Synthesis of Phosphorus Solution for n⁺ Si Selective Emitter Solar Cell by Spin on Doping

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Abstract. A strong requirement in manufacturing of high-efficiency solar cells is its cost reduction. One approach of aim is to merge several steps of n^+ Si selective emitter processing into one step without degrading the performance of solar cells. By varying the doping level in the selective area, intrinsic fields can be built into solar cells with potential benefits long recognized. In this paper, the spin-on doping (SOD) method was used for the purpose of important tasks, different phosphorus diffusion to form n^+ Si selective area consisting of the lightly and heavily doping emitter areas with 35 Ω/sheet and 121 Ω/sheet. The main solution containing different concentrations of phosphorus doped-SOD source was synthesized in this work. The sheet-resistance dependence of n-Si emitter layers on the concentration of phosphorus acid in the SOD solution was studied in term of the volume ration of TEOS: H_3PO_4, as well as the thermal diffusion temperature. The suitable condition for forming n^+ Si selective emitters in one process step is 1000°C diffusion temperature for 30 minutes with the complementary SOD volume ratio of 4:1 and 2:1. SOD solution can be patterned by a screen printing or an inkjet printing.

1 Introduction

In last 40 years several types of crystalline silicon (c-Si) solar cells were increasingly developed for high efficiency laboratory cells where the processing relies on all available high-quality materials and techniques to reduce losses. Silicon solar cell efficiency of energy conversion to reach the fundamental efficiency limits at as high as 24% has achieved on laboratory [1]. On the other hand, the typical solar cell efficiency of industrial c-Si cells is in the range of 15-17%. However, the efficiency from the industrial process can approach the efficiency as high as laboratory cells with attenuating the technological factors. The main loss influencing cell efficiency is surface recombination losses. The major contributor is to look at an available and simple implementation to improve passivated surfaces of c-Si solar cells [2]. There are two different regions of surfaces in a c-Si solar cells to be concerned in order to reduce surface recombination velocity. Non-metalized region at interfaces of passivating and n-emitter layers is concerned in order to avoid the formation of a dead layer. Metal-heavy dope (n^+) emitter interfaces need to form for increasing blue light responsibility and reducing contact resistance. Therefore, an effective method as n^+ selective emitter layer on p-type Si wafer leads to these requirements. The most commercial selective emitter silicon (SE Si) solar cell involves lightly doping n^- emitter layer on front p-Si surface substrate followed by the standard antireflection process and heavy doping n^+ emitter region underneath silver contacts completed by screen printing after firing [3]. This common method to achieve n^+ type Si region is compatible with mass product technique to form front contact using silver paste with quickly firing. However, over firing may occur to result in silver migration through the junction that cause the leakage current. Recently various commercialized methods have been proposed to optimize the lightly-doped and heavily-doped region for applying SE technology to Si solar cell in mass production scale such as phosphorus ink [4], doped Si ink [5], and laser doped-SE [6]. Many SE techniques have involved the additional diffusion process steps which effect on low fabrication cost [7].

In this work, the preparation of different sheet resistances was presented to form lightly doped- and heavily-doped emitters in one diffusion process step. This method is an alternative to prepare lightly n-type emitters and heavily n^+ type emitters regions [8]. The different resistivity of emitter regions would completely feature with using minimum process sequences without using an acid-resistant mask to make shallow trenches. Firstly, a typical thermal diffusion method was exploited to drive dopant atoms into p-type Si substrates. Resistivity value of emitter layer finally obtained under one condition of thermal diffusion can be simply adjusted by varying the phosphorus concentrations in SOD solution. The different phosphorus doped-spin-on doping (SOD) sources were synthesized from the main solution of Tetraethylorthosilicate (TEOS) containing different concentrations of phosphorus acid. The dependence of sheet resistance of the emitter layer on the concentration of phosphorus acid in the SOD solution as well as the thermal diffusion temperature was studied.

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The optimal ratios of TEOS: H_3PO_4 with the same appropriate time and temperature conditions were investigated.

2 Experimental Methods

2.1 Synthesis of P doped-SOD solution

Lightly doped- and heavily doped-emitter layers were prepared by using SOD solution as a precursor. SOD solutions with different phosphorus concentration are the different SOD sources for the thermal diffusion process. Firstly, the SOD solution was obtained from starting solutions of tetraethylorthosilicate (TEOS, 98%), ethanol absolute (EtOH, 99%) and H2O in a volume ratio of 10:20:3. Subsequently, the prepared solution was stirred for 5 minutes at room temperature to ensure homogeneity. Phosphoric acid (H_3PO_4, 85%) was then added by different volume ratios of TEOS: H_3PO_4 such as at 5:1, 4:1, 3:1 and 2:1 and then stirred for 60 minutes. In general, the hydrolysis reaction of the TEOS mixture solution was catalysed at 70°C. While the SOD solution was stirred at room temperature for 30 minutes, it was cooled down at the same time. The schematic diagram of the process step for preparation of SOD solution is depicted in Fig.1.
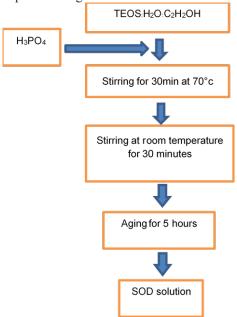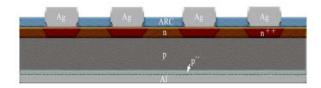

Fig. 1. Schematic diagram of process sequence for preparing phosphorus doped-SOD solution

2.2 Preparation of n-emitters

The P doped-SOD solution was coated on p-type Si substrates by spin-coating method. P dopant concentrations were controlled by a different amount of phosphoric acid in the volume ratios of TEOS: H_3PO_4. A thickness profile of SOD region covered on crystalline silicon (100) wafers ($1 - 20$ $\Omega \cdot cm$) used as substrates were cleaned with standard cleaning of Radio Corporation of America (RCA) and then dipped in dilute

5% hydrofluoric solution for 20 seconds and rinsed in deionized water in order to remove the native oxide on the Si surface. After aging of the SOD solutions for 5 days except for 2:1 and 3:1 SOD solutions without aging condition due to featuring higher viscosity than others, each solution was spun on the Si substrates at 2-speed rates automatically at 500 rpm/min for 5 seconds. and then 3000 rpm/min for 30 seconds. The p-type Si substrates coated with P doped-SOD films containing different phosphorus were dried at 200°C for 30 minutes in air and then thermally diffused in a high temperature furnace for the thermal diffusion process in a N_2 atmosphere. The dopant diffusion was operated at the temperature of 1000°C with various diffusion time from 30 minutes to 90 minutes. P atoms effectively forced by the high temperature were driven into the p-type Si wafer to form the n-emitter layer with different resistivity values obtained. Four-point probes measurement was employed to measure sheet resistance. It is possible to achieve a variety of doping profiles in the SOD coated regions.

Different SOD solution was used to form the n-emitter layer with an n^+ selective region by a spin-on-dopant technique and subsequently, thermal diffusion. Metal contacts on selective doping Si wafers were provided by screen printing and fired under rapid temperature annealing (RTA) process with temperature 915°C for 7 seconds. The selective emitter solar cell shows the structure in Figure 2.

Selective Emitter Solar cell

Fig. 2. Structure of selective emitter solar cell in this work by using different doped-SOD solution

3 Results and discussions

Figure 3 shows the thickness profile of the coated SOD region with 4: 1 ratio (TEOS: H_3PO_4) by verifying the optical profiler (VEECO) measurement. The SOD and PSG film thicknesses with the different volume ratios of TEOS: H_3PO_4 were plotted in Fig.4. The range of SOD film thickness between 64 nm and 609 nm range after drying results in the presences of PGS film after thermal diffusion process. The range of PSG film thickness is between 103 nm and 297 nm. It was presented that SOD thickness was not significantly related to PSG thickness. Typically, about 100 nm the thickness of the silicon oxide layer is chosen for designing antireflection coating (ARC) layer for Si solar cells in order to minimize reflectance for a wavelength of 600 nm. With feathering results, it seems that PSG film from a starting material of SOD solution in the ratio of 4: 1 TEOS: H_3PO_4 could be used for ARC to have an agreement with Yujie Tang's

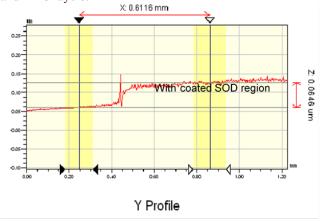work [9] that involved dual tasks for preparing n^+ emitter and ARC layers.

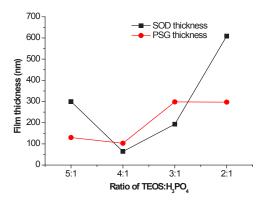**Fig. 3.** A thickness profile of the SOD region layer

Fig. 4. SOD and PSG film thicknesses

Dopant density in the coating regions and in the field emitter can be adjusted independently from varying TEOS: H_3PO_4 ratio. Dependence of sheet resistance of n-type emitter layer on various phosphorus concentrations in the term of the SOD film and diffusion time was depicted in Fig. 5.

The results show that the period of time in the diffusion process effects to the decrease of sheet resistance of the n-emitter layer in all ratio conditions. The volume ratio of TEOS: H_3PO_4 = 5: 1 obtains sheet resistance in the range of 183 - 446 Ω/ sheet with decreasing time in diffusion from 90 min to 30 min. The volume ration at 4: 1 and 3: 1 obtained the sheet resistance in the minimum range of 12-35 Ω/ sheet and 16-36 Ω/ sheet, respectively. It is noticed that too large amount of H_3PO_4 for the volume ratio at 2: 1 resulted in the sheet resistance became increasing. It is mostly due to the presence of more defects from heavy dopants. Therefore, at the same condition of a diffusion process, different n^+ Si selective emitter regions can feature with complementary SOD solutions to form lightly doping n-type (<50 Ω/sheet) and heavily doping n^+ Si type (80-100 Ω/ sheet) emitters. The coating alignments such as screen printing needs in this technique. This result suggests that the complementary volume ratios of 4: 1 and 2: 1 or 3: 1 and 2: 1 can be chosen for diffusion process at 1000°C for 30 min to form the n^+ selective emitter underneath silver contacts and at the illuminated

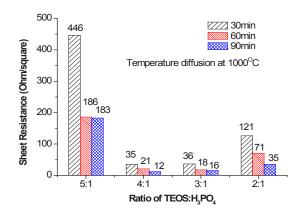area. In addition, PSG film occurs inevitably after process can be used as an ARC.

Fig. 5. Sheet resistance of N-type emitter layers as a function of TEOS:H3PO4 volume ratio with the different time in diffusion conditions

Figure 6 shows the comparison of J-V curve between the p/n Si solar cell and the selective solar cell with the n^+ Si region, respectively. It is noted that the SE solar cell generates the gain current density and the higher open voltage by 12% and 3.7%, respectively compared with a typical p/n Si solar cell. It also directly leads to gain its power conversion efficiency by 1.74% due to the enhancement of blue light absorption in lightly doping emitter.
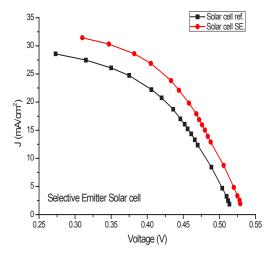

Fig. 6. J-V curve of the SE solar cell

4 Conclusions

In this work, the SOD solution was developed by a using mixture of TEOS and H_3PO_4 as a phosphorus source for using in the n^+ selective emitter purpose. After the thermal diffusion process, PSG residue obtained the suitable thickness for ARC with the minimal reflectance at 600 nm in the light wavelength. Complementary SOD solutions with 4: 1 and 2: 1 or 3: 1 and 2: 1 were coated in the silver contact region and illuminated region to form lightly (121 $\Omega/\square$) and heavily (35 $\Omega/\square$) doping

emitters as an n^+ selective emitter layer after the thermal diffusion process at 1000°C for 30 minutes.

This alternative technique can be a simple implementation to merge several steps of n^+ Si selective emitter processing into one step without degrading the performance of solar cells. Both important factors of the SE solar cell including current density and open voltage increase by 12% and 3.7%, respectively compared with a typical p/n Si solar cell. These enhancement values directly result in the gain of its power conversion efficiency by 1.74%

Acknowledgement

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