramp [°C/min]	reorganization time [min]
A	1150	10	5
B	1150	100	5
C	1150	100	30
D	1150	100	90

An approximately 40 µm thick p-type epitaxial layer with an aimed doping density of $8 \cdot 10^{16}$ cm^{-3} was deposited on all samples at 1150 °C for 47 min directly after reorganization in hydrogen atmosphere. Table 1 summarizes the reorganization parameters compared in this work. A variation of the heating ramp and the reorganization time was conducted. The cooling ramp was kept similar for all studied processes.

Samples for defect density measurements were Secco· etched for 40 seconds. The remaining samples were used to look at cross-sections, to determine the detachment properties and to measure the lifetimes on freestanding silicon foils. For the latter the 4 x 4 cm² area for detachment was predefined with a Nd:YAG laser.

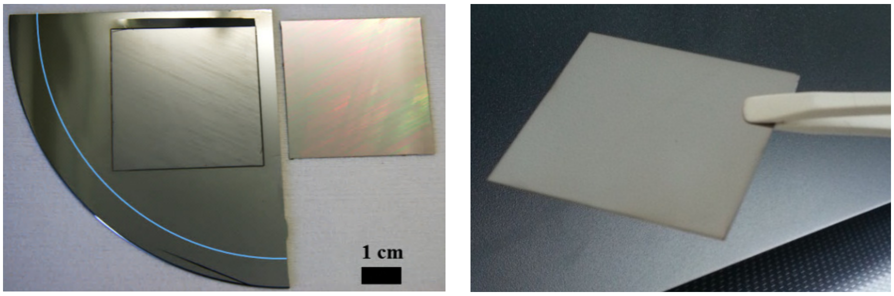

Fig. 1. Left: A 4 x 4 cm² detached silicon foil next to the corresponding substrate (the blue line marks the area without porous layer); Right: A freestanding etched and passivated 4 x 4 cm² silicon foil.

After mechanical detachment the residual porous silicon layer on the rear side was etched with CP71 and the samples were passivated with 20 nm Al_2O_3 on both sides followed by an annealing step for 25 min at 425 °C. Fig. 1 shows a 40 µm thick foil directly after detachment (left) and after etching and passivation (right).

3. Layer structure after reorganization and detachment properties

Samples reorganized shortly after porosification show almost exclusively spherical or facetted pores in the low porosity layer and only a few remaining pillars in the high porosity layer even after 5 min of reorganization at 1150 °C. This allows easy detachment from the substrate. We suppose that long storage leads to an oxidation of the porosified samples to an extent that the oxide cannot be removed sufficiently in hydrogen atmosphere for proper reorganization. In the following experiments we processed only samples that were aged over 300 days in clean room atmosphere.

First, the influence of the heating ramp was investigated comparing 10 °C/min (process A) to 100 °C/min (process B). Fig. 2 (a) and (b) show cross-sections of reorganized porous layers resulting from these processes. The structure of process A looks less reorganized than Process B although the samples were both tempered for 5 min at 1150 °C after reaching the process temperature. The only difference was the lower heating ramp of 10 °C/min which seems to affect the reorganization strongly. One explanation for this effect could be that keeping the sample longer at a temperature below 1150 °C leads to a closing of the silicon surface before the native oxide in the lower layer is sufficiently removed. This hinders the rest of the layer from reorganizing. Fig. 3 fortifies that theory showing cross-sections of porous layers reorganized at two different temperatures, 950 °C and 1000 °C. The porous structure shows a still opened surface after 30 min annealing at 950 °C and already a closed surface after 30 min reorganization at 1000 °C. A longer reorganization at 1000 °C seems for that reason obstructive for a good reorganization process. For all further processes the ramp was therefore kept at 100 °C/min.

In the following experiments a comparison of different reorganization times is shown. The cross-sections of Process B and C suggest that almost the same structures are formed after reorganization between 5 and 30 min (see Fig. 2 (b) and (c)). The highly porous layer is not yet reorganized to a separation layer that might allow good detachment. The epitaxially grown foils were therefore only partially detachable. Additionally the low porosity layer shows only a few facetted pores and close to the surface almost solely elongated pores.

For Process D the reorganization time was enhanced to 90 min. The cross-section of the porous structure shows further reorganization compared to process B and process C (see Fig 2 (d)). Still the bottom high porosity layer

· Secco-etch: HF + $K_2Cr_2O_7$ + H_2O in a ratio of HF : H_2O = 2 : 1 with 44 g $K_2Cr_2O_7$ dissolved in 1 l of H_2O. It etches defects on all surfaces.

exhibits a higher amount of pillars than newly etched samples. The low porosity layer, however, seems to have reorganized properly. Detachment was still not possible on the whole area. Enhancing the reorganization time even further might therefore lead to the desired structure but would question the industrial feasibility of the concept.

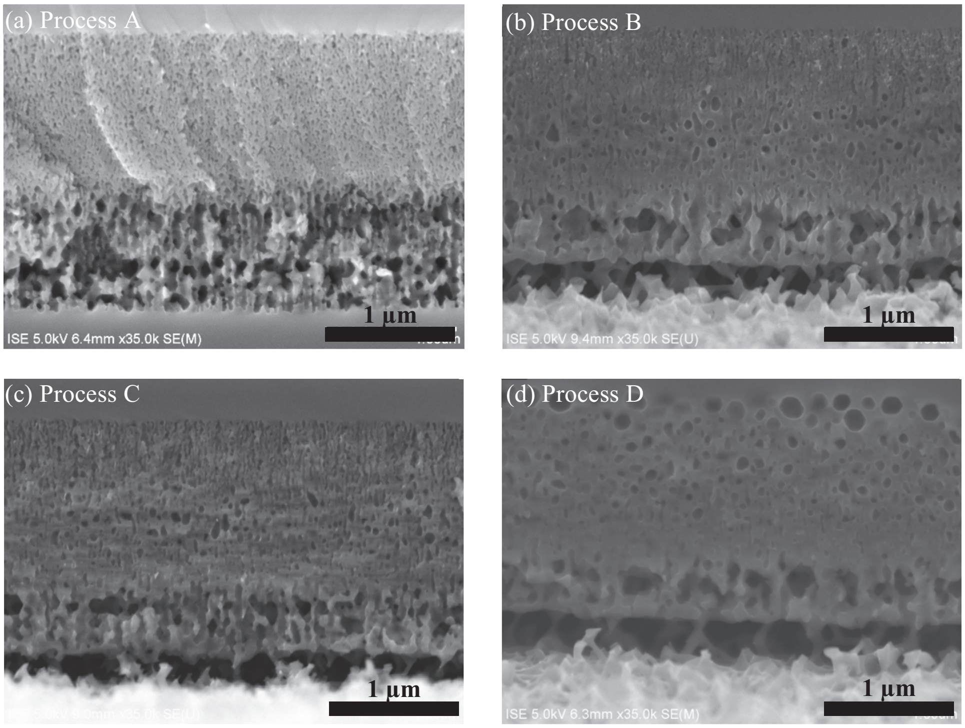

Fig. 2. SEM pictures showing cross-sections of samples without an HF-Dip processed with (a) process A, (b) process B, (c) process C and (d) process D.

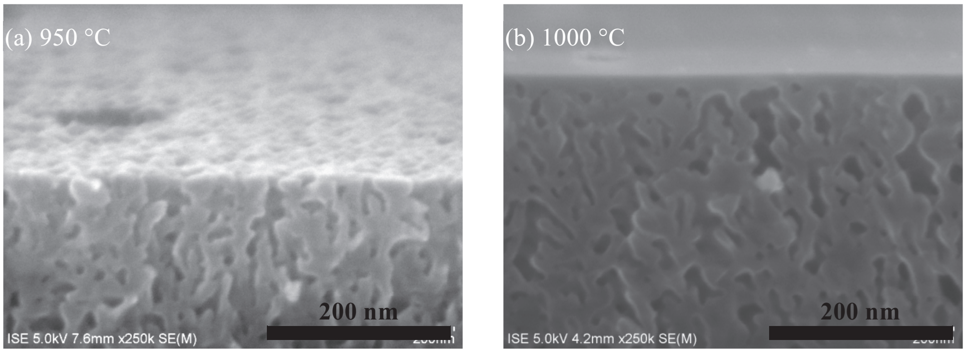

Fig. 3. SEM picture of the porous silicon surface of a sample without an HF-Dip after 30 min reorganization at (a) 950 °C and (b) 1000 °C.

A possible way to determine whether an oxide is responsible for the decelerated reorganization is to perform an HF-dip on the samples prior to processing. Fig. 4 (a) and (b) show that in these samples the second high porosity layer reorganized for process A and process B to such a degree that the foil already detached from the substrate after the process. Only a few remaining pillars could be observed (see Fig. 4 (b)). The low porosity layer shows facetted pores already after 5 min of reorganization. All foils could be successfully detached from these substrates. These results support the assumption that long storage of porosified samples leads to stronger "bulk" oxidation that hinders the desired reorganization of the porous layers. An HF-dip can restore the sample constitution to a comparable state of samples right after porosification.

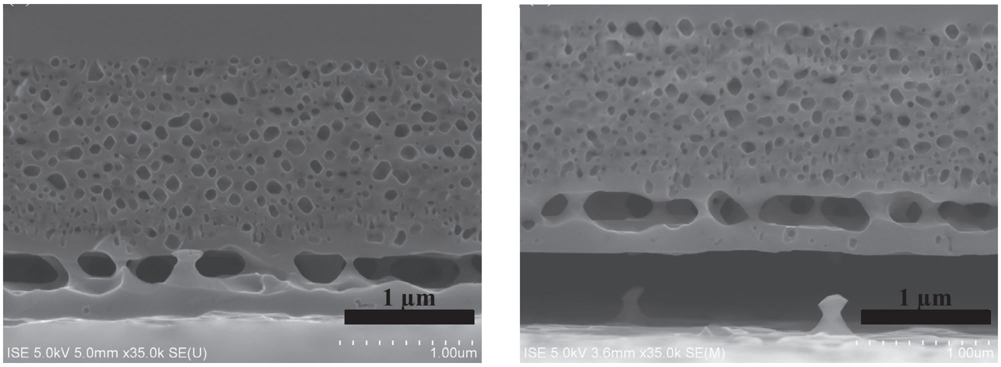

Fig. 4. SEM pictures showing cross-sections of samples with an HF-dip prior to processing with (a) 5 min and (b) 30 min of reorganization followed by 47 min of epitaxial growth.

4. Quality of deposited silicon layers grown on porous silicon

The quality of an epitaxially grown silicon foil can be determined by defect density measurements and effective carrier lifetime measurements. The defect density measurements summarized in Table 2 show that aged samples with a porous intermediate layer have a much higher stacking fault density (SFD) compared to reference layers on polished and cleaned CZ wafers. For processes with longer reorganization times a reduction of the SFD can be observed. This indicates an improvement of the template with increasing time which strongly affects epitaxial growth. The low porosity layer that serves as a template for epitaxy is not yet sufficiently reorganized after 30 min. SFD of epitaxial layers grown on porous layers reach almost reference values after 90 min of reorganization which suggests that the surface closed completely. High SFD are expected to affect the minority carrier lifetime negatively.

The exact etch pit densities (EPD) for those samples were hard to determine because EPs located in and on SF cannot be accounted for during the automated measurement. Therefore only the EPD value of process D can be trusted which is also in the range of the reference values.

The HF-dipped sample reorganized with process C shows defect densities in the same range as the samples without pre-conditioning, which rules out that the pre-treatment degrades the porous structure.

To determine spatial resolved lifetime values MWPCD measurements on passivated free standing silicon foils were performed. The determined effective carrier lifetimes are averaged over 50 measurement points leading to a quite big error due to an inhomogeneous distribution on the 4 x 4 cm² foils. The reason for this will be discussed later on in this paper.

Table 2. Defect densities on and effective carrier lifetimes of epitaxial foils for four different process sequences of reorganization.

Process	etch pit density [1/cm²]	stacking fault density [1/cm²]	τ_{eff} [µs]
B (without HF-Dip)	$(7\pm3)\cdot10^2$	$(38\pm18)\cdot10^3$	9±2
B (with HF-Dip)	not measured	not measured	7±2
C (without HF-Dip)	$(2\pm1)\cdot10^3$	$(5\pm1)\cdot10^3$	16±7
C (with HF-Dip)	$(6\pm5)\cdot10^3$	$(6\pm2)\cdot10^3$	**22±5**
D (without HF-Dip)	$(7\pm3)\cdot10^3$	$(2\pm1)\cdot10^2$	11±6
Reference	$(5\pm7)\cdot10^3$	< 10	-

Increasing the reorganization time from 5 min to 30 min leads to a noticeable improvement in the effective carrier lifetime of the deposited epitaxial layer both with and without HF-Dip. Although no difference in the porous layer structure could be observed with SEM investigations the lifetime measurements suggest that the template for epitaxy is enhanced after 30 min reorganization. Process C and D, however, show in the range of the measurement error comparable values for the effective carrier lifetime, although lower defect densities were measured for the latter. This might be related to the mechanical detachment process that can also affect the quality of the foils by inducing cracks and stress respectively. Process D was only performed with aged samples and following experiments have to reveal whether a longer reorganization performed on HF-dipped samples reduces the defect density and therefore increases the effective carrier lifetime further.

A reorganization time of 30 min led to an average effective carrier lifetime of 22 µs on an HF-dipped sample. This corresponds to a diffusion length of about 200 µm for the 40 µm thin epitaxial silicon foil. Locally values of 40 µs were measured showing that epitaxial layers with even higher quality can be processed. These are sufficiently high values for high-efficiency solar cell manufacturing. The effective carrier lifetimes for the remaining processes are summarized in Table 2.

To investigate the inhomogeneity of the effective carrier lifetimes on the epitaxial foils we performed MWPCD mappings and PL measurements. Fig. 5 shows a MWPCD mapping next to a PL image of a sample reorganized with process B that received an HF-dip before processing. The upper circle in the PL image marks a line-shaped conglomeration of stacking faults (see Fig. 6 left) which has a negative effect on the otherwise good effective carrier lifetime in this region. The lower circle marks a scratch (see Fig. 6 right) on the surface which can also clearly be seen in the lifetime mapping. Another observation from the MWPCD measurement is that apparently the edges of the samples exhibit a higher effective carrier lifetime than the center. µRaman measurements in both areas confirmed a remaining highly doped p-type layer in the inner region of the sample. The origin of this was a by mistake deposited highly doped back surface field layer which was not sufficiently etched away before Al_2O_3 passivation. Highly doped p-type material leads to a higher surface recombination velocity and therefore to a lower effective carrier lifetime [5]. The bulk lifetime of the silicon foils might therefore be in a higher range than the measured effective once. Following experiments have to confirm this.

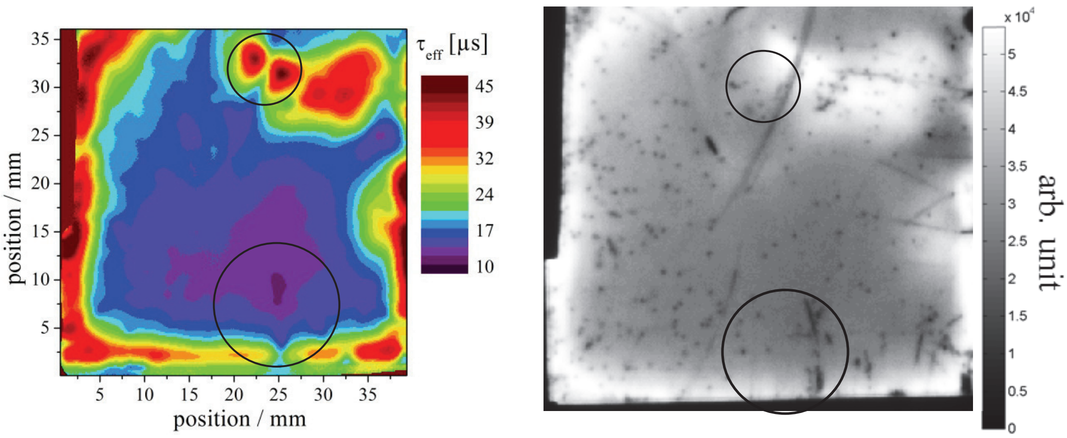

Fig. 5. MWPCD mapping (left) and PL imaging (right) of a 4 x 4 cm² sample that was processed with process B.

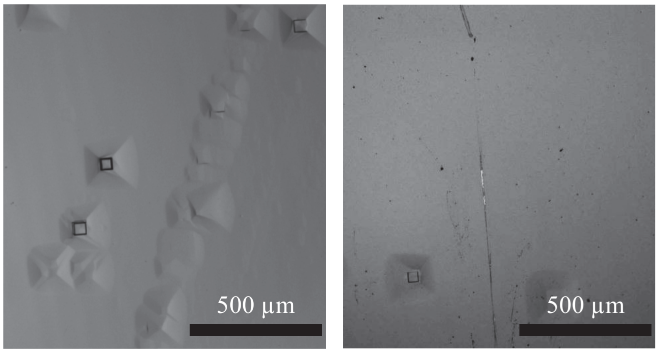

Fig. 6. Microscopic pictures of the stacking faults (left) and the scratch (right) leading to a locally decreased effective carrier lifetime on the sample shown in Fig. 4.

5. Conclusion

This paper presented results of the reorganization processes applied on porous silicon layers. Their effect on defect densities, detachment properties and effective carrier lifetimes of the epitaxially deposited foils was investigated. Aged porosified substrates exhibit an oxide that hinders the layer from proper reorganization. The constitution of the samples could successfully be restored with a simple HF-Dip leading after reorganization to the desired separation layer and the closed template required for high quality epitaxial growth. Successful mechanical detachment of 4 x 4 cm² foils after reorganization and epitaxy could be performed on these samples. The epitaxially deposited layers show still higher stacking fault densities compared to reference values of epitaxial layers deposited on cleaned Cz substrates. But a reduction of the defect densities could be achieved with longer reorganization times. The best averaged effective carrier lifetime was 22 µs and could be reached with a medium reorganization time of 30 min prior to epitaxy. This corresponds to a sufficiently high diffusion length of 200 µm for a 40 µm thin silicon foil. An inhomogeneous lifetime distribution due to a remaining highly doped p-type layer was observed which could be removed with a longer etching step prior to passivation. In areas without that highly doped layer local values over 40 µs could be measured showing the high material quality of epitaxial layers grown in a quasi-inline APCVD reactor.

Acknowledgments

The authors would like to thank IMS for supplying the samples and our colleagues M. Winterhalder, M. Kwiatkowska, K. Zimmermann, L. Mundt and F. Heinz for helping with sample preparation and measurements.

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