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Fabrication of silicon solar cell with >18% efficiency using spin-on-film processing for phosphorus diffusion and SiO_2/graded index TiO_2 anti-reflective coating

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ABSTRACT

This study employed spin-on film (SOF) technology for the fabrication of phosphorus diffusion and multi-layer anti-reflective coatings (ARCs) with a graded index on silicon (Si) wafers. Low cost and high efficiency solar cells are important issues for the operating cost of a photovoltaic system. SOF technology for the fabrication of solar cells can be for the achievement of this goal. This study succeeded in the application of SOF technology in the preparation of both phosphorus diffusion and SiO_2/graded index TiO_2 ARCs for Si solar cells. Optical properties of TiO_2, SiO_2, and multi-layer SiO_2/TiO_2 deposition by SOF are characterized. Electrical and optical characteristics of the fabricated solar cells are measured and compared. An impressive efficiency of 18.25% was obtained by using the SOF processes.

1. Introduction

The formation of shallow p–n junctions in silicon (Si) is an important step in the fabrication of photovoltaic devices [1–5]. Using ion implantation, excimer laser annealing, and thermal diffusion of dopants into the Si wafer forming a p–n junction are expensive approaches [2,6–11]. Typically, thermal diffusion is produced by heat treatment in a conventional furnace at temperatures above 900 °C for durations ranging from minutes to hours. But this method often results in junctions, which are too deep for applications requiring shallow p–n junctions. Rapid thermal annealing (RTA) using various dopant sources, such as planar dopants or doped spin-on film (SOF), has been developed for the fabrication of shallow p–n junction solar cells [12,13,3,14–20]. In addition, anti-reflective coatings (ARCs) are commonly used to improve the efficiency of solar cells by reducing reflectivity at the air-semiconductor interface. ARCs films are generally applied using vacuum processes, such as thermal evaporation, reactive sputtering, and plasma-enhanced chemical vapor deposition, but little reported on using SOF for ARC [21–30]. The proposed SOF fabrication method is relatively inexpensive and highly scalable for large volume batch processing, making it a strong candidate for the further development of solar cells [31].

This study demonstrates the application of SOF technology in the preparation of both phosphorus diffusion and SiO_2/graded index TiO_2 ARCs for Si solar cells. Optical properties of TiO_2, SiO_2, and multi-layer of SiO_2/TiO_2 deposition by SOF process are characterized. Electrical and optical characteristics of the fabricated solar cells are measured and compared under dark and AM 1.5G illumination.

2. Experimental methods

2.1. TiO_2 and SiO_2 films deposition and phosphorus diffusion using SOF technique

To obtain the designed optical properties and thickness of TiO_2 and SiO_2 films by using SOF technique, the baking temperature of 200–500 °C for 10–30 min and the spin speed between 2000 and 8000 rpm are proposed in this study. After cleaning the silicon (Si) sample, Titaniumsilicafilm-C (Emulsitone Company, NJ, USA) solution was applied on the clean sample surface and then spinning coated with the specific speed on the Si sample surface. Next, the Si sample was baked at 200 °C for 15 min and followed by baking at 300–500 °C for 15 min in air ambient to form a solid TiO_2 film. In which, Titaniumsilicafilm ingredients are tetra-isopropyl titanate, silica, methyl alcohol (3–5%), ethyl alcohol (70–80%), and

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ethyl acetate. Thinner TiO_2 films can be obtained by diluting the solution with ethyl alcohol (C_2H_5OH) or by increasing the spin speed. Films of Titaniumsilicafilm can be removed by soaking in dilute HF solution followed by a spray of water to wash away the TiO_2 particles which do not dissolve in HF. Similarly, SiO_2 layer obtained using Silicafilm (Emulsitone Company, NJ, USA) by SOF processing with spin speed of 6000 rpm for 20 s, followed by prebaking at 200 °C for 15 min and then 400 °C for 15 min in an RTA-chamber. In which, Silicafilm ingredients are polysilicate, methyl alcohol (3–5%), ethyl alcohol (70–80%), and ethyl acetate. Thus, Silicafilm is an alcohol solution which is applied to a semiconductor surface to yield a pure SiO_2 film similar in characteristics to a pyrolitic oxide. The thickness and refractive index (n) of the obtained TiO_2 (SiO_2) film was depending on the spin speed and baking temperature, and can be adjusted by varying the diluting ratio of Titaniumsilicafilm-C:C_2H_5OH for obtaining a desired TiO_2 layer. The thickness and refractive index of the deposited TiO_2 and SiO_2 films were measured by n&k analyzer 1280 (n&k Technology, Inc.). For the broadband ARC applications, the combination of two graded-index TiO_2 layers ($n_1 = 2.31$ and $n_2 = 2.20$) and a SiO_2 layer ($n_3 = 1.46$) structure using a spin-on-film technique was proposed in this study, as shown in Fig. 1. The novel in this work is achieved higher refractive index TiO_2 layer ($n = 2.20$, 2.31) and constructed graded-index TiO_2 layers using SOF method. In general, the SOF TiO_2 film yielding index of refraction was from about 1.50–2.00 and the graded-index TiO_2 layers constructed by hybrid deposition. The proposed method is a simply and low cost process. The optical reflectance of silicon substrates coated with and without multi-layer ($SiO_2/TiO_2/TiO_2$) ARCs was characterized using an UV/Vis/NIR spectrophotometer (PerkinElmer LAMBDA 35).

The diffusion of phosphorus atoms through p-type crystalline silicon was implemented with a liquid-type Phosphorosilicafilm (Emulsitone Company, NJ, USA) on the p-Si samples using SOF technique at a speed of 6000 rpm for 20 s, followed by prebaking at 200 °C for 15 min and then 400 °C for 15 min in an RTA-chamber. Then, a 200-nm thick SiO_2 film was capped on the surface of the post-baking p-Si samples using the SOF processing and treated at 900 °C for 1–5 min to facilitate the diffusion of phosphorus. In which, Phosphorosilicafilm ingredients are phosphorus pentoxide, silica, methyl alcohol, ethyl alcohol, and ethyl acetate. In addition, the phosphorous doped silica film is easily removed in dilute HF solution. Secondary ion mass spectrometry (SIMS; Cameca IMS-4f) measurement was used to gain a more complete understanding of the diffusion of phosphorus atoms through p-Si as well as the

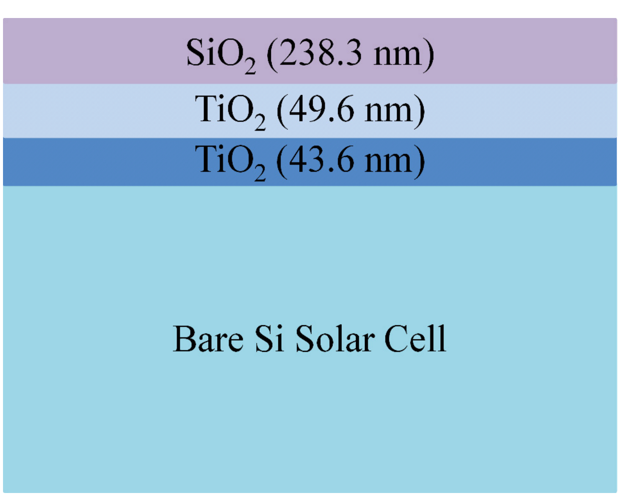

Fig. 1. Schematic diagram of a broadband triple-layer ARC, two graded-index TiO_2 layers ($n_1 = 2.31$ and $n_2 = 2.20$) and a SiO_2 layer ($n_3 = 1.45$) combination using a spin-on-film technique.

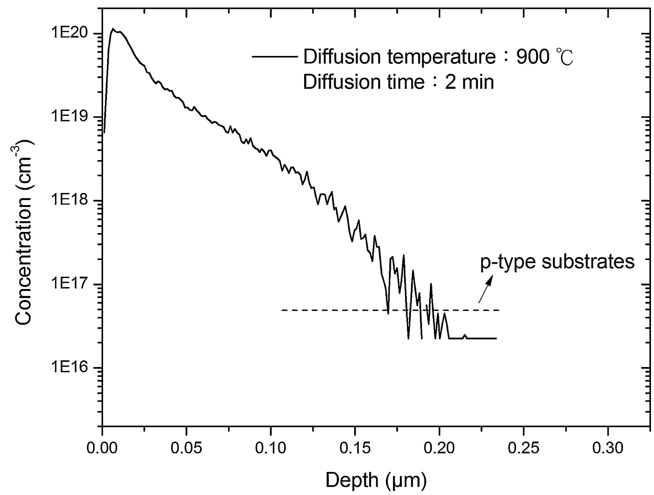

Fig. 2. Phosphorus profile of phosphorus diffuses into a silicon substrate using SIMS measurement.

carrier concentration distribution throughout the sample following diffusion. The novel in the proposed SOF diffusion using Phosphorosilicafilm and RTA heat treatment at 900 °C for 2 min was a simply and low cost process and obtained a high quality shallow p–n junction.

2.2. Solar cells fabrication using SOF technique

To fabricate C-Si solar cells, a p-type Si-wafer polished on one side with a resistivity of 1–10 Ω cm and (1 0 0) orientation was employed in this work. Following standard cleaning processes, the Si wafer was coated with liquid phosphorus and capped with 200-nm SiO_2 using the SOF coating technique. The SOF processing was at a speed of 6000 rpm for 20 s, followed by prebaking at 200 °C for 15 min and then 400 °C for 15 min in an RTA-chamber. The samples were then subjected to heat treatment at 900 °C for 2 min to facilitate the diffusion of phosphorus. Following the diffusion process, the sample was soaked in an HF-solution to remove the SiO_2 and phosphorus-oxide. The diffusion of phosphorus atoms through single crystal silicon materials is shown in Fig. 2. According to SIMS measurement, we produced a 0.18 μm-thick n^+-Si layer with a surface concentration of 1.1×10^{20} cm^{-3}. Finally, films of 200-nm Al and 20-nm Ti/200-nm Al were applied using e-beam evaporation on the back and front sides and annealed at 450 °C for 20 min to obtain good ohmic-contacts for the bare-type Si solar cells. Finally, the solar cells were coated with multi-layer anti-reflective coatings ($SiO_2/TiO_2/TiO_2$) using SOF processes.

The photovoltaic $I–V$ characteristics of the fabricated solar cells were measured using a source meter (Keithley 2400) under one-sun AM 1.5G (100 mW/cm^2) illumination at 25 °C. The solar simulator (XES-151S, San-Ei Electric Co., Ltd.) was calibrated according to an NREL-certified crystalline silicon reference cell (PVM-236) before conducting measurements on the samples. The external quantum efficiency (EQE) responses of the bare solar cells (without surface coating) were measured and compared with those of solar cells coated with multi-layer anti-reflective coatings ($SiO_2/TiO_2/TiO_2$) at wavelengths between 300 and 1200 nm (EQE-RQE-R3015, Enli Technology Co., Ltd.).

3. Results and discussion

The proposed SOF method for photovoltaic device processing has three main advantages: (1) more convenient in films deposition compared to traditional physical and chemical deposited methods,

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