Effects of annealing temperature on crystallisation kinetics, film properties and cell performance of silicon thin-film solar cells on glass

Yuguo Tao [a],*, Sergey Varlamov [a], Oliver Kunz [b], Zi Ouyang [a], Johnson Wong [a], Thomas Soderstrom [a], Michael Wolf [b], Renate Egan [b]

[a] Photovoltaics Centre of Excellence, University of New South Wales, Sydney, NSW 2052, Australia
[b] CSG Solar Pty Ltd, Sydney, NSW, Australia

ABSTRACT

Solid-phase crystallisation (SPC) of Si films on glass prepared by three deposition methods, plasma enhanced chemical vapour deposition (PECVD), electron-beam evaporation, and a combination of both, are compared for different annealing temperatures. Three independent techniques, optical transmission microscopy, UV reflectance spectroscopy, and X-ray diffraction, are used to characterise the crystallisation kinetics and film properties. The activation energy for the incubation is estimated to be 2.7–3.0 eV. The scanning electron microscopy images of polycrystalline Si films after Secco etching show a gradually decreasing average grain size in each film type for higher SPC temperatures. The crystal quality of all film types degrades at higher crystallisation temperatures. Solar cells fabricated from these polycrystalline Si films were characterised by Suns-V_{oc} and spectral response measurements. According to both the resulting open-circuit voltage and the short-circuit current, the electronic quality of all polycrystalline Si film types and the corresponding cell performance degrade for higher crystallisation temperatures but to a different extent depending on the film deposition method.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

1. Introduction

Polycrystalline silicon (*poly*-Si) on glass thin-film solar cell technology is one of promising photovoltaic (PV) technologies. It can potentially combine some advantages of Si wafer-based technology, such as long-term stability, use of abundant and non-toxic materials, a large portfolio of available well-developed processes, with a low material usage and large area monolithic integration typical for the thin-film approach [1–3]. An additional benefit of *poly*-Si on glass solar cells as compared to all other thin-film technologies is avoidance of transparent conductive oxide (TCO), which simplifies manufacturing and improves solar module reliability [4]. *Poly*-Si solar cell fabrication involves high temperature processing steps for film crystallisation and defect annealing. However, glass used as a film substrate or superstrate cannot withstand prolonged treatments at temperatures much higher than its critical points. Hence, a number of either low temperature or high temperature but short time approaches to crystallisation of amorphous silicon (*a*-Si), such as solid phase crystallisation (SPC) [5,6], rapid thermal annealing (RTA) [7], laser crystallisation [8], have been being explored. Of these, SPC has

become the most common and important for obtaining *poly*-Si thin films with the relatively good crystalline and electronic properties for solar cell application [5,10]. The *poly*-Si on glass solar modules are manufactured from precursor *a*-Si films prepared by either Plasma Enhanced Chemical Vapour Deposition (PECVD) [1] or electron-beam (E-beam) evaporation [11,12]. To obtain *poly*-Si material with acceptable electronic quality the precursor *a*-Si thin films are typically crystallised at the standard temperature of 600 °C for 20 h [13,14]. However, this lengthy annealing time results in a very large thermal budget and a low throughput, thus diminishes the attractiveness of *poly*-Si thin-film on glass solar cell technology as compared to both silicon wafer-based technology [15] and other thin film technologies [16]. A shorter SPC process would be much preferred.

Although the film preparation conditions, such as deposition method [13,14], deposition temperature [17], dopant type and concentration [18,19], substrate surface morphology [20–22] all affect the crystallisation kinetics of *a*-Si film to a certain extent, according to Blum's formulae [23] the crystallisation time of *a*-Si films can be shortened by a factor of about 2 if the annealing temperature is increased by 10 °C. It has been demonstrated previously that higher crystallisation temperatures lead to smaller grain size [13,24], which can degrade electronic quality of *poly*-Si if the grain boundaries are not well passivated [25]. However, it is becoming clear more recently that a smaller grain

---

size does not necessarily lead to lower open circuit voltage (V_{oc}) and poorer cell performance [26]. Instead, intragrain defects can be potent enough to limit the minority carrier lifetime by a few nanoseconds and V_{oc} by about 500 mV [27–29]. According to authors' previous research, the performance of poly-Si thin-film cells prepared by PECVD degrades significantly when the SPC temperature increases from 600 °C to 640 °C [30].

On the other hand, the currently preferred Si film deposition method is E-beam evaporation due to its much higher rate (up to 1 μm/min) and lower equipment cost as compared to PECVD [11,12]. Therefore, this work further expands the study of the effects of the annealing temperature on the SPC kinetics and properties of a wider range of poly-Si films and solar cells prepared by different methods: E-beam evaporation, PECVD, and a combination of both. The SPC kinetics and poly-Si film properties were characterised by the following techniques: optical transmission microscopy (OTM), UV reflectance spectroscopy (UV-R), X-ray diffraction (XRD), scanning electron microscopy (SEM), and the solar cells' electrical properties were evaluated by the Suns-V_{oc} [31], external quantum efficiency (EQE) measurements, and the capacitance–voltage (C–V) analysis [32,33].

2. Experiments

Planar borosilicate glass (Schott Borofloat33) coated with a 65 nm thick SiN antireflection and barrier layer was used as a substrate. The precursor a-Si films with the standard solar cell n+/p-/p+ structure deposited in the KAI800 PECVD tool at CSG Solar are hereinafter defined as "PECVD" films; the precursor a-Si films with the same structure all deposited by E-beam evaporation are regarded as "E-beam" films, and the films with the emitter layer prepared by PECVD while the absorber and back surface field (BSF) layers evaporated by E-beam are called "Hybrid" films. The main benefit of the combination of PECVD emitter and E-beam evaporated absorber, rather than the opposite combination, is that the PECVD method is well-proven but with low deposition rate (suitable for depositing thin layer: emitter), and the E-beam evaporation has high deposition rate (suitable for preparing thick layer: absorber). In addition, the Hybrid structure can eliminate the phosphorous doping source in the deposition chamber, so there is only Boron doping source in the chamber, which makes the engineering control much easier. The substrate temperatures during all Si film depositions were controlled in the range of 250–300 °C. All samples' size is 2.5×2.5 cm^2. The PECVD films were cut from the same 70×80 cm^2 deposition sheet, while E-beam and Hybrid films were from different 10×10 cm^2 deposition sheets. To dehydrogenate PECVD films while keeping the same post-deposition thermal history for all film types, all films were pre-annealed at ~470 °C for about 1 h in nitrogen ambient. Crystallisation was performed in a nitrogen-purged atmospheric pressure tube furnace at temperatures of 600, 640 and 680 °C for subsequently

increasing times. In this work, different samples are annealed for different times to study the crystallisation kinetics.

Fully crystallised samples were treated at ~1000 °C for ~60 s to activate dopants and to anneal defects. Hydrogen passivation was performed in a cold-wall vacuum system with an inductively coupled remote plasma source at a temperature of ~650 °C for ~20 min, a plasma power of ~3200 W, hydrogen gas flow of ~200 sccm and argon gas flow of ~60 sccm [34]. The metallisation scheme used in this work consists of two interdigitated comb-like metal grids, as described elsewhere [35], and each 2.5×2.5 cm^2 sample features one solar cell of 1.6×1.25 cm^2 size. The described solar cells are used in the superstrate configuration, and the cell design parameters are summarised in Table 1.

The hemispherical UV reflection spectra were recorded by Varian Cary 5G double-beam spectrophotometer equipped with the integrating sphere. The XRD spectra were measured by the Philips X'pert Materials Research diffractometer operated at a voltage of 40 kV and a current of 40 mA, using Cu K_a radiation ($\lambda = 1.54$ Å). The parameter setting for all XRD scans is 2°/min and a step size of 0.02° in a 2θ range of 20–60°. A Hitachi S4500 field emission scanning electron microscope was used for taking SEM images. The microscope was typically operated at voltage of 8 kV, and routinely used for imaging at $10,000\times$ magnification. The sheet resistances of the whole poly-Si films and the back surface field (BSF) layers were measured by the Napson contactless tool and by the four-point-probe method respectively, while the sheet resistance of the emitter layer was deduced from the combined sheet resistance data [35]. The doping level in the absorber was extracted by means of the capacitance–voltage analysis. The detailed description of the Suns-V_{oc} method can be found in [31]. The EQE measurements were performed on the QE/1PCE system in the wavelength range of 300–1100 nm with a wavelength step size of 5 nm.

3. Results and discussions

3.1. Crystallisation kinetics

The crystal grain nucleation and growth in a-Si has been experimentally investigated since the middle of the 1970s [23,36]. It is shown in these studies that the crystalline fraction exponentially increases with time. To study the SPC stages in Si films on glass, in this work the characteristic incubation time is defined as a period after the setpoint temperature is reached and before nucleation and crystal growth start, while the characteristic crystallisation time is defined as the time needed to fully crystallise the a-Si layer (starting from the instant when the SPC temperature setpoint is reached).

OTM allows convenient visual identification of the start and the end of crystallisation, although it is not easily possible to estimate the crystallisation fraction at the intermediate stages. The OTM images in Fig. 1 show that crystal grains in E-beam Si

Table 1
Design parameters of the solar cells in superstrate configuration.

Parameter	Details	PECVD	E-Beam	Hybrid
Glass	3.3 mm; Borofloat33, planar			
AR coating	~65 nm; PECVD SiN; $n \approx 2.1$			
Emitter	~ 0 nm, n+; P~1×10^{20} cm^{-3}	PECVD	E-Beam	PECVD
Absorber	~1400 nm; p-; B~5×10^{16} cm^{-3}	PECVD	E-Beam	E-Beam
BSF	~100 nm; p+; B~2×10^{19} cm^{-3}; 1.5 kΩ/□	PECVD	E-Beam	E-Beam
SPC	At 600 °C, 640 °C, 680 °C for various times			
RTA	1 min at ~1000 °C			
Hydrogenation	20 min at ~650 °C; remote plasma			