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Study of boron precipitates formed during front side emitter formation with boron spin on dopant (BSOD) diffusion in *n*-type c- Si solar cells

B Singha^a and C S Solanki^{b*}^{a,b}Department of Energy Science and Engineering, Indian Institute of Technology, Bombay, Maharashtra, PIN-400076, India

Abstract

Boron precipitates formed during boron source diffusion is an unwanted phenomenon during front side emitter formation in *n*-type crystalline silicon solar cells. Boron spin on dopant (BSOD) is one of the mostly preferred alternative dopant sources to conventional liquid BBr₃, used for *p*-type emitter formation, but has problems of forming boron precipitates during its diffusion. In this work, we have studied boron precipitates formed by BSOD diffusion and characterized borosilicate glass layer (BSG) and boron rich layer (BRL) at different process parameters. We have tried different process controlled steps to get very less amount of boron precipitates on the surface during diffusion of BSOD source and were successful in reducing boron precipitates from 56% atomic and 36% weight percentages to 0% values for optimized sheet resistance value of 50±5 Ω/sq for the front side emitter.

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Keywords: Boron spin on dopant (BSOD); borosilicate glass layer (BSG); boron rich layer (BRL); sheet resistance

1. Introduction

Crystalline silicon (c-Si) solar cell covers 80% of the total solar cell market [1] and almost 85% of these cells are based on *p*-type substrate with phosphorus doped *n*-type emitter [2]. In recent years, research interest on *n*-type solar cell has increased because of various advantages of *n*-type c-Si over *p*-type; such as- avoidance of B-O complexes under illumination (hence no light induced degradation (LID)), higher minority carrier (holes) lifetime, superior tolerance to common impurities, ease of thermal

* Corresponding author. Tel.: +912225767895; fax: +912225764890.

E-mail address: chetanss@iitb.ac.in.

oxide passivation, less misfit dislocation etc [3-8]. So, people are trying to work on lowering the cost and improving the efficiency of solar cells with *n*- type c- Si substrates [8].

Liquid boron tri-bromide (BBr₃) is mostly used dopant source for fabricating *p*- type emitter in *n*- type c-Si solar cells. However, this source is hazardous and extra safety precautions increase cost in the fabrication process [9]. In order to lower the cost, it is necessary to study and experiment on new dopant sources which are able to give a good quality *p*- type emitter. BSOD is one of the alternatives to BBr₃ liquid source. A high concentration of boron dopant, like BSOD, in general, has problems of forming boron precipitates during its diffusion process. These precipitates result in boron rich layer (BRL) with thicknesses ranging from some Angstroms to nanometers and deteriorate the emitter properties and make the emitter inactive for solar cell purpose. It is very essential to remove BRL by different physical and chemical means and by controlling the process parameters.

In this work, we have tried different BSOD concentrations to obtain the lowest BRL on the diffused surface after removal of borosilicate glass (BSG) layer formed during diffusion process. An optimized in-situ oxidation, during ramping down of the diffusion process, is also used to reduce the formation of boron precipitates. After deglazing (removal of BSG layer), a chemical treatment with 2% HF and hot HNO₃ (at 80°C) helps in reducing the BRL thickness to almost zero. Different characterization techniques with and without BSG and BRL, have shown significant variation in the results and have helped in optimization of the *p*- type emitter for different sheet resistance values.

2. Experiments

2.1. Fundamentals related to BSOD diffusion

Boron diffusions are carried out by surface reaction between B₂O₃ and Si which takes place at diffusion temperatures, 850°C to 950°C [10] as shown in equation (i).



The elemental boron diffuses into the silicon surface at diffusion temperature and forms a doped glass layer having boron concentration corresponding to the silicon solid solubility limit at that temperature [10]. When boron supply to the surface is more compared to its diffusion into the silicon surface, then excess boron precipitates over the surface forming BRL and it is not easily removed by simple deglazing techniques that are used for removing BSG layer formed during diffusion process. BRL is generally represented by SiB_x. It is mostly SiB₆ [11] and gets easily attacked by nitric acid and by fluorine at high temperatures. So, any BRL left after deglazing can be removed by hot HNO₃ (generally at 80°C) and HF. Formation of BRL can also be minimized by controlling the process step parameters. In-situ oxidation during ramping down of the diffusion process helps in minimizing the formation of BRL. For reproducible diffusion results, a baking step just after spinning of BSOD is necessary to avoid moisture trapping by B₂O₃ to form boric acids i.e. H₃BO₃ and HBO₂ at room temperature and so it is preferable to insert the baked BSOD coated wafers into the hot diffusion furnace just after the baking step [11].

2.2. Experimental procedure of SOD diffusion

Starting wafer of the experiment was *n*- type c-Si with <100> orientation and 1-5Ωcm resistivity. As a necessary cleaning step, RCA1 with H₂O (DI): NH₄OH: H₂O₂ and RCA2 with H₂O (DI): HCl: H₂O₂, both

taken in the ratio 7:1:2 were used respectively to remove the organic and metallic impurities from the wafer. Thereafter BSOD was spun over the sample surface at 3000rpm and then wafers were baked at 200°C for 15mins to remove the moisture trapped by the coated film. The diffusion temperature used in this process was 900°C. In situ oxidation at 700°C for 20mins, during ramping down of the diffusion process, was used to reduce the boron precipitates from the surface. Just after removal of BSG layer, concentrated HNO₃ (at 80°C) followed by 2% HF dip was further used to remove all the boron precipitates (approximately) from the surface. The process flow diagram of the experiment is shown in figure 1.

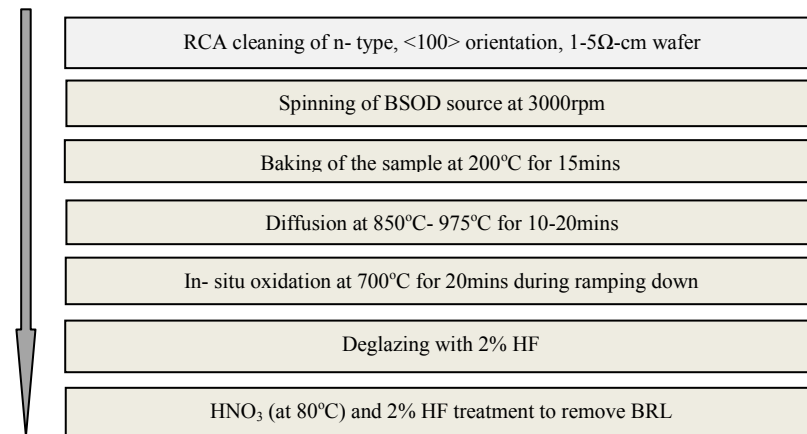


Figure 1. Process flow diagram of the experiment

Different characterization and measurement techniques were used to analyze the samples with BSG and BRL. These include TEM (transmission electron microscopy), SIMS (secondary ion mass spectroscopy), SEM (scanning electron microscopy), EDAX (energy dispersive x-ray), four point probes, QSSPC (quasi steady state photo conductance), FTIR (Fourier transform infrared spectroscopy) and UV-VIS spectroscopy.

3. Analysis of experimental results and discussion

For studying BSOD diffusion in *n*- type c-Si wafers and to characterize different samples due to different concentrations of BSOD, giving different thicknesses of BRL, we had taken five different types of samples as follows-

- Type 1: BSOD diffusion was done on RCA cleaned samples without diluting the dopant source and no in- situ oxidation was applied during ramping down of the diffusion process i.e. no process control steps were used to reduce the formation of BRL. The 'type 1' samples had BSG layer and BRL (boron precipitates) formed during BSOD diffusion.
- Type 2: Removal of BSG layer of 'type 1' samples with 2% HF solution which could not remove BRL from the surface, i.e. surface of 'type 2' samples was having BRL after removal of BSG layer.

- Type 3: BSOD, diluted with acetone in the ratio BSOD: acetone= 8:1, was used for diffusion and in- situ oxidation was done at 700°C for 20mins during ramping down of the diffusion process. So, ‘type 3’ samples were with BSG layer and some amount of BRL, formed during controlled BSOD diffusion process.
- Type 4: Removal of BSG layer of ‘type 3’ samples with 2% HF. ‘Type 4’ samples were having small amount of BRL at the surface.
- Type 5: Hot HNO₃ (at 80°C) and 2% HF were used on ‘type 4’ samples. So, ‘type 5’ samples were having approximately zero boron precipitates at the surface.

3.1. TEM (transmission electron microscope) analysis of BSG layer formed after B- diffusion

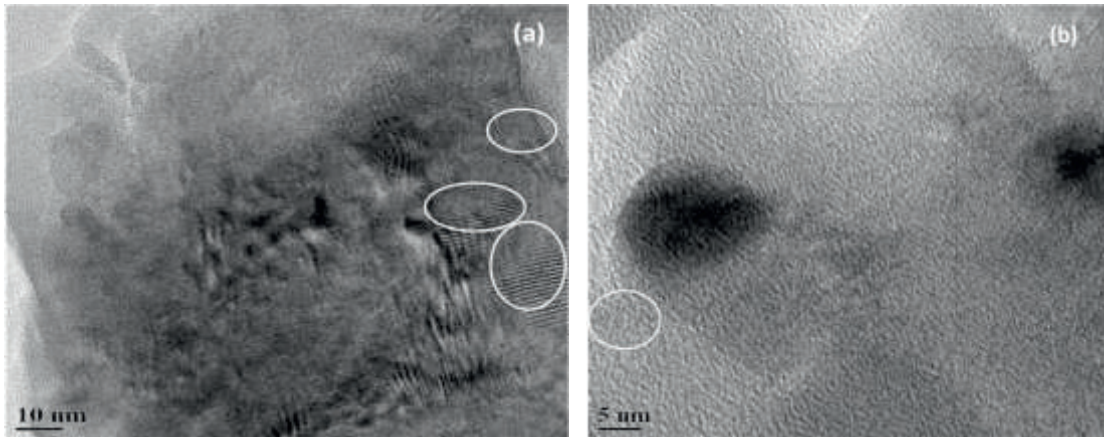


Figure 2. TEM images of BSG layers under high resolution which shows presence of SiB_x crystal structures in the amorphous BSG layer (a) sample where diffusion was done only with BSOD (without diluting with acetone) and no in- situ oxidation was used during ramping down process (b) sample diffused with BSOD: acetone taken in 8:1 ratio and in- situ oxidation at 700°C for 20mins.

TEM images of BSG layers of ‘type 1’ and ‘type 3’ samples are shown in figure 2 (a) and 2 (b) respectively. More numbers of crystal structures are found in BSG of figure 2 (a) where no process controlled steps were used. Elemental analysis at these regions could not give the exact constituents of the crystals. But one reason of these crystal formations is boron precipitates, SiB_x, formed during BSOD diffusion, which gradually decreases with process controlled steps, as seen in figure 2(b).

3.2. SIMS analysis

The diffusion temperatures for ‘type 1’ samples were 950°C and 900°C for 15 minutes. The resulting boron profiles, after deglazing with 2% HF solution (‘type 2’ sample), are shown in figure 3(a) where the presence of thick BRL with boron concentration in between 10²¹ to 10²² atoms/cm³ was prominent at the surface. X- axis of figure 3 plots can be used to measure the thickness of BRL. For ‘type 3’ samples, diffusion temperature was 900°C and the resulting BRL at the surface, after removing BSG layer (‘type 4’ sample), as shown in figure 3(b), was having less thickness compared to ‘type 2’ samples. This clearly indicates that controlled process steps could reduce the formation of boron precipitates at the surface.

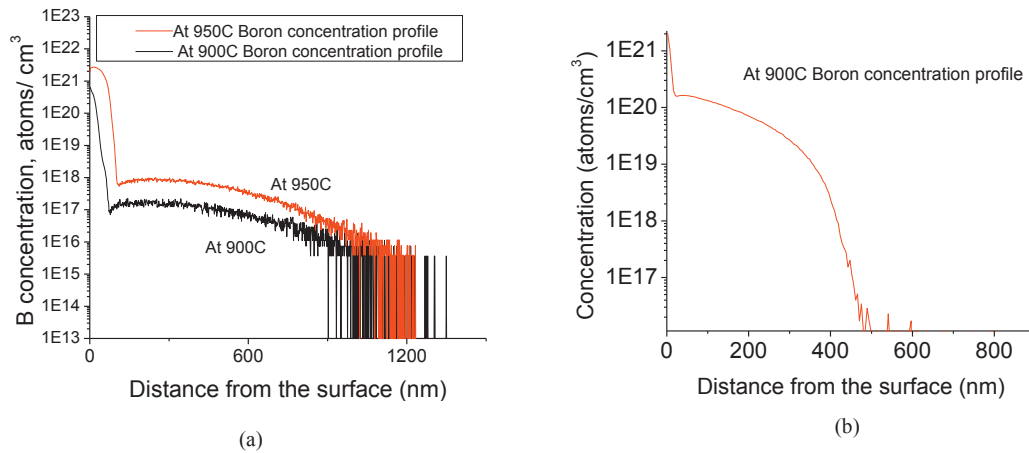


Figure 3. Boron concentration profile obtained from SIMS analysis (a) BSOD diffusion with no in- situ oxidation and no dilution of the dopant source (b) BSOD diffusion with diluted dopant source (here BSOD: Acetone= 8:1) and with in- situ oxidation at 700°C for 20mins during ramping down of the diffusion process

3.3. SEM and EDAX analysis

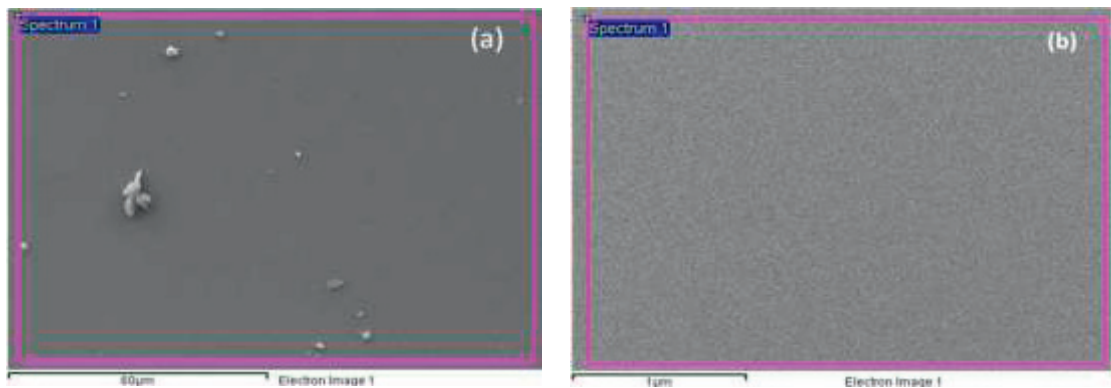


Figure 4. SEM images of BSOD diffused surface after deglazing (a) surface with no in- situ oxidation and no dilution of BSOD (b) surface with diluted BSOD (with acetone in 8:1 ratio) diffused and with in- situ oxidation at 700°C followed by hot HNO₃ (at 80°C) dip and 2% HF treatment

SEM (Scanning electron microscopy) was used to study the surface morphology of BRL left after deglazing. But boron precipitates don't show any significant detectable structures on the sample surface as shown in figure 4(a) and 4(b) for 'type 2' and 'type 5' samples respectively. However, EDAX analysis for the chosen area ('spectrum 1' in both the figures of figure 4) showed significant boron amounts at the surface for type 2 samples where no process controlled steps were used to reduce BRL. With 'type 5' samples, the BRL thickness at the surface almost reduces to zero.

EDAX analysis of the sample is presented in table 1. Comparative study of different weight% and atomic% of boron, carbon, oxygen and silicon under the chosen area, 'spectrum 1', represents that boron

percentages on the surface reduces to zero values when treated with hot HNO_3 (at 80°C) followed by 2% HF (at room temperature). Hot HNO_3 oxidizes BRL and 2% HF dip will remove the oxide layer. Carbon is found on both the sample surfaces but its weight% and atomic% are less for 'type 5' samples which was fabricated under controlled process. Oxygen is found in the sample where detectable BRL is present. Presence of oxygen on the surface generally deteriorates the emitter properties and should be removed before processing further fabrication steps of the solar cell. For 'type 5' samples, BRL is completely removed from the surface and so weight % and atomic % of silicon on the sample surface increases compared to 'type 2' samples.

Table 1. Comparison of EDAX analysis of the samples chosen under 'spectrum 1' of SEM images of figures 4(a) and 4(b)

Element	Type 2 samples		Type 5 samples	
	Weight%	Atomic%	Weight%	Atomic%
	(With BSOD diffusion and no-situ oxidation)		(BSOD: acetone= 8:1 as diffusion source and in-situ oxidation)	
Boron	36.95	55.91	-----	-----
Carbon	7.65	10.42	4.61	10.16
Oxygen	3.19	3.27	-----	-----
Silicon	52.20	30.40	95.39	89.84

3.4. Sheet resistance and minority carrier lifetime measurement

Sheet resistance of the deglazed sample was measured by four point probe method and minority carrier lifetime for different samples was measured by QSSPC (quasi steady state photo-conductive) measurement at minority carrier density 1×10^{14} atoms/cm³. The different sheet resistance and lifetime values obtained for different concentrations of boron with acetone are shown in table 2. In-situ oxidation at 700°C and for 20mins, during ramping down of the diffusion process, was maintained in all the BSOD+ acetone mixtures. From these measurements, BSOD: acetone ratio in 8:1 corresponding to sheet resistance values $50 \pm 5 \Omega/\text{sq}$ was optimized for further process steps. This dopant concentration could result very less or negligible BRL on the surface.

Sheet resistance values of the emitter are directly related to its doping concentration. When the dopant amount and mixed acetone was of the same volume, the sheet resistance value of the emitter was high indicating lower boron concentration of the emitter. The boron concentration at this range was lower than 10^{18} dopant atoms/cm³ (determined by SIMS), and good emitter properties could not be availed. As the boron amount in the dopant source had increased, the measured sheet resistance value got decreased and consequently boron concentration of the emitter got increased. High BSOD concentration, as in only BSOD source without mixing it with acetone, was also not desirable as it led to the formation of BRL which was sometimes difficult to remove with hot HNO_3 (at 80°C) followed by 2% HF dip.

Table 2. Sheet resistance and minority carrier lifetime values after deglazing and removal of BRL

Samples with BSOD: Acetone conc.	Sheet resistance values after deglazing with 2% HF	Minority carrier lifetime value after deglazing (in μsec)	Sheet resistance value after chemical (2% HF-HNO ₃ -2%HF) treatment to remove BRL (in Ω/sq)	Minority carrier lifetime after 2%HF-HNO ₃ -2%HF treatment (μsec)
1:1	250± 25	15.6	265± 25	15.3
2:1	170± 20	18.2	185±25	17.7
4:1	100± 15	18.3	135±15	18.2
8:1	45± 5	21.3	50± 5	20.7
Only BSOD	43± 5	20.3	41± 2	20.3

3.5. FTIR characterization of B- diffused samples

Fourier transform infrared (FTIR) spectroscopy was used to study different bonds present in ‘type 1’ and ‘type 5’ samples to compare the BSOD diffusion without any process control techniques and with all controlled process steps to reduce BRL thickness at the surface. The results for the same are shown in figure 5(a) and 5(b) respectively.

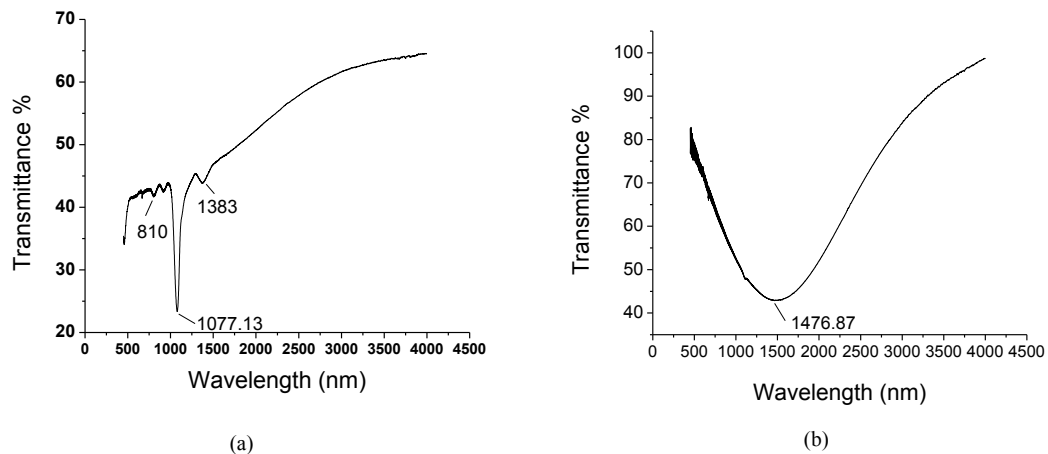


Figure 5. FTIR analysis of BSOD diffused samples (a) for samples without applying any process controlled steps to lower the thickness of BRL i.e. no lowering of BSOD concentration, no in- situ oxidation, no chemical treatment. The sample is with BSG (b) for samples with all the process controlled steps i.e. with in- situ oxidation, lowering of boron concentration with acetone and chemical treatment with hot HNO₃ and 2%HF dip to remove BRL from the surface.

The ratio of the B–O band peak intensity at a frequency near 1370 cm^{-1} to the Si-O-Si stretching absorbance maximum near 1075 cm^{-1} is widely used to determine the boron content for glass films of thicknesses up to 2.5 mm [12]. In our characterization, the peak positions have been found to be shifted to slightly higher positions as shown in figure 5(a). Intensity of B-O peak was found to be less compared to Si-O-Si peak indicating the dominance of Si oxides over B oxides. Peak corresponding to 810 cm^{-1} represent Si-O-Si bending bands. So presence of silicon oxides/ dioxides and boric oxides are prominent in BSG layer, formed after BSOD diffusion.

FTIR analysis, as shown in figure 5(b), didn't give any significant peak for the samples processed with controlled steps to reduce BRL at the surface. Also, hot HNO_3 (at 80°C) followed by 2% HF dip removed most of the BRL and the Si oxides present on the sample surface. So, no detectable peaks were found in 'type 5' samples.

4. Conclusion

In order to reduce the cost due to extra safety precautions in BBr_3 liquid source use in fabricating *n*-type c-Si solar cells, it is necessary to work with other boron dopant sources. BSOD is suitable to meet this goal with some process controlled steps to reduce the formation of BRL which deteriorates the emitter properties. In this paper, three different process steps were studied which could together reduce the boron precipitates formed at the sample surface to almost zero. Boron mixed with acetone in a suitable ratio, in- situ oxidation at 700°C for 20mins during ramping down of the diffusion process and hot HNO_3 + 2%HF treatment to remove the BRL were the three important process steps, as discussed in this paper, which enable BSOD to give good doping concentration for forming *p*- type emitter with no boron precipitates at sample surface.

TEM images of BSG layer, formed during diffusion process, showed more crystal like structures/ precipitates for samples prepared with only BSOD diffusion and no in- situ oxidation. SIMS analysis clearly indicated the presence of a thinner BRL, left after deglazing with 2%HF, for the samples prepared with controlled process steps. EDAX analysis of the samples, after deglazing, showed reduction of boron concentration to zero when the surface was treated with hot HNO_3 followed by 2%HF dip. Sheet resistance measurement showed the suitable dopant to acetone ratio for optimizing the emitter dopant concentration. Minority carrier lifetime value which varied with different dopant concentrations helped in determining the appropriate doping steps for the emitter. FTIR analysis showed the presence of B-O and Si-O-Si bands in BSG layer, but no significant peaks were seen for the samples treated with hot HNO_3 and 2% HF solutions used for removing BRL which clearly indicated a good emitter surface for further process steps of the solar cell.

So, with controlled process parameters, BSOD can give good boron doping concentrations according to our requirement and no BRL at the surface. It has good future for forming *p*- type emitter in *n*- type c-Si solar cells.

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