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Design of Solar Cells p^+/n Emitter by Spin-On Technique

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In this paper spin-on dopant diffusion has been investigated as a technique for fabrication of p^+/n monocrystalline silicon solar cell emitters. A homogeneous spreading onto the front wafer surface has been achieved by using 2 ml of boron-dopant solution and three-step spin-profile. Study of the wafers stacking arrangement has revealed that the highest doping level and the best emitter sheet resistance uniformity were obtained using the back-to-back wafers arrangement. The N_2/O_2 gas ratio variation during the diffusion process has shown that a higher percentage of nitrogen yields a slightly lower emitter sheet resistance. Study on temperature dependence of as-processed emitter resistivity revealed that 910 °C results in targeted sheet resistance of around 48 Ω/sq. Using these preliminary experimental results, a batch of 6 silicon wafers was processed. After BSG and BRL chemical removal, the batch average sheet resistance of the emitter was 49.50 Ω/sq. The uniformity of a wafer and of the batch was below 7% and 13%, respectively. The ECV and SIMS depth profiling have shown the electrically active and the total boron surface concentration of 1.5×10^{20} atoms/cm^3 and 2.5×10^{20} atoms/cm^3, respectively. The junction depth was around 0.3 μm. Finally, by increasing the oxygen flow rate we reached an average sheet resistance of 51 Ω/sq. and a junction depth of 0.35 μm.

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1. Introduction

The n-type silicon (Si) offers a way of avoiding the disadvantages related to p-type silicon. The former type has several advantages: (i) it has no light-induced degradation (LID) effect due to absence of boron-oxygen complexes [1, 2]; (ii) it has a higher minority carrier diffusion length because it is less sensitive to metallic impurities; (iii) it is less prone to degradation during high temperature processes such as boron (B) diffusion.

Thus, the n-type silicon seems to be a more interesting material and its advantages will probably make it the predominant wafer material for industrial solar cells manufacturing in the future [3].

There are several different methods of forming silicon solar cell p^+ emitter. Gaseous phase diffusion of boron using hazardous BBr_3 or BCl_3 liquid source, that needs extra safety precautions, leading to the increase of the process cost [4]. Alternative B-dopant sources have also been investigated to lower the cost involved in B diffusion. Boron spin-on dopant (BSOD) method is one of them and compared to BBr_3 source, no special safety requirements are needed. In addition, it requires a little control of the diffusion process parameters.

Other advantages of BSOD technique are convenient application of the dopant, easy control of the doping concentration and of the junction depth, preventing unnecessary boron coating on the other side by tuning the coating process parameter [5]. However, the particular challenge for boron diffusion process is the formation of Si-B_x compound named boron rich layer (BRL) [6–10] on the surface. This layer is detrimental for the surface and bulk carrier lifetime [11, 12] and its removal is problematic [13]. As the subject is important, there is a number of reports on this subject [14–19].

The objective of this study is the formation of homogeneous p^+ emitter, adapted for n-type solar cells, using the BSOD method.

2. Experimental

The experiments consisted of spin-coating of the liquid boron compound onto the surface of NaOH etched n-type <100> monocrystalline 4 inch silicon wafers. The diffusion step was performed in quartz tube furnace in N_2:O_2 environment. The emitter sheet resistance (SR) was measured using a four-point probe. The total and active phosphorus profiles were measured by CAMECA secondary ion mass spectroscopy (SIMS) and Accent electrochemical capacitance-voltage profiler (ECV), respectively. The BSG is removed by 2% HF dipping and the BRL layer was chemically etched to hydrophobicity by successive cycles of hot HNO_3 followed by 2% HF dip.

3. Results and discussion

A preliminary work has been conducted in order to obtain a homogeneous spreading of the dopant solution, leading to a uniform surface coating. We have found that a volume of 2 ml per wafer is necessary to wet the entire wafer front surface. Moreover, three-step time-rotation speed profile (spin profile, SP) was selected. After dopant deposition and DI step, the best homogenous doped layer was obtained using the following SP: 10 s at 500 rpm, 7 s at 4000 rpm, 7 s at 5000 rpm.

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3.1. Determination of the optimal wafers stacking arrangement

The batch to be processed is constituted of 6 test-wafers. As illustrated in Fig. 1, every two wafers are placed together in one slot of the quartz boat using two arrangements, back-to-back (BtB) and face-to-face (FtF). Dummy wafers were used to allow a homogeneous gas distribution. The DI process was performed at 900 °C and 3 standard litres per minute (slm) of nitrogen.

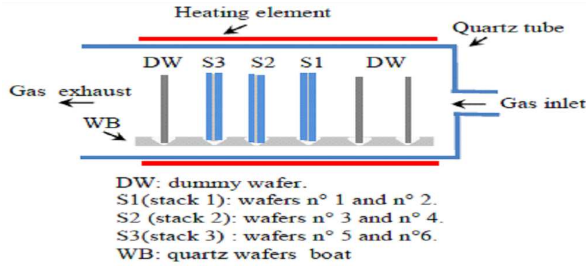

Fig. 1. Schematic of the wafers arrangement in the diffusion quartz tube.

The measured SR lies between 46 Ω/sq.–52 Ω/sq. and 41 Ω/sq.–46 Ω/sq. for FtF and BtB arrangements, respectively. The BtB arrangement produces a more doped wafer surface. The loss of the dopant in gaseous form is reduced. In addition, the BtB wafers configuration leads to improved sheet resistance uniformity. Its value is below 12%, in contrast to FtF arrangement, where it is higher than 12%. The selected arrangement is then the BtB.

3.2. Determination of the diffusion process parameters

The two main characteristics of an emitter are its SR and its junction depth. These two characteristics will be determined by studying the effect of process conditions on n^+/p structure.

3.2.1. Effect of N_2/O_2 ratio variation

In these experiments the total flow rate (N_2+O_2) was kept constant at 3 slm. A slight increase of SR was observed by increasing oxygen flow rate during the DI process. The average SR increases between 0.5 Ω/sq. and 5 Ω/sq. with oxygen rate increase from 0 slm to 3 slm. The same behaviour is observed for BRL-etched processed wafers.

3.2.2. Effect of DI temperature

Due to boron atoms activation, the SR decreases from around 48 Ω/sq. to 28 Ω/sq. with temperature increase from 910 °C to 950 °C, for 20 minutes duration and gas ratio of 2/1. The SR was measured on processed wafers, coated with BRL. Taking into account that the SR increases after the BRL etching, the temperature of 910 °C and process time of 20 minutes lead to a SR of around 50 Ω/sq. Thus, the diffusion process parameters selected are 910 °C and 20 minutes.

3.3. Emitter formation

Using the chosen parameters, several processes were performed using a batch of six wafers. The gas ratio was 2/1. Figure 2 shows the average SR before and after BRL etching of the six processed wafers. The sheet resistances of the doped wafers before BRL etching were below 50 Ω/sq. After BRL etching, the SR value increased by a few Ohms/square. It is between 46 Ω/sq and 52.4 Ω/sq and has an average value of 49.50 Ω/sq.

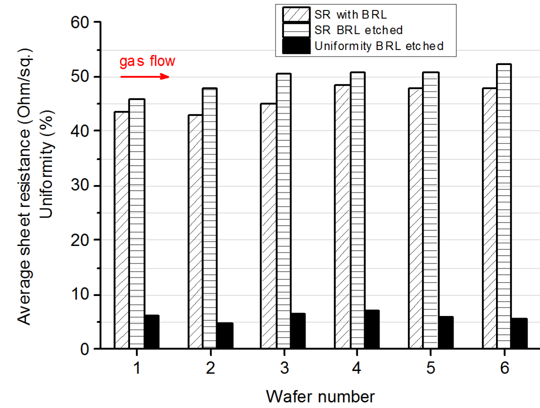

Fig. 2. Sheet resistances and uniformity of the wafer.

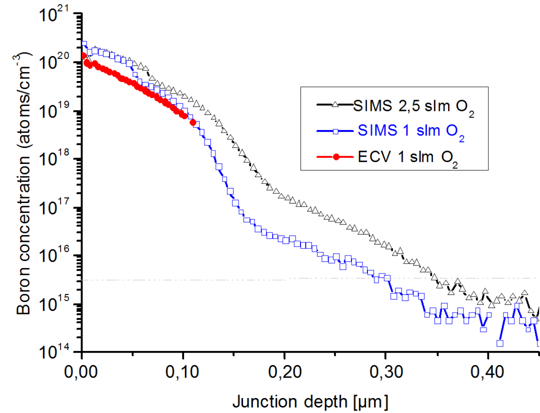

Fig. 3. SIMS and ECV depth profiles of the p^+ emitter.

The SR uniformity of a wafer is below 7%, as shown in Fig. 2. However, the uniformity of entire batch is 13%, which is considered relatively high. This is visible in Fig. 2 where a slight but constant increase of the SR from the first wafer to the sixth wafer is observed. Considering the gas flow direction (see Fig. 1) and due to cumulative effect of the boron exdiffusion from the doped surface of wafers, one can expect the opposite situation. In other words, the sixth wafer must have the lowest SR because it is more doped. The possible reason for that is the presence of only one dummy wafer in the wafer loading zone of the tube, where the gas is not well confined, as at its end. Another possible cause is an inadequate gas flow rate. The total amount of boron diffused through the silicon substrate is illustrated by the SIMS profile in Fig. 3. The surface concentration is around 2.5×10^{20} atoms/cm^{-3} and the junction depth is 0.30 μm.

Meanwhile, the distribution of the active boron measured by ECV, presented in the Fig. 3, shows that the surface concentration is 1.5×10^{20} atoms/cm^{-3}. The amount of the inactive boron, remaining near the surface, is rather significant to constitute recombination centers. This quantity can be reduced by reducing the deposited volume of the BSOD solution or by diluting it with acetone or propanol.

As mentioned in Section 3.2.1, in order to increase the SR, we have increased the flow rate of oxygen to 2.5 slm. Figure 4 shows that the SR increases with oxygen flow rate increase. The average SR has increased from 49.50 Ω/sq. to 51 Ω/sq. The highest uniformity on wafer is around 10% and the uniformity on batch had remained relatively high due to the reasons cited above.

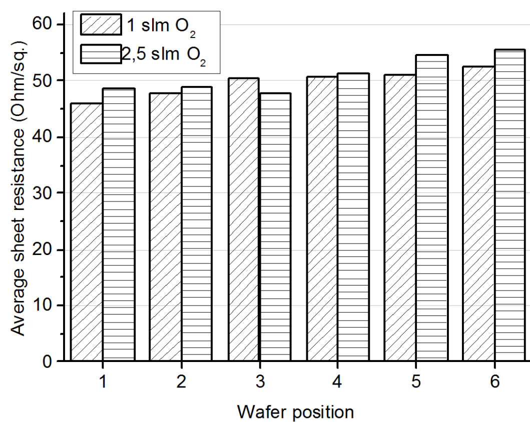

Fig. 4. Variation of the average SR with oxygen flow rate.

The SR increase is due to the decrease of the surface boron concentration, as shown in Fig. 4. Indeed, during the DI step the atoms of boron oxidize in presence of oxygen and are then etched away by the HF dip. Figure 3 reveals that the junction depth increased by 0.05 μm.

The obtained emitter is characterized by surface concentration of 1.3×10^{20} atoms/cm^{-3}, a junction depth of 0.35 μm and an average SR of 51 Ω/sq. Figure 3 also reveals that the BRL has not been removed completely in spite of the hydrophobic character of the emitter surface. As reported in [11] complete removal of BRL is not possible even if thermal oxidation is used.

4. Conclusions

Using a spin-on technique and a boron liquid dopant source, we have realized a p$^+$ emitter for n-type monocrystalline silicon solar cells. The boron diffusion process which consisted of the deposition step and drive-in step was performed on a batch of 6 silicon wafers stacked back-to-back. Emitter sheet resistance with an average value of 49.50 Ω/sq. and junction depth of around 0.3 μm were obtained for a drive-in temperature of 910 °C. The ECV and SIMS depth profiling have shown the electrically active and the total boron surface concentration of 1.5×10^{20} atoms/cm^3 and 2.5×10^{20} atoms/cm^3, respectively. The sheet resistance uniformity of wafer and of entire batch were below 7% and 13%, respectively. By increasing the oxygen flow rate during the drive-in step we have observed an increase in the sheet resistance and the junction depth. With a sheet resistance of around 50 Ω/sq. and junction depth of 0.35 μm, this developed emitter is suitable for solar cells application. However, the batch sheet resistance uniformity should be reduced by adjusting the gas flow rate or the wafer arrangement.

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