

# Epitaxially grown polycrystalline silicon thin-film solar cells on solid-phase crystallised seed layers



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## ABSTRACT

This paper presents the fabrication of poly-Si thin film solar cells on glass substrates using seed layer approach. The solid-phase crystallised P-doped seed layer is not only used as the crystalline template for the epitaxial growth but also as the emitter for the solar cell structure. This paper investigates two important factors, surface cleaning and intragrain defects elimination for the seed layer, which can greatly influence the epitaxial grown solar cell performance. Shorter incubation and crystallisation time is observed using a simplified RCA cleaning than the other two wet chemical cleaning methods, indicating a cleaner seed layer surface is achieved. Cross sectional transmission microscope images confirm a crystallographic transfer of information from the simplified RCA cleaned seed layer into the epi-layer. RTA for the SPC seed layer can effectively eliminate the intragrain defects in the seed layer and improve structural quality of both of the seed layer and the epi-layer. Consequently, epitaxial grown poly-Si solar cell on the RTA treated seed layer shows better solar cell efficiency,  $V_{oc}$  and  $J_{sc}$  than the one on the seed layer without RTA treatment.

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## 1. Introduction

Polycrystalline silicon (poly-Si) on glass thin-film solar cells combine advantages of crystalline silicon-wafer based technology with a low material usage and large area monolithic integration typical for thin-film technologies [1]. Solid phase crystallisation (SPC) of amorphous Si (a-Si) thin films is one of the simplest techniques to obtain poly-Si at relatively low temperature (600 °C) and it is commonly used for poly-Si films solar cell fabrication [2,3]. A thin heavily P-doped SPC poly-Si film can be used as a seed layer for epitaxy and it can also act as the emitter in a respective solar cell [4].

Solid phase epitaxy is reported suitable for thickening of the SPC seed layer [4]. The SPE technique consists of a-Si deposition and ex-situ annealing for the crystallisation. SPE can occur when an amorphous thin film is in direct contact with an adjoining crystalline seed layer. The crystalline material provides a template for ordered crystallisation of the amorphous film, a process which occurs as a layer-by-layer conversion of atoms from the amorphous to the crystalline phase [5]. Thus, a crucial prerequisite for good epitaxy is a clean, contamination-free seed layer surface. The usual surface contamination on silicon is a thin native

oxide film. Furthermore, metallic and organic contaminants are always present. These contaminants mask the crystalline information of the underlying crystalline seed layer and thus take away its beneficial function [6]. Therefore, the surface cleanliness of the seed layer is most essential for achieving good epitaxy [7].

In this paper, different wet chemical cleaning methods are introduced to achieve a clean seed layer surface for epitaxy. SPE kinetics can be used to evaluate the seed layer surface cleanliness. Theoretically, SPE should start right away without any incubation time. However, the SPE growth is always preceded by a long “delay period” which varies between 6 h and 25 h for an ex-situ annealing at a temperature of 600 °C [8]. The cleanliness of the initial amorphous-crystalline can affect this long “delay period” [9]. Thus, analysing the “delay period”, or the incubation time, can identify which surface cleaning method generates the cleanest seed layer surface.

Moreover, a large number of intragrain defects in SPC poly-Si thin films impedes its use as the seed layer for epitaxy since the quality of the epi-layer is mostly determined by the quality of the seed layer [10]. In our previous report, intragrain defects in the SPC seed layer can be greatly eliminated by rapid thermal annealing (RTA) [11]. Therefore, in this paper, we are aiming to identify whether RTA treatment for the seed layer can effectively improve the epi-layer quality and performance of the epitaxial grown poly-Si thin film solar cell.

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## 2. Experimental

### 2.1. Seed layer preparation

The seed layer precursor (80 nm  $\text{SiN}_x$ /200 nm a-Si with P-doping concentration of about  $3.3 \times 10^{20} \text{ cm}^{-3}$ ) was deposited on a planar glass substrate (Schott Borofloat33) by plasma-enhanced chemical vapour deposition.  $\text{SiN}_x$  acts as a barrier and anti-reflection layer. After deposition, all seed layer precursors were crystallised at  $600^\circ\text{C}$  in a tube furnace purged with nitrogen.

### 2.2. Seed layer surface cleaning

Before loading the seed layer into the deposition chamber, surface cleaning should be applied firstly because that a clean, contamination-free substrate surface is a crucial prerequisite for good epitaxy. Three different wet chemical cleaning methods were applied to the seed layer as following:

#### (1) HF dip only (HF)

The SPC poly-Si seed layer was dipped in a 5% HF solution ( $\sim 1$  min) to get a hydrophobic surface, rinsed in DI water ( $\sim 3$  min) and then dried by  $\text{N}_2$  (1 min). HF dip method creates oxide-free silicon surfaces terminated mostly with hydrogen. From IR measurements, monohydride predominates on the Si(1 1 1) surface and dihydride on the Si(1 0 0) surface [12]. This hydrogen-termination is expected to suppress re-oxidation of the Si surface before loading sample into the deposition chamber.

#### (2) Standard RCA cleaning process followed by an HF dip (standard RCA)

RCA cleaning is developed in the 1970s at Radio Corporation of America [13]. This wet chemical cleaning process usually consists of two steps: RCA-1 and RCA-2. RCA-1 solution is mixed by  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  (30%) and  $\text{NH}_4\text{OH}$  (27%) with volumetric ratio at 5:1:1. RCA-2 solution is mixed by  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  (30%) and HCl (37%) with volumetric ratio at 5:1:1. RCA-1 reduces organic contamination and light metals such as Cu, Ag, Ni, Co and Cd; and RCA-2 removes heavier metals [14]. The sample was firstly cleaned in RCA-1 solution for 5 min at  $80^\circ\text{C}$ , rinsed and HF dipped. Then it was cleaned in RCA-2 solution for 5 min at  $85^\circ\text{C}$ , rinsed, HF dipped and dried in  $\text{N}_2$  (1 min).

#### (3) Simplified RCA process (simplified RCA)

HF dip step between RCA-1 and RCA-2 was omitted in this method to reduce excessive etching of the poly-Si seed layer by HF dip.

### 2.3. Epitaxial growth on seed layer

After surface cleaning, the seed layer was loaded into the vacuum chamber as soon as possible to prevent any further contamination from the environment. The absorber and back surface field (BSF) were deposited on the cleaned seed layers by E-beam evaporation at 300 nm/min with the doping profile as follows:  $\sim 2 \mu\text{m}$ ,  $2 \times 10^{16} \text{ cm}^{-3}$  B-doped absorber and  $\sim 100 \text{ nm}$ ,  $2 \times 10^{19} \text{ cm}^{-3}$  B-doped BSF at  $250^\circ\text{C}$ . Afterwards, SPE was performed ex-situ in the furnace under nitrogen flow at temperature of  $580^\circ\text{C}$ . These epitaxially grown samples were then rapid-thermal annealed at  $950^\circ\text{C}$  for 3 min to activate dopants and to reduce the defect density. Following up, high-temperature hydrogenation treatment was applied to passivate the grain boundaries. Hydrogen passivation was performed in a cold-wall vacuum system with an inductively coupled remote plasma source at a temperature of  $650^\circ\text{C}$  for 20 min, a plasma power of 3200 W, hydrogen gas flow of 200 sccm and argon gas flow of 60 sccm [15].

### 2.4. Solar cell metallisation

SPE grown samples were cut to size of  $5 \text{ cm} \times 5 \text{ cm}$  and were metallised with interdigitated Al line contacts on the heavily doped layers, the emitter and BSF. All cells were in the superstrate configuration, had an area of  $2 \text{ cm}^2$  and did not have any light trapping features. More details on the metallisation scheme used in this work are given in reference [16].

The structural quality of the Si film was analyzed by Raman spectrum (Renishaw inVia Raman Microscope) and X-ray diffraction (Philips X'pert Materials Research diffractometer). Two different excitation wavelengths of the laser for the Raman investigation are used in this paper. The 442 nm laser with estimated penetration depth of about 330 nm was used for the  $\sim 200 \text{ nm}$  thick seed layer. The 785 nm laser with estimated penetration depth of about  $10 \mu\text{m}$  was used for the  $2 \mu\text{m}$  thick epitaxially grown poly-Si. Intragrain defects in the epitaxial Si layers were analyzed by cross-sectional transmission electron microscopy (TEM) (Philips CM200 with a field emission gun).

External quantum efficiency (EQE) measurements were performed by a QEX10 spectral response system from PV Measurements, Inc. The current–voltage ( $I$ – $V$ ) measurements were performed using an IV5 solar cell  $I$ – $V$  testing system from PV Measurement, Inc. (using a Keithley 2400 source meter) under illumination power of  $100 \text{ mW cm}^{-2}$  by an AM 1.5G solar simulator (Oriel model 94023A).

## 3. Results and discussions

### 3.1. Seed layer surface cleaning effects on the SPE process

Monitoring the real-time in-situ transmission of Si films is a commonly used method for the crystallisation kinetics analysis [8,17]. It is used to monitor the SPE process in this work. A low power (5 mW) 632 nm-wavelength laser was introduced into the furnace. After passing the sample the transmitted intensity was recorded by a photodiode outside the furnace. The laser probe area is a round circle with the diameter of 2 mm (relatively large enough compared with  $1 \pm 0.5 \mu\text{m}$  average poly-Si grain size).

Fig. 1 shows the evolution of the transmission during the annealing which reflects the SPE kinetics of the samples on the seed layers treated by different surface cleaning methods. As is obvious, a remarkable increase of transmission starts after about 620 min to 760 min annealing at  $580^\circ\text{C}$ , due to an increasing amount of crystalline fraction in the film. This is an indication of the incubation

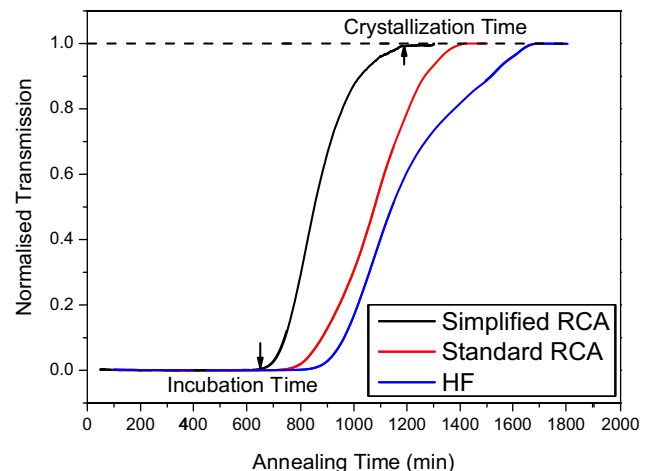


Fig. 1. Optical transmission of Si films on the seed layers during SPE at  $580^\circ\text{C}$ . The seed layers were cleaned by different wet chemical methods.

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