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SILICON SOLAR CELLS WITH BORON BACK SURFACE FIELD FORMED BY USING BORIC ACID

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ABSTRACT: This paper presents a novel boron diffusion process using nontoxic boric acid solution as a boron source to form a boron back surface field (BSF). It is shown that the boric acid provides excellent BSF quality and high bulk lifetimes when combined with a proper dielectric passivation. Boron emitters with a sheet resistance of $\sim 100 \Omega/\text{sq}$ have been obtained by diffusion at 925°C for 60 min. SiO_2 -based dielectric passivation of the boron emitter yields J_{oe} values of $\sim 100 \text{ fA}/\text{cm}^2$. The effective bulk lifetime of completed cells are measured to be $> 500 \mu\text{s}$ in $1.3 \Omega\text{cm}$ p-type FZ wafers. Cell efficiency up to 19.2 % has been achieved on $2 \times 2 \text{ cm}^2$ cells with the phosphorus emitter and the boron BSF formed with phosphoric acid and boric acid, respectively.
Keywords: boric acid, silicon, boron

1 INTRODUCTION

A High quality back contact with low back surface recombination velocity (BSRV) and high back surface reflectance (BSR) is one of the key requirements for achieving high efficiency crystalline silicon solar cells. This requirement is even more critical for achieving high efficiency on thinner substrates, which is the current strategy adopted by PV industry for reducing the cost of crystalline silicon solar cells. However, the most widely used technique for back contact formation in industrial crystalline Si solar cells, screen-printed Al-back surface field (Al-BSF), typically gives high BSRV (over 400 cm/s) and low BSR (60-70 %). In addition, the process causes wafer warping, which is a serious issue for thin and large area wafers.

A boron BSF is one of the promising techniques for achieving high quality back contact. It has three advantages over the screen-printed Al-BSF as: 1) it can be formed without inducing high stress in the substrate, 2) it can be used in conjunction with a dielectric passivation to further enhance the passivation and optical properties, and 3) it can provide higher p^+ doping concentration because of its higher solid solubility limit in Si allowing better passivation to be achieved[1]. Boron can be diffused into Si in several different ways. Liquid BBr_3 was used as a boron source to fabricate high efficiency solar cells. However, the BBr_3 source is a hazardous chemical, and requires an extra masking step to allow diffusion only on one side of the sample. Although solid boron sources provide a simple and safe diffusion method, they were found to degrade bulk lifetime during the high temperature processing. Diffusion processes using spin-on dopants (SOD) films are also another common choice since a simultaneous diffusion process is possible through coating of p-type source on one side and n-type on the other side[2,3,4]. The drawback of the SOD is that it leaves a thick diffusion glass and has also tends to significantly degrade the bulk lifetime after the diffusion process. In this paper, a novel process for boron diffusion is presented where boric acid diluted in deionized (DI) water is used as a boron source[5]. In this paper, the boron diffusion process and the boron diffused layer were investigated analyzing 1) sheet resistance and boron doping profiles

extraction, 2) dark saturation current density (J_{oe}) measurement, 3) effective lifetime through the process sequence, and 4) cell performance with the boron BSF.

2 EXPERIMENTAL

2.1 Boron diffusion

The boric acid solution was prepared by dissolving boric acid ($>99.999\%$, Aldrich Co.) in DI water. The phosphoric acid solution for n^+ emitter diffusion was also prepared by dissolving phosphoric acid in the DI water. The inclusion of metal impurities in these sources is minimized by using only high-purity acid and DI water. The B diffusion process started with wafer cleaning in 2:1:1 $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$, and 2:1:1 $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$, where the chemical oxide formed by the H_2SO_4 solution was left on the surface of the wafer to allow uniform coating of the boric acid solution. The boric acid solution was spin-coated on the wafer, followed by a drying process. Subsequently, boron diffusion process was performed either in a rapid thermal processing (RTP) system or a quartz tube furnace at temperatures in the range of 925 - 1000°C . The borosilicate glass (BSG) is removed in a HF solution after the furnace diffusion.

2.2 Characterization

Polished n-type Cz wafers of $10 \Omega\cdot\text{cm}$ were used to extract the boron doping profile from the spreading resistance measurement. Float zone (FZ) silicon wafers with high bulk resistivity $\geq 500 \Omega\cdot\text{cm}$ were used for sheet resistances and emitter saturation current density (J_{oe}) measurements. P-type $<100> 1.3 \Omega\cdot\text{cm}$ FZ wafers were used for solar cell fabrication. For the J_{oe} study, boric acid solution was spin-coated on both sides of the wafer. After the B-diffusion and the BSG removal, different dielectrics were formed on both sides of the wafers to passivate the surface. The dielectrics of interest include: spin-on dielectric-A, spin-on SiO_2 , thermal SiO_2 , and low-frequency plasma enhanced chemical vapor deposited (PECVD) SiN_x . Spin-on SiO_2 is commercially available while the spin-on dielectric-A was developed for the passivation of p-type Si substrate[6]. After spin-coating, the spin-on dielectrics were annealed at a temperature of 875°C . The thermal SiO_2 used in this

study was grown in the quartz tube furnace at the same temperature. The J_{oe} was measured by using photoconductance (PC) technique[7] at different process steps: after dielectric passivation, forming gas annealing (FGA), and firing at 850 °C in an infrared belt furnace.

2.3 Cell fabrication

Solar cells were fabricated by first spinning the boric acid solution onto one side of the wafer followed by a drying and a diffusion process. After BSG removal, phosphoric acid was coated on the other side, dried, and annealed (in the same quartz tube used for boron diffusion) at temperature above 875 °C. A dielectric was then spin-coated on the boron diffused surface followed by an annealing at 875 °C for back surface passivation. Subsequently, SiN_x films were coated on the front side of the wafer for anti-reflection coating as well as emitter passivation. The front and rear metal contacts were defined by a photolithography process. Front contacts were formed by an evaporation of Ti, Pd, Ag followed by a lift-off process. Additional Ag was plated to reduce the series resistance. The rear contact was formed by local openings in the back dielectric followed by an evaporation of Al, Ti, Pd and Ag. Nine 4 cm² cells were fabricated on each wafer and isolated using a dicing saw followed by a 30 min forming gas anneal at 400 °C. The structure of the completed solar cell and the process sequence are shown in Fig. 1 and Fig. 2 respectively.

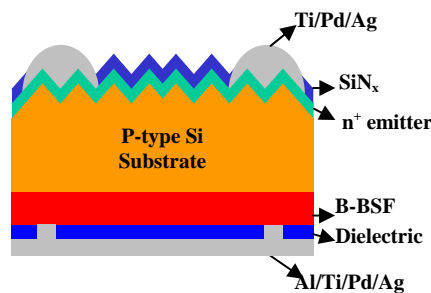


Fig. 1 Schematic diagram of a completed Si solar cell with boron BSF and dielectric passivation on the back.

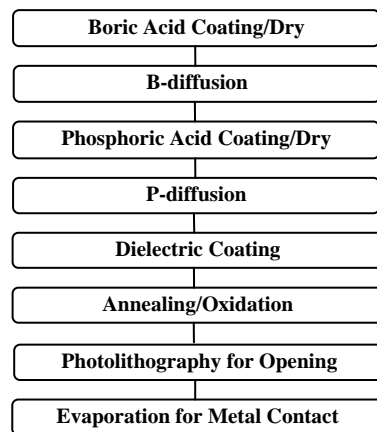


Fig. 2 Process sequence for solar cell fabrication

3 RESULTS AND DISCUSSION

3.1 Boron diffusion

The chemical formula of boric acid is H_3BO_3 (orthoboric acid), which is considered to be a hydrate of boric oxide (B_2O_3), and exists in the crystalline phase. The boric acid solutions with various concentrations can be prepared by dissolving different amount of the boric acid in DI water. DI wafer/boric acid solutions of up to 6 wt% of boric acid can be dissolved in the water at room temperature. No hazardous materials or procedures are required for the solution preparation and the diffusion process because the boric acid solution is only weak acidic. A dilute water solution of boric acid is widely used in pharmacy, leather manufacture, electroplating, insecticide and cosmetics since it has mild antiseptic properties[8]. It is also used as a flame retardant. Orthoboric acid results in orthorhombic metaboric acid (HBO_2) when it is heated below 130 °C. On continued heating, orthorhombic metaboric acid is converted to monoclinic polymorph above 130 °C, forming cubic crystalline metaboric acid and tetraboric acid at above 150 °C and 300 °C, respectively[9]. Anhydrous boric oxide (boron oxide) begins to soften at about 325 °C. The boron oxide reacts with silicon to form SiO_2 and B, which diffuses into silicon at high temperature.

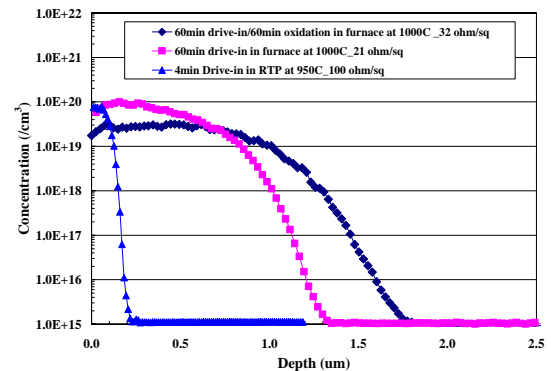


Fig. 3 Active boron profiles of the p+ emitters formed by the boric acid as a doping source.

Fig. 3 shows the boron doping profiles measured by the spreading resistance method. An RTP (rapid thermal processing) system and a quartz tube furnace were used for the boron drive-in process. The surface concentration of boron was found to be in the range of $1.8-7.5 \times 10^{19} \text{ cm}^{-3}$ and the junction depth was in the range of 0.2-1.8 μm depending on the diffusion time and temperature. This demonstrates that boric acid can be used as a diffusion source to obtain both shallow and deep boron profiles. When in-situ oxide was grown after the boron diffusion, sheet resistance increases due to out-diffusion of boron.

Fig. 4 shows the sheet resistance of boron diffused emitters as a function of the boric acid concentration for 60 min diffusion at temperature of 950 °C and 1000 °C. Sheet resistance can be varied from 20 to 180 Ω/sq by adjusting the diffusion temperature and the concentration of the boric acid. This ability to control the sheet resistance over a wide range shows that boric acid is a

viable source for making both emitters (on n-type substrates) and BSFs (on p-type substrates). For both the diffusion temperatures, the sheet resistance decreased with increasing boric acid concentration until the boric acid concentration reaches 0.5 wt%. For higher concentrations the reduction in sheet resistance is minimal. This implies that 0.5 wt% boric acid solution provides enough boron to saturate the surface after a 60 min diffusions at least up to 1000 °C. It should be noted that the boron diffusion at 950 °C for 4 min in the RTP system gave p⁺-emitter with sheet resistance of around 100 Ω/sq and a junction depth of 0.2 μm. This process can likely be used to form a p⁺ emitter for n-type solar cells.

3.2 Emitter saturation current

Fig. 5 summarizes J_{oe} , measured at different process steps, on boron emitters formed at 925 °C for 60 min passivated with different dielectrics. Except for SiN_x, all the dielectrics exhibited very low J_{oe} in the range of 90-115 fA/cm², corresponding to open circuit voltage (V_{oc}) limits in the range of 681-687 mV. For both the thermal SiO₂ and the spin-on SiO₂ layers, J_{oe} decreased after FGA and then increased drastically after a firing in the belt furnace at 850 °C. This is attributed to the degradation of the Si/SiO₂ interface during the firing. On the other hand, the passivation provided by the spin-on dielectric-A was found to be much more resistant against a firing resulting in a very low J_{oe} value of ~100 fA/cm² even after the firing in the belt furnace. In contrast, the SiN_x passivated p⁺-emitter exhibits J_{oe} value in the range of 900-950 fA/cm² that is almost an order of magnitude higher than those obtained using the other SiO₂ based dielectrics. It should be noted that the same PECVD SiN_x layer was found to give ~100 fA/cm² on 100 Ω/sq phosphorus emitters.

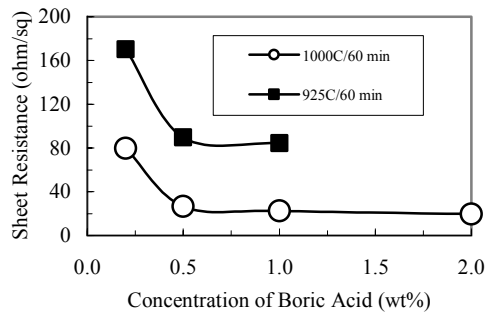


Fig. 4 Sheet resistance of the boron diffused emitters as a function of boric acid concentrations.

This difference in J_{oe} values for different types of emitters is attributed to the field effect passivation of the SiN_x film due to its high density positive charge in conjunction with a capture cross section area difference between electrons and holes. For the p⁺-emitter, the positive charge in the SiN_x attracts electrons which are minority carriers, reducing minority carrier recombination in the emitter. For the lightly doped p-type substrate or the n⁺-emitter, the positive charge in the SiN_x induces the inversion or accumulation with high concentration of electrons retarding holes away from the interface. Note that J_{oe} values of the emitters formed with

boric acid are comparable to the ones obtained with BBr₃[10].

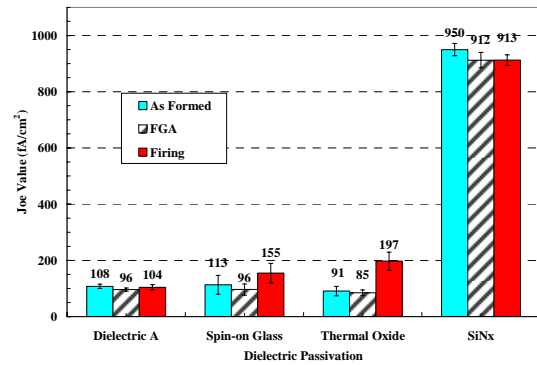


Fig. 5 Measured J_{oe} values of the 100 Ω/sq boron emitters created by diffusion at 925 °C with different dielectric passivation layers after different process steps.

3.3 Effective lifetime

The effective lifetime of the 1.3 Ωcm p-type FZ wafers was measured at each process steps as shown in Fig.6. The average effective carrier lifetime after the boron diffusion was ~255 μs, which is considerably higher than those reported in the literature using other spin-on or screen printing sources. The average carrier lifetime is further improved to 547 μs after the phosphorus diffusion with phosphoric acid on the opposite side of the wafers at 870 °C. Nevertheless, it was found that the lifetime was very sensitive to the boron diffusion process parameters and the equipment status. It is expected that higher lifetime can be achieved if boric acid with higher purity is available.

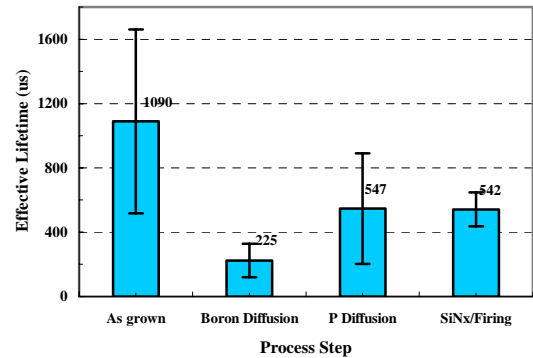


Fig. 6 Effective bulk lifetimes of 1.3 Ωcm, p-type FZ wafers after each process step.

3.4 IQE and cell performance

IQE and reflectance for the solar cells with B-BSF and Al-BSF are shown in Fig. 7, where the cell parameters of the solar cell with B-BSF are also included. The Al-BSF is formed by a firing a screen printed Al-paste in a conventional belt furnace. The benefits of B-BSF in the IQE and back reflectance are clearly shown by the enhanced long wavelength response of IQE and reflectance. The reflectance values at above 1030 nm wavelength indicate that BSR of B-BSF contact is higher than that of the Al-BSF contact. The blue response is also seems to be high due to the oxide passivation of the emitter during the annealing of rear dielectric. Efficiency

of ~19.2 % was achieved on the solar cell with B-BSF due to the enhanced back contact performance. However, the V_{oc} (~640 mV) of the completed cells is significantly lower than the implied V_{oc} (660-665 mV) measured before the metal contact formation process. We are currently investigating the interaction between the dielectric and the metal contact as well as the cause of high diode ideality factor in order to improve the cell efficiency.

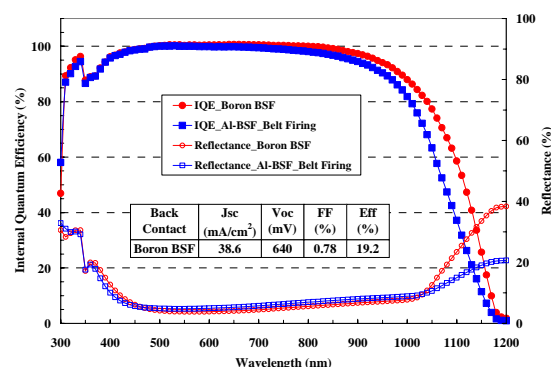


Fig. 7 IQE and reflectance as a function of wavelength for solar cells with the B-BSF and Al-BSF.

4 CONCLUSION

A low-cost non-toxic novel boron diffusion source was prepared by dissolving high-purity boric acid into DI water. Heavily doped boron emitter was formed by spin coating the boric acid onto Si wafers followed by annealing the coated wafers in the diffusion furnace or an RTP chamber. Various sheet resistances and profiles were obtained by adjusting a diffusion temperature, time and concentration of the boric acid solution. J_{sc} values of ~100 fA/cm² were obtained on a ~100 Ω /sq boron emitter with SiO₂-based dielectric passivation. The effective bulk lifetime of completed cells are measured to be > 500 μ s in 1.3 Ω cm p-type FZ wafers. Cell efficiency up to 19.2% has been achieved on 2x2cm² PL contact cells with the boron BSF.

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