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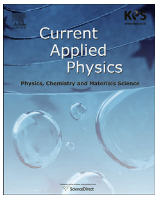

Effect of rapid thermal oxidation on structure and photoelectronic properties of silicon oxide in monocrystalline silicon solar cells

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ABSTRACT

This paper concerns the topic of surface passivation properties of rapid thermal oxidation on p-type monocrystalline silicon wafer for use in screen-printed silicon solar cells. It shows that inline thermal oxidation is a very promising alternative to the use of conventional batch type quartz tube furnaces for the surface passivation of industrial phosphorus-diffused emitters. Five minutes was the most favorable holding time for the rapid thermal oxidation growth of the solar cell sample, in which the average carrier lifetime was increased 19.4 μs. The Fourier transform infrared spectrum of the rapid thermal oxidation sample, whose structure was Al/Al-BSF/p-type Si/n-type SiP/SiO_2/SiN_x/Ag solar cell with an active area of 15.6 cm^2, contained an absorption peak at 1085 cm^{-1}, which was associated with the Si–O bonds in silicon oxide. The lowest average reflectance of this sample is 0.87%. Furthermore, for this sample, its average of internal quantum efficiency and conversion efficiency are respectively increased by 8% and 0.23%, compared with the sample without rapid thermal oxidation processing.

1. Introduction

The world will need about 20 TW of non-CO_2 energy to stabilize CO_2 in the atmosphere by mid-century. The simplest scenario to stabilize CO_2 by mid-century is one in which photovoltaics and other renewables are used for electricity, hydrogen for transportation, and fossil fuels for residential and industrial heating [1]. As the crystalline silicon photovoltaic industry seeks to use thinner wafers to reduce costs, the importance of surface passivation of the front and rear surfaces of such wafers is increasing.

Crystalline silicon is the most frequently used material in solar cells because it enables highly efficient and low-cost production using a simple manufacturing process. Approximately 80% of the solar cells in that are used in the photovoltaic industry worldwide are currently fabricated using crystalline silicon [2]. Various methods for increasing the efficiency of crystalline silicon solar cells have been investigated for more than 20 years. They include gettering, dry texturing, use of selective emitters, hydrogen surface passivation and the use of silicon nitride (SiN_x) as the surface passivation layer on the surface of the emitter. It is known that thermal silicon oxides are effective in the surface passivation of highly phosphorus-doped silicon surfaces [3]. To reduce the cost of crystalline silicon solar cells, crystalline photovoltaics is developing the use of cells that are much thinner than 200 μm [4].

Increasing the conversion efficiency of crystalline-silicon (c-Si) solar cells is the most important goal of c-Si photovoltaic research. Highly efficient solar cells are obtained only when both the loss of photo-generated carriers and the loss of sunlight that enters the solar cells are low [5]. Therefore, both the optical and the electrical quality of the c-Si solar cell wafer must be optimized. SiO_2 is precisely the preferred material for this purpose. This material had effectively been used in c-Si solar cells, which were produced by the University of New South Wales and set it to be the world-record for efficiency [6]. Since the surface recombination of charged carriers will strongly influence the efficiency of thin silicon cells, the formation of a high-quality SiO_2 layer with a low interface state density is a critical for thin silicon cells [7–9].

A SiO_2 layer with low interface state density deposited on a moderately-doped silicon substrate had been obtained by using high-temperature thermal oxidation processes. However, the high-temperature process may degrade the bulk silicon and reduce the bulk carrier lifetime, especially for silicon materials of lower quality than float-zone silicon [10]. In 2011, Zhuo et al. [11] utilized gas mixtures of 0.5–5% O_2 and He to fabricate SiO_2/Si structure by means of atmospheric-pressure (AP) plasma oxidation at 400 °C. By

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optimizing formation conditions, the SiO_2/Si structure with a low interface state density of 1.4×10^{10} cm^{-2} eV^{-1} can be obtained. On the other hand, the positive fixed charge density in the AP-plasma oxide film is relatively high at 5.3×10^{11} cm^{-2}. These characteristics are useful for effective field-effect passivation of Si surfaces for photovoltaic application. Accordingly, the low-temperature processing is favored for producing SiO_2 layers with a low interface state density for Si surface passivation. SiO_2 layers with an interface state density of the order of 1.1×10^{10} cm^{-2} eV^{-1} have been formed by plasma-enhanced chemical vapor deposition (PECVD) at (200–400 °C) followed by annealing using a forming gas of nitrogen [12,13].

Depending on the deposition conditions, however, the properties of SiO_2 layers prepared by PECVD will be influenced by impurities, such as H, N, H_2O, and Si–OH groups, etc., and characterized by their higher porosity than that of SiO_2 layers that are thermally grown at higher temperatures [14]. In addition, the deposition of other dielectric layers, such as silicon nitride and aluminum oxide, has been studied extensively in the silicon solar cell material as the surface passivation [15,16]. Plasma oxidation that requires only O_2 and inert gas as plasma gases has attracted much attention as an alternative means preparing high-quality SiO_2 layers. For nanoscale silicon device processes, gate oxide layers must be fabricated at low temperatures of under 700 °C to prevent undesirable diffusion-related and temperature-sensitive effects. Hence, plasma oxidation process has been extensively studied with the goal of fabricating ultra-large-scale integrated circuits [17].

According to the literature reported by S. Narasimha and A. Rohatgi [18], a passivation scheme involving plasma silicon nitride deposition on top of SiO_2 grown by rapid thermal oxidation had been developed to attain a low surface recombination velocity (S) of nearly 10 cm/s on the 1.25 Ω-cm p-type (100) silicon surface. Such low S value is achieved by the stack structure even when the rapid thermal oxide or plasma silicon nitride films individually yield poorer surface passivation. In this work, the processing of Rapid thermal oxidation (RTO) had been fully applied for monocrystalline silicon cells. Through widely investigating, it revealed that electrical properties of the surface of a monocrystalline silicon solar cell would be obviously affected by the RTO processing. The effect of the RTO layers on the surface is investigated, resulting in an important improvement of the electrical properties of the surfaces of the monocrystalline silicon solar cells.

2. Experimental

Fig. 1 schematically depicts the sample structure that is investigated herein. In this solar cell, it mainly includes a p-type monocrystalline silicon wafer with a resistivity of 1–3 Ω-cm and a thickness of 200 μm. For this cell, a structure of Al-BSF/p-type Si/n-type $SiP/SiO_2/SiN_x/Ag$ has been fabricated, whose active area is 15.6 cm^2, and related processing flow is shown as in Fig. 2. After alkaline texturing, a shallow diffusion will be performed by $POCl_3$ phosphorus, and this can yield a sheet resistance of 80 Ω/sq. Successively, the phosphosilicate glass was cleaning by wet chemical method, thus samples were divided into two groups – one group (sample A) was without RTO processing and the other one group (sample B) was processing through RTO.

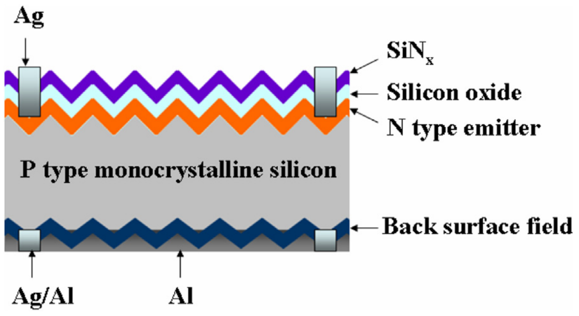

Fig. 1. Monocrystalline silicon solar cell sample structure.

According to the literature reported by S. Narasimha et al. [18], a passivation scheme involving plasma silicon nitride deposited on top of SiO_2 by RTO could attain a low S of nearly 10 cm/s on the 1.25 Ω-cm p-type (100) silicon surface. For doing so, RTO layers were grown in a rapid thermal processing (RTP) unit at 850–900 °C in less than 5 min. The SiO_2 layer grown by RTO could obtain a value of S smaller than 10–20 cm/s aforementioned. The oxide-thickness of a RTO layer, which was grown in an RTP unit at 850 °C for 2 min, prepared by S. Narasimha et al. [18] was 4.3 nm, whereas the oxide-thickness of a RTO layer, which was at 800 °C for 7.3 min, prepared by A. Stadler et al. [19] was 5 nm. On the other hand, in our inline-walking string, a high-quality batch-type quartz-tube furnace system was utilized, in which the temperature and the growth time of RTO were 810 °C and 5 min, respectively, as well as the gas-flow ratio of $N_2:O_2$ was 6.5:1. For sample B, its oxide-thickness obtained is approximately 5 nm.

For increasing incident light, an antireflection coating layer of SiN_x was coated on the top of RTO layer by plasma-enhanced chemical vapor deposition. For screen-printing, Ag glue was firstly printed on the layer of SiN_x, and then dried. Subsequently, glues of AgAl and Al would be separately printed on the back of the wafer. It is noticed that each printed layer should be dried after printing. Positive and negative electrodes can be formed through a sintering process of 700–900 °C to complete a whole solar cell.

3. Results and discussion

3.1. Microstructural observations

A p-type monocrystalline silicon wafer with a thickness of 200 μm and a resistivity of 1–3 Ω-cm was fabricated for use in solar cells, whose related processing sequence could be found in Fig. 2. Texturization was performed in KOH – isopropyl alcohol (IPA) – surfactant additives (GP Solar, GP ALKA-TEX. +2) – deionized water at a temperature of 78 °C for 20 min to form randomly micron-sized pyramids. The KOH etchant used herein was an aqueous solution with a volume of 5.2 L, 7.3 L added IPA, 120 L of deionized water, and 0.5 L of surfactant additives.

In principle, texturization is a result of anisotropic etching of silicon in an alkaline solution, such as NaOH or KOH, with a low hydroxide concentration [20–22]. An efficient release to the hydrogen bubbles that are formed during the etching from the

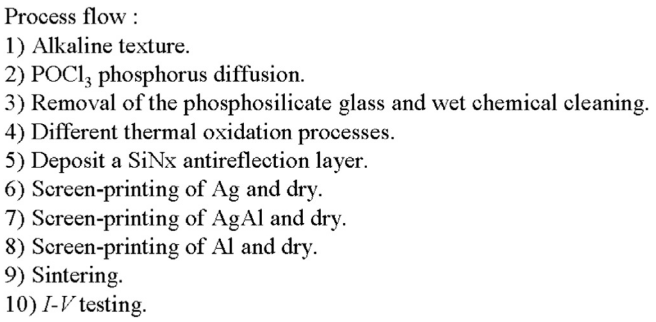
Process flow :
1) Alkaline texture.
2) $POCl_3$ phosphorus diffusion.
3) Removal of the phosphosilicate glass and wet chemical cleaning.
4) Different thermal oxidation processes.
5) Deposit a SiNx antireflection layer.
6) Screen-printing of Ag and dry.
7) Screen-printing of AgAl and dry.
8) Screen-printing of Al and dry.
9) Sintering.
10) I-V testing.

Fig. 2. Process flow for fabrication of monocrystalline silicon solar cell sample test structures.