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Fabrication of selective-emitter silicon heterojunction solar cells using hot-wire chemical vapor deposition and laser doping

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ABSTRACT

The Si heterojunction (HJ) solar cells were fabricated on the textured p-type mono-crystalline Si (c-Si) substrates using hot-wire chemical vapor deposition (HWCVD). In view of the potential for the bottom cell in a hybrid junction structure, the microcrystalline Si (μ c-Si) film was used as the emitter with various PH₃ dilution ratios. Prior to the n- μ c-Si emitter deposition, a 5 nm-thick intrinsic amorphous Si layer (i-a-Si) was grown to passivate the c-Si surface. In order to improve the indium-tin oxide (ITO)/emitter front contact without using the higher PH₃ doping concentration, a laser doping technique was employed to improve the ITO/n- μ c-Si contact via the formation of the selective emitter structure. For a cell structure of Ag grid/ITO/n- μ c-Si emitter/i-a-Si/textured p-c-Si/Al-electrode, the conversion efficiency (AM1.5) can be improved from 13.25% to 14.31% (cell area: 2 cm × 2 cm) via a suitable selective laser doping process.

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1. Introduction

Recently, thin-film silicon/crystalline silicon (c-Si) heterojunction (HJ) solar cells have been studied extensively due to their promising performance and low-temperature fabrication process. In this type of cell, a Si thin-film emitter layer is typically deposited by plasmaenhanced chemical vapor deposition to form a p–n junction at low temperatures (<400 °C) [1,2]. The emitter layer in the HJ cell is usually highly doped with a very thin thickness which helps to reduce the series resistance and to minimize the recombination of photogenerated carriers in the layer. It is well known that the performance of the HJ cell is strongly dependent on the emitter properties and the quality of the thin-film Si/c-Si interface [3].

Efforts to improve the material quality of the Si thin-film emitter itself have focused on the development of various deposition techniques, such as hot-wire chemical vapor deposition (HWCVD) [4], very highfrequency plasma CVD, and electron cyclotron resonance CVD. Among them, the HWCVD has attracted considerable attention because both amorphous silicon (a-Si) or microcrystalline silicon (μ c-Si) films can be achieved with higher deposition rate [5,6] and lower deposition temperature [7,8]. In this paper, the n- μ c-Si/p-c-Si HJ solar cell was investigated, where this type of cell could be further used for the bottom cell in a hybrid junction structure [9,10]. All cells in this work were fabricated on textured c-Si substrates by HWCVD. A systematic study of various PH₃ dilution ratios in the HWCVD process was carried out to optimize the n- μ c-Si emitter properties for the Si HJ cell applications. The influence of the contact property between indium-tin oxide (ITO) and n-µc-Si on the cell performance is also investigated. Especially, a laser doping technique was employed to improve the ITO/n-µc-Si contact via the formation of the selective emitter structure. Finally, the photovoltaic properties like open-circuit voltage ($V_{\rm oc}$), short-circuit current density ($J_{\rm sc}$), fill factor (FF), and conversional efficiency (η) of the µc-Si/p-c-Si HJ cells with and without the selective emitter will be characterized.

2. Experimental

All Si thin films used in this study were deposited using a HWCVD apparatus as described previously [11], where the filament temperature was monitored by an optical pyrometer and the substrate temperature was measured using a thermocouple embedded in the substrate holder. A textured Czochralski c-Si wafer (250 μ m thick, boron-doped, 1–5 Ω cm) was used as the substrate. The 1-µm-thick Al back contact was deposited by electron-beam evaporation and then annealed at 600 °C in order to achieve both effective back surface field and ohmic contact [4]. Before loading the sample, a chamber cleaning process was performed using the atomic H generated on the hot tungsten wires [12] and the substrate was dipped in 1% diluted hydrofluoric acid for H-termination. The c-Si substrate was then subjected to the H atom pre-treatment process to passivate the c-Si surface [13], which was carried out by decomposing H₂ in the same HWCVD chamber. A 5 nm-thick intrinsic a-Si layer (i-a-Si) has been inserted between the c-Si substrate and n-µc-Si emitter layer [14]. Details of the i-a-Si layer effect on the characterization of Si HJ solar cells have been reported elsewhere [15]. Following, a 20nm-thick n-µc-Si emitter layer was deposited under various PH₃ dilution ratios $[R_{PH_2} = PH_3 / (SiH_4 + H_2 + PH_3)]$. Table 1 summarizes the HWCVD pretreatment and deposition parameters for the i-a-Si and n-µc-Si films.



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Table 1

Deposition parameters of Si thin films by HWCVD used in this study for Si heterojunction solar cells.

Deposition parameters	H-treatment	i-a-Si	n-µc-Si
Wire temperature (°C)	1650	1650	1750
Substrate temperature (°C)	150	250	200
Pressure (mTorr)	200	100	100
Process gas flow (sccm)	$H_2 = 80$	$SiH_4 = 5$	$SiH_4 = 2$
			$H_2 = 17.82 - 17.98$
			$PH_3 = 0.02 - 0.18$

After the n-µc-Si emitter deposition, a laser doping technique was used to improve the ITO/n-µc-Si contact performance. A phosphorusdoped SiO₂ solution was prepared as a dopant source using a sol-gel process. It was spun on the n-µc-Si emitter film, prebaked at 80 °C for 20 min and then postbaked at 200°C for 1 h under atmosphere. An Nd-YAG laser (wavelength: 355 nm; repetition rate: 10 Hz) with various power densities (64 to 318 mJ/cm², beam size = 7.85×10^{-3} cm²) was scanned through a metallic mask with periodic circular hole to make the heavily doped selective emitter. The hole diameter is kept at 0.5 mm with different spacings from 0.625 to 5 mm. After the laser irradiation process, the residual dopant source was removed using a wet etching process. Then the ITO front contact (80 nm thick) and Ag grid contact (1 µm thick) were successively deposited on the emitter film using an electron beam evaporator. Finally, the cell structure (Ag grid/ITO/n-µc-Si selective emitter/i-a-Si/textured p-c-Si/Alelectrode) was fabricated and shown in Fig. 1. The cell characteristics (area: $2 \text{ cm} \times 2 \text{ cm}$) were obtained through the current–voltage (I–V) measurements at 100 mW/cm² with an AM 1.5-like spectrum.

3. Results and discussion

The control of the dopant concentration in the emitter layer is the key point in the photovoltaic properties of a HJ cell since it determines the equilibrium between defect density and position of Fermi level at the interface [16]. The first step in the present work was the deposition of singly doped films in order to determine the doping efficiency of phosphine in our system. Here the energy level at absorption coefficient of 10^4 cm^{-1} (E04) of the n-µc-Si film was obtained from the transmission spectrum [17]. The carrier concentration (N_c) of the doped emitter film was determined using the Van der Pauw-Hall measurement. Fig. 2 shows the dependence of E04 and N_c of the n-µc-Si films on the PH₃ dilution ratio (R_{PH_3}). It is found that both the E04 and N_c are strongly dependent on the R_{PH_2} . When the R_{PH_2} increases from 0.1 to 0.9%, the N_c increases rapidly from 5×10^{15}



Fig. 1. Schematic cross-section (a) and fabrication process (b) of Si heterojunction solar cell used in this study.



Fig. 2. Variation of optical band gap (E04) and carrier concentration (N_c) of n-type μ c-Si emitter layer as functions of PH₃ dilution ratio [$R_{PH_3} = PH_3 / (SiH_4 + H_2 + PH_3)$].

to 3.7×10^{19} cm⁻³, indicating a good PH₃ doping efficiency in the emitter layer. On the other hand, the E04 first increases intensively from 1.81 to 2.01 eV when the $R_{\rm PH_3}$ increases from 0.1 to 0.3% and then gradually increases to 2.08 eV when the $R_{\rm PH_3}$ increases to 0.9%.

The photovoltaic parameters (J_{sc} , V_{oc} , FF, and η) of the HJ cells as functions of R_{PH_3} in the n-µc-Si emitter are shown in Fig. 3. Apparently, the cell performance can be improved when the R_{PH_3} increases from 0.1 to 0.5%. An optimum η value of 13.25% was achieved under a R_{PH_3} of 0.5%. It was found that both the J_{sc} and FF values dropped when the R_{PH_3} increased from 0.5 to 0.9%. These results indicate that a decrease of the doping concentration in the n-µc-Si emitter allows a shift of the Fermi level toward midgap and thus a reduction of the electric field at the interface. Under higher phosphorus doping levels, the increase of defect density in the emitter could cause recombination and a dramatic reduction of photovoltaic properties of the HJ cell [16].

In order to improve the ITO/emitter front contact without using the higher PH₃ doping concentration, a selectively doped emitter via a metal mask was performed using the laser doping technique. The effect of laser irradiation density on the photovoltaic parameters of the HJ cell is illustrated in Fig. 4. As shown in this figure, all cells were



Fig. 3. Photovoltaic characteristics of Si heterojunction solar cells (Ag grid/ITO/n- μ c-Si emitter/i-a-Si/p-c-Si/Al electrode) fabricated under various PH3 dilution ratio (R_{PH_3}) using HWCVD.

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