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Influences of oxygen contamination on evaporated poly-Si thin-film solar cells by solid-phase epitaxy

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ABSTRACT

The influences of the oxygen contaminations on the crystal quality and performances of the evaporated polycrystalline silicon (poly-Si) thin-film solar cells prepared by solid-phase epitaxy were investigated by applying different deposition rates and base pressures. The experimental results show that although the evaporated poly-Si thin-film solar cell obtained at high base pressures (9.33×10^{-5} Pa) and high deposition rate (300 nm/min) has small amount of SiO_2 precipitations, it still shows the similar good material quality and performances as the cell prepared at low base pressure (1.33×10^{-6} Pa) and high deposition rate (300 nm/min) with oxygen interstitials. On the other hand, the poly-Si thin-film solar cell deposited at low base pressure (1.33×10^{-6} Pa) and low deposition rate (50 nm/min) has large amount of SiO_2 precipitations and resulting worse material quality and hence cell performances. Therefore, the high deposition rate is desirable to maximize the solar cell performance, as well as the throughput. It is a more influential factor than the base pressure.

1. Introduction

Polycrystalline silicon (Poly-Si) thin-film solar cells are becoming increasingly important in recent years due to their potential of significantly reduced manufacturing cost when compared to Si wafer based solar cells [1,2]. At the University of New South Wales, poly-Si thin-film solar cells are being developed utilizing solid-phase epitaxy (SPE) of a-Si films by both e-beam evaporation [3] and plasma-enhanced chemical vapor deposition (PECVD) [4]. Comparing with the PECVD method, the key advantage of e-beam evaporation is the exceptionally high Si deposition rate of up to 1 µm/min, which is obviously beneficial from a cost point of view due to the capability of high throughput. Additional advantages of the method include the absence of toxic gases, optimal Si source material usage, and compatibility with a continuous in-line deposition mode. Thus, if performed in a non-ultra-high vacuum (non-UHV) environment (base pressure $>1.33\times10^{-6}$ Pa, pressure during Si evaporation $>1.33\times10^{-5}$ Pa), e-beam evaporation could potentially be a low-cost Si deposition method for thin-film solar cells. The base pressure and Si evaporation rate are the two key parameters during deposition, which can affect impurities (e.g. oxygen) and defect densities in films and hence the crystal quality and resulting minority carrier lifetime of the poly-Si thin-film solar cells. It has been established that Czochralski Si wafer solar cells still exhibit a high minority carrier lifetime with oxygen concentration levels of up to several 10^{18} cm^{-3} as a result of strong Si–O bonds that saturate the dangling bonds [5]. In poly-Si thin-film solar cells, high short-circuit current densities can be achieved with a small minority carrier diffusion length in the range of the film thickness of ~2 µm in conjunction with good light trapping [6]. Moreover, the poly-Si thin-film solar cells are more than two orders of magnitude thinner than Si wafer solar cells. Therefore, the tolerable oxygen contamination levels could be much higher than in Si wafer solar cells. In this work, different base pressures and deposition rates will be tested and the impact of the oxygen contaminations on the crystal quality and performance of the resulting SPE poly-Si thin-film solar cells will be investigated using various in-situ and ex-situ characterization techniques.

2. Experimental details

Initial experiments were conducted with SPE poly-Si films on double-side polished intrinsic (100) float zone Si wafers for the purpose of Fourier Transformation Infrared Spectroscopy (FTIR) measurement. Prior to the Si evaporation process, the Si wafers were chemically cleaned with piranha solution (a 1:1 mixture of H_2SO_4 and H_2O_2), followed by a dip into 5% HF to remove the surface oxide. The a-Si films of 1.5 µm thickness were then deposited at either low rate (50 nm/min) or high rate (300 nm/min) by e-beam evaporation, using a substrate temperature in the range of 200–220 °C. The base pressures of the evaporator was ~1.33×10^{-6} Pa for the low base pressure setting, and deliberately increase up to ~9.33×10^{-5} Pa with continuous air flow via

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a capillary valve for the high base pressure setting. Three sets of Si thin films were prepared with the following conditions: (1) high deposition rate and low base pressure; (2) high deposition rate and high base pressure; (3) low deposition rate and low base pressure. After the depositions, the a-Si thin film samples were transferred in air to a tube furnace for crystallization at 575 °C for 24 h with continuous nitrogen flow.

In order to observe the impacts of base pressure and deposition rate on cell performances, poly-Si thin-film solar cells were fabricated with the lightly-doped absorber layers being deposited at different based pressures and deposition rates by aluminium-induced crystallization epitaxy (ALICE). The concept of ALICE comes from the SPE poly-Si thin film on seed layer by aluminium-induced crystallization (AIC). Both heavily-doped emitter and back surface field (BSF) layers were deposited at a low rate due to the heating limitation of doping sources. The settings of the base pressures and deposition rates corresponded to the above experiments with poly-Si thin films on Si wafers. The structure of the ALICE cells is glass (superstrate configuration)/SiN(70 nm)/p^+ (75 nm, $\sim 1\times10^{19}$ cm^{-3}, Al, AIC seed layer)/p^+ (50 nm, $\sim 1\times10^{19}$ cm^{-3}, B, emitter)/n (1500 nm, $\sim 8\times10^{16}$ cm^{-3}, P, absorber)/n^+ (100 nm, $\sim 1\times10^{20}$ cm^{-3}, P, BSF). Al, B, P stand for aluminium, boron and phosphorous doping, respectively. After crystallization in tube furnace, the ALICE cells received a rapid thermal annealing (RTA) process at 900 °C for 4 min to activate doping and reduce the defect density. Then, high-temperature hydrogenation treatments were applied to the ALICE cells to passivate the grain boundaries in the poly-Si thin films. The hydrogenation processes were performed in a cold-wall vacuum system featuring an inductively coupled remote plasma source with glass temperature of 610 °C for 20 min and plasma power of 3300 W, hydrogen flow of 200 sccm and argon flow of 60 sccm.

The hydrogenated ALICE cells were bifacially metallized by contacting the emitter layers and BSF layers with 900 nm Al separately. This metallization scheme has less than 5% Al shading as the air-side contact in order to be compatible with back surface reflectors. The total size of the test structure is 1.25×0.8 cm^2 [7]. A final phosphoric etching was applied to the metallized ALICE cells to eliminate the local shunts by removing the Al residues left in the voids of poly-Si films.

The partial pressures of background gases during the deposition process were monitored in-situ using residual gas analyzer (RGA) from Stanford Instruments. The bonded oxygen contents in the poly-Si films were measured by FTIR, using a Nicolet 5700 system. The UV reflectance measurements were applied with a Varian Cary 5G double-beam spectrophotometer in the wavelength range from 250 nm to 400 nm to determine the crystal quality of poly-Si films. Moreover, cross-sectional Transmission Electron Microscopy (XTEM) was used to reveal the structural quality of poly-Si films by Philips CM12 and CM200.

Open-circuit voltage (V_{oc}) of ALICE cells was measured using a quasi-steady-state V_{oc} (*Sun*-V_{oc}) method. *Sun*-V_{oc} curves were fitted with a two-diode model, (ideality factors $n=1$, $n=2$) which includes a shunt resistance, illuminated current–voltage (*I*–*V*) curves. External quantum efficiency (*EQE*) measurements of the ALICE solar cells were performed on an Oriel system, with a wavelength step size of 5 nm. The *EQE* spectra were converted to internal quantum efficiency (*IQE*) spectra by calculating with the total hemispherical reflectance. PC1D simulations were applied to calculate the minority carrier diffusion lengths.

3. Experimental results and discussions

3.1. Vapor compositions in the non-UHV Si evaporator

Using a RGA, the partial pressures of selected molecules (N_2, O_2, H_2, and H_2O) were monitored during a standard a-Si evaporation process onto a SiN-coated glass substrate. The base pressure of the Si evaporator just prior to the deposition was about 3.99×10^{-6} Pa. The pump system on the Si evaporator chamber consists of a mechanical roughing pump and a liquid helium-cooled cryogenic pump. The Si deposition occurs in a stationary mode (i.e., non-moving substrate). The results obtained with the RGA are shown in Fig. 1. It can be seen that the base pressure of the system, prior to the loading of the sample, is dominated by the presence of N_2 gas. Upon insertion of the SiN-coated glass substrate into the evaporation chamber via a loadlock and switching on of the heaters, the sample mainly releases H_2 and H_2O. Switching on the e-beam eliminates O_2 and H_2O from the gas phase, but leaves the N_2 concentration unaffected. This shows that O_2 and H_2O are very efficiently gettered by the Si vapor and are thus incorporated into the deposited Si film. The partial pressure of H_2 increases drastically during the Si melting process as H_2 releases from the Si pellets in the crucible. H_2 is considered to be benign impurity in Si, hence this pressure increase during Si evaporation is not expected to have a detrimental effect on the Si thin film material quality. The RGA clearly is a very useful tool for the optimization and the control of the Si evaporation process.

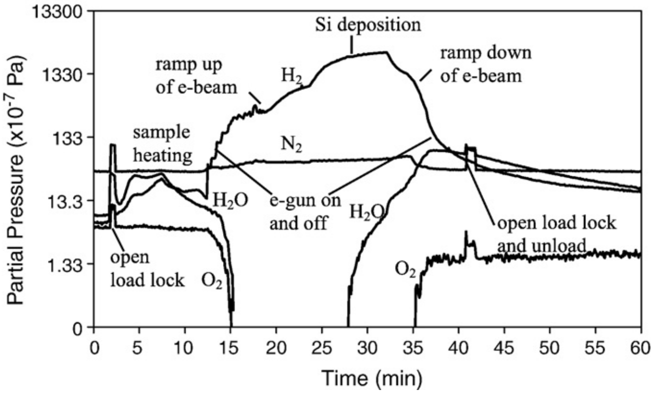

Fig. 1. Partial pressures of selected background gases (H_2, N_2, O_2, and H_2O) in the vacuum chamber during the a-Si precursor thin-film deposition process on SiN-coated glass.

3.2. Oxygen contents in Si films

FTIR measurements are non-destructive and can yield information on impurities in poly-Si thin films. It can distinguish the difference between interstitial (O_i) and precipitated SiO_2 cluster, which cannot be performed in SIMS. Furthermore, the oxygen detection limit for FTIR is about 10^{16} atoms/cm^3, which is one order of magnitude better than SIMS detection limit ($\sim10^{17}$ atom/cm^{-3}). Oxygen can dramatically affect the charge carrier diffusion length by either acting as recombination center (e.g., a B–O complex) [8] or by disrupting the Si crystal by inclusion of SiO_2-like clusters [9,10]. FTIR was used to identify the oxygen contents in Si films on intrinsic Si wafers prepared at different deposition rates and base pressures. Prior to the measurements, the Si films were dipped into a 5% HF solution to remove the surface SiO_2 layer. From Fig. 2, it can be seen that there is acceptable interstitial oxygen [11] in poly-Si thin films prepared at high deposition rate and low base pressure, while detrimental SiO_2 precipitates [12] in films prepared at either high rate/high pressure or low rate/low pressure.

It is noted that the high base pressure in this experiment is 17 times higher than low base pressure, while low deposition rate is 6 times lower than high deposition rate. This indicates that most of oxygen was not gettered by Si vapor during deposition in the high base pressure environment. This phenomenon is confirmed by RGA showing that the oxygen partial pressures are consistent during the deposition process. It is most likely that the deposition rate of Si is so high at 300 nm/min that oxygen has much less time/chance to be gettered by the Si vapor although there is plenty of oxygen in the chamber. Additional experiments show that the oxygen content levels are proportional to the base pressure if the deposition rate is