



SELECTIVE BORON DIFFUSION WITHOUT MASKING LAYER USING BORIC ACID FOR SOLAR CELL EMITTER FORMATION

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Abstract

In this article, we have used boric acid source to form the boron emitter in a selective way. And, the conditions of boron diffusion process were investigated. It was found that for 5% boric acid in DI water, the spinning of 3000 rpm for 15 sec and dry out process at 200°C are the most appropriate conditions.

Also, in this study, by using boric acid source, a selective doping method was developed. Therefore, it can be possible to have both light and heavy (under contacts) dopings on different areas of the wafer but without any extra masking layer (e.g. silicon dioxide) and undergoing only one drive-in process.

Keywords: *Boric acid, Emitter formation, Solar cell*

1. Introduction

Solar cells based on n-type c-Si wafers have raised growing interest since they feature clear advantages compared to the standard p-type Si; because of having lower sensitivity to metallic impurities and not degraded by the boron-oxygen pairs [1, 2].

Recently, there has been a remarkable increase in investigating spin-on or spray-on dopant (SOD) sources particularly in solar cell research and production. Low cost and neither toxic nor pyrophoric are advantages of these sources [3, 4]. Boron diffusion using BBr_3 is toxic and needs an additional etching step in order to diffuse either on one side of the sample or on specific areas. Since diffusion processes using Boron SOD films are common, we have used and developed a SOD process applying boric acid source to have boron emitter formation. By controlling the boric acid concentration in the solutions, temperature and the diffusion time, we have obtained a wide range of sheet resistances and doping profiles for solar cell applications. In this paper, the conditions of boron diffusion process, which includes the appropriate rotation (spinning speed) and temperature to drive out the excess solvents, were investigated. The output parameters such as carrier lifetime, sheet resistance and diffusion profile have also been measured. Finally, using this method, we were able to produce samples with selective diffusion areas without any extra masking layer, which can be used as the selective emitter for solar cell applications.

2. Experimental

In order to achieve the desired properties of the boron emitter, n-type Cz <100>-oriented wafers of 1-3 Ωcm were used as the substrates. After standard Piranha cleaning, the solution of boric acid, known as H_3BO_3 (orthoboric acid), was spin-coated on the samples. Later, all samples were dried in the oven to remove the solvent. Subsequently, boron diffusion process was performed in a quartz tube furnace at different temperatures in the range of 950-1050 $^\circ\text{C}$. The borosilicate glass (BSG) is removed in a HF solution after the furnace diffusion. Next, a thorough characterization of the process was performed using various techniques. The sheet resistance and the minority carrier lifetimes were measured respectively using four point probes and $\mu\text{-PCD}$ method. Electrochemical capacitance voltage profiler (ECVP) was applied to investigate the emitter surface doping concentration and the dopant profiles.

3. Result and Discussion

a. Boron Diffusion

The boric acid which exists in the crystalline phase was used as the solid source in this study. H_3BO_3 solutions with various concentrations can be prepared by dissolving different amounts of boric acid in DI water. The solubility in DI water at most at room temperature reaches up to 5wt% [1]. The formed anhydrous boron oxide (boron oxide) begins to soften at 325 $^\circ\text{C}$ [1]. The boron oxide then reacts with silicon to form SiO_2 and B, which then diffuses into the silicon by manipulating the temperature. After boric acid was dissolved in DI water, the samples were placed on a spinner and the SODs were drop-coated on the center of the sample. The required SOD solution (boric acid/DI water) for 1cm \times 1cm samples was 100 μl . In order to choose the appropriate layer deposition, we have first investigated various speeds and times. Then, the coated samples were baked at several different temperatures for 15 min to drive out the excess solvent (also called pre-deposition). Afterward, the samples were loaded in the diffusion furnace for 14 min consisting of N_2 gas as the ambient gas (drive-in step). Fig. 1 shows the optical microscope images of samples primarily dispersed by 5% boric acid solution after diffusion and BSG layer removal for different spinning speeds. It can be seen that 3000 rpm for 15 sec is appropriate for conformal coating. The process was also optimized for the appropriate temperature to drive out the excess solvents. It was examined at 50, 100, 150 and 200 $^\circ\text{C}$ to check which gives the best uniformity of the final layer. It found that 200 $^\circ\text{C}$ can result in the optimum layer (shown in Fig. 2).

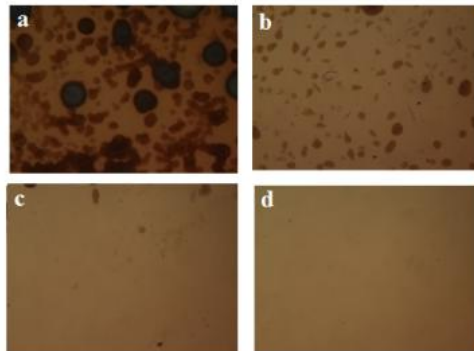


Fig. 1: Optical Microscopy image for different spin coat speed (a: 500 rpm, b: 1000 rpm, c: 2000 rpm, d: 3000 rpm) after drive-in step: 1050 $^\circ\text{C}$ and 5% boric acid/DI water concentration.

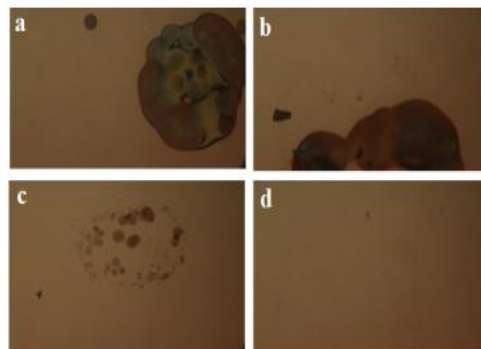


Fig. 2: Optical Microscopy image for different predep temperature (a: 50 $^\circ\text{C}$, b: 100 $^\circ\text{C}$, c: 150 $^\circ\text{C}$, d: 200 $^\circ\text{C}$) after drive-in step: 1050 $^\circ\text{C}$ and 5% boric acid/DI water concentration.

In addition, the effects of different concentrations of acid boric in DI water (1-5%) and different drive-in temperatures (950-1050°C) on the sheet resistance and the lifetime were studied and the results are shown in Table I & II. It can be seen that when the boric acid concentration or drive-in temperature increases, the sheet resistance decreases. On the other hand, the carrier lifetime unfortunately decreases as well. This results in an increase in the probability of contamination, and this is the reason. Fig. 3 shows the boron profile for different concentrations of boric acid solution, measured using ECVP. The surface concentration was assumed to be increasing in the range of $5.71-19.8 \times 10^{19} \text{ cm}^{-3}$ for different solutions used in the study. The junction depth was estimated to be in the range of 0.32-0.65 μm . The effects of different drive-in temperatures (950-1050°C) on the sheet resistance and the lifetime were also studied. The results are shown in Table II. According to this table, when the drive-in temperature increases, both sheet resistance and carrier lifetime will be decreased.

According to a previous report [5], two mechanisms of contamination and generation of dislocations due to a high B doping using this solid source are the reasons why the lifetime decreases. Fig. 4 shows the boron doping profiles at different temperatures, showing that we can have a good control on the depth of the profile (the both shallow and deep boron profiles) using boric acid as a diffusion source.

Table I: Sheet resistance and lifetime from different concentration of acid boric: pre-deposition time:15 min, drive-in time: 14 min, drive-in temp:1050°C.

Boric acid concentration (%)	Rsh (Ω/\square)	τ (μs)
1	47.7	3.81
2	40.6	2.78
3	35.1	2.62
4	30.1	1.85
5	17.5	1.6

Table II: Sheet resistance and lifetime at different drive-in temperatures: pre-deposition time:15 min, drive-in time: 14 min, boric acid concentration:5%.

Temperature ($^{\circ}\text{C}$)	Rsh (Ω/\square)	τ (μs)
950	386.6	4.93
975	148.8	2.27
1000	58.8	2.01
1025	25.4	1.75
1050	17.5	1.6

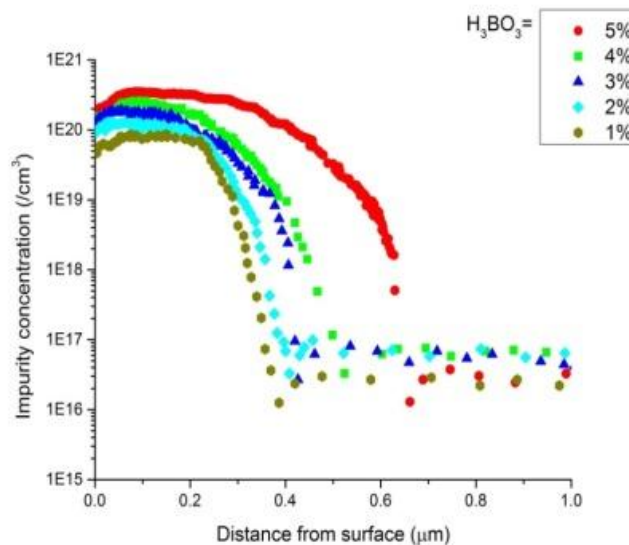


Fig. 3: Depth profile of boron in samples shown in Table I.

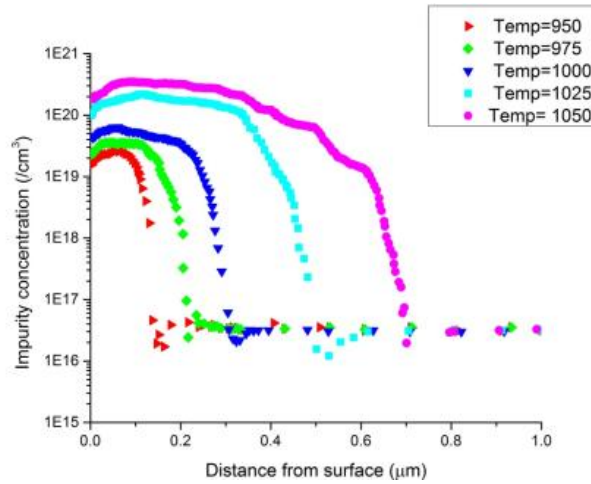


Fig. 4: Depth profile of boron in samples shown in Table II (Temp=°C).

b. Selective B Diffusion

The most interesting feature of this process compared to normal diffusion process is the ability to have a selective diffusion without having additional etching process. At first, photolithography was used to define windows in which the diffusion must be performed (shown Fig 5 b and c). After developing and post baking the resist, 200μl of 5% acid boric/DI water solution was applied on the patterned sample using spin-coating (see Fig. 5 d). Then, the sample was placed in an oven at 100°C for 15 min to drive out the solvent. Afterwards, the over-photoresist part of the boric acid was removed by lift off using acetone followed by DI water (Fig. 5 e). Finally, the sample was placed in the diffusion furnace in N₂ gas environment for 15 min at 1050°C.

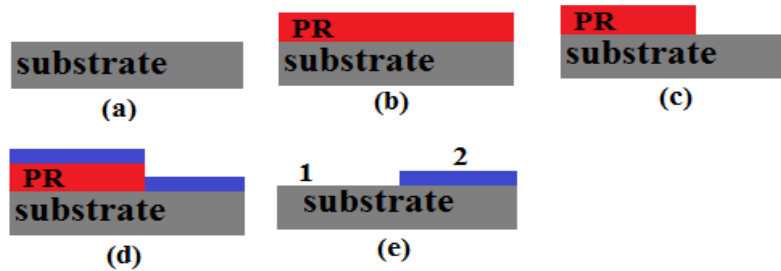


Fig. 5: Selective diffusion process with boric acid/DI water source. a) sample cleaning, b) photoresist spin coat, c) lithography, d) SOD & baking, e) photoresist (PR) lift off.

The ECVP measurements on these samples (shown in fig 6) show a remarkable difference in the surface concentration as a result of this selective process.

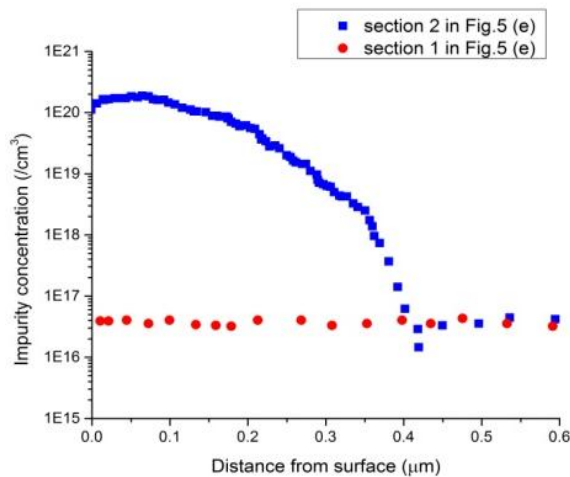


Fig.6: Depth profile of boron on a sample prepared as mentioned in Fig. 5. Section 1 and 2 are shown in Fig. e. Temperature: 1050°C, drive-in time 14 min.

In order to study the selective diffusion effect on the lifetime and sheet resistance, another experiment was designed. Therefore, after SODs were formed on the samples (100µl, 3000rpm and 15 sec), the coated samples were baked at different temps (50, 100, 150 and 200°C) to drive out the excess solvent. Next, samples were placed on the hotplate stirrer containing DI water in at 90°C for 3h so that the layer would be removed. Then, the samples dried and were loaded in diffusion furnace for 14 min with 4slm flow of N₂ gas.

The results of lifetime and sheet resistance are shown in Table III and Table IV respectively.

Table III: lifetime results at different pre-deposition temperatures: pre-deposition time:15 min, drive-in time: 14 min, boric acid concentration:5%.

Pre-dep Temp (°C)	τ (µs) : after 3h in the DI water	τ (µs): after drive-in diffusion
50	1.293	2.994
100	1.206	2.914
150	1.114	2.272
200	0.942	2.189

Table IV: sheet resistance results at different pre-deposition temperatures: pre-deposition time:15 min, drive-in time: 14 min, boric acid concentration:5%.

Pre-dep Temp(°C)	R _{sh} before process	R _{sh} after Dry	R _{sh} (Ω/□): after 3h in the DI water	R _{sh} (Ω/□): after drive-in diffusion
50	81.6	83	80	24.86
100	79.3	82.5	82	17.02
150	76.5	72.5	75.5	15.42
200	87.2	80.1	83.8	14.8

These tables clearly show that hot DI water can dissolve the solid layer formed on the samples and can be used as the potential etchant for this material. The ECVP measurements on the sample with and without etching with hot DI water are shown in Fig.7. This figure illustrates a remarkable difference in the surface concentration. In the other words, we have both light and heavy dopings in different areas of the wafer.

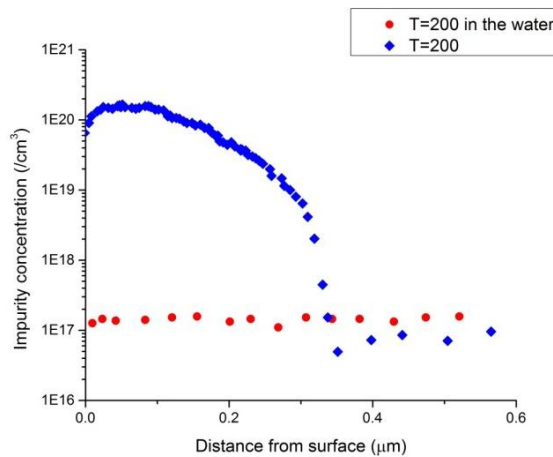


Fig.7: Depth profile of boron diffusion. Temperature:1050°C, drive-in time 14 min.

4. Conclusion

In this paper, we used boric acid source to formed boron emitter selectively on the n-type substrates. A thorough investigation of the effective parameters was performed to obtain the optimum conditions of boron diffusion process. It was found that spinning speed of 3000 rpm for 15 sec and 200°C drive-out bake result in a uniform dopant seed layer for the diffusion. The depth profile can be carefully controlled by monitoring the

boric acid solution concentration and the drive-in temperature. For selective cases, patterning can be done either by optical lithography and etching the unwanted parts using hot DI water or lift-off process. ECV measurements after selective process showed that the pre-deposition step (SOD) will not change the doping unless samples undergo a high temperature drive-in process.

5. References

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