

**Record-High-Efficiency Solar Cells on Multicrystalline Materials Through Understanding and Implementation of RTP-enhanced SiN<sub>x</sub>-induced Defect Hydrogenation**

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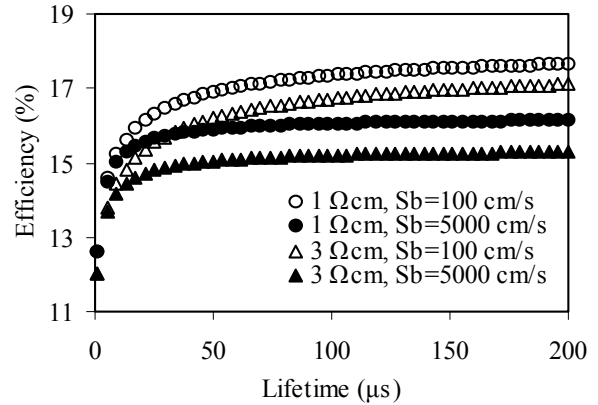
**ABSTRACT**

This paper presents results on five record-high-efficiency 4 cm<sup>2</sup> solar cells on three different multicrystalline silicon materials through effective hydrogen passivation of bulk defects during cell processing. Silicon ribbon solar cell efficiencies of 18.2% and 17.9% were achieved on EFG and String Ribbon Si cells fabricated with photolithography front contacts, screen-printed Al-doped back surface field, and double layer anti-reflection coating. In addition, high-efficiency, screen-printed, manufacturable cells were achieved on HEM (16.9%), EFG (16.1%), and String Ribbon (15.9%) Si. It is found that proper implementation of a fast co-firing of front and back screen-printed contacts in a belt furnace can significantly enhance the bulk lifetime to ~100 μs and simultaneously produce high quality contacts with fill factors approaching 0.78. The firing process involves fast ramp-up and cooling rates to enhance PECVD SiN<sub>x</sub>-induced hydrogen passivation of defects and the quality of Al back surface field.

**1. Introduction**

Multicrystalline cast and ribbon silicon are promising materials for low-cost, high-efficiency solar cells. However, these materials have high impurity concentrations and crystalline defect densities, resulting in low as-grown lifetimes, typically less than 10 μs, which are not sufficient for achieving high-efficiency solar cells. Therefore, effective impurity gettering and defect passivation during the cell fabrication are essential to achieve low-cost, high-efficiency cells from these materials. Model calculations in Fig. 1 show the requirements for achieving >17% efficient untextured screen-printed cells with a 45 Ω/sq. emitter, single layer anti-reflection (AR) coating and fill factor of 0.78. Solar cell simulations reveal that a bulk minority carrier lifetime of ~150 μs is required, in conjunction with back surface recombination velocity (S<sub>b</sub>) of ~100 cm/s to achieve manufacturable planar efficiency of >17% on 3 Ω-cm Si.

This paper reports on the implementation and optimization of rapid-firing-enhanced SiN<sub>x</sub>-induced hydrogenation to achieve record-high-efficiency solar cells with both screen-printed and photolithography (PL) contacts. In this work, cells benefited from optimized firing cycles designed for PECVD SiN<sub>x</sub>-induced hydrogen



**Fig. 1** Device simulations for 1 and 3 Ωcm screen-printed planar solar cells with BSRV of 100 and 5000 cm/s.

passivation of bulk defects, good ohmic contacts, and the formation of an effective Al-doped back surface field (Al-BSF).

**2. Experimental**

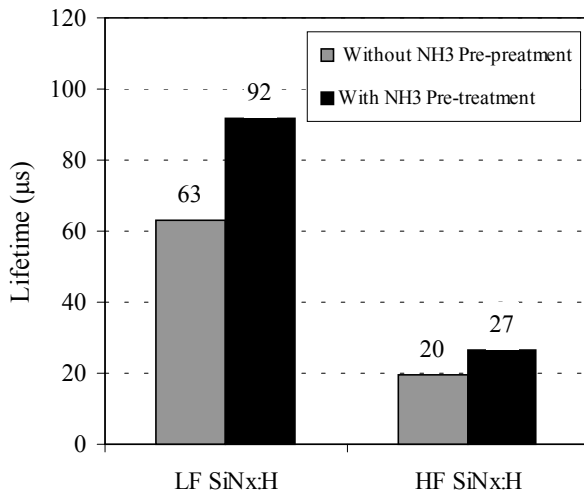
Solar cells with screen-printed and PL contacts were fabricated on ~300 μm thick, p-type cast mc-Si, EFG and String Ribbon Si using a very simple n<sup>+</sup>-p-p<sup>+</sup> cell design. Phosphorus diffusion was performed in a POCl<sub>3</sub> tube furnace to form the n<sup>+</sup> emitter with a sheet resistance of 45 Ω/sq. For cells with PL contacts, the POCl<sub>3</sub> diffusion temperature was adjusted to obtain a sheet resistance of 90 Ω/sq. A silicon nitride (SiN<sub>x</sub>) AR coating was deposited on top of the n<sup>+</sup> emitter in a commercial low-frequency (50 kHz) or high-frequency (13.56 MHz) PECVD reactors. In addition, SiN<sub>x</sub> films were grown with and without an NH<sub>3</sub> plasma pretreatment to understand and improve defect passivation. SiH<sub>4</sub>, NH<sub>3</sub>, and N<sub>2</sub> gases were used to deposit the SiN<sub>x</sub> coating with an average refractive index of 2.1 and thickness of 775 Å. A commercial Al paste was printed on the entire backside of all the wafers. A grid pattern was screen printed using a commercial Ag paste on top of the SiN<sub>x</sub> AR coating and fired through SiN<sub>x</sub> rapidly in a belt furnace or an RTP system to form ohmic contact to the n<sup>+</sup> emitter. This simultaneous anneal of Al and SiN<sub>x</sub> involves fast ramp-up and cooling rates to promote and enhance PECVD SiN<sub>x</sub>-induced hydrogen passivation of defects in Si.

Cells were isolated using a dicing saw and annealed in forming gas at 400°C for ~10 min. Minority carrier lifetime measurements were performed at various stages of cell processing to understand and optimize defect passivation. Before minority carrier lifetime measurements, the metallization, SiN<sub>x</sub> film, and diffused layers were removed. The surfaces were passivated by immersion in an I<sub>2</sub>/methanol solution during the lifetime measurement. Lifetime measurements were made using the QSSPC technique at an injected carrier concentration of 10<sup>15</sup> cm<sup>-3</sup> [1].

### 3. Results and Discussion

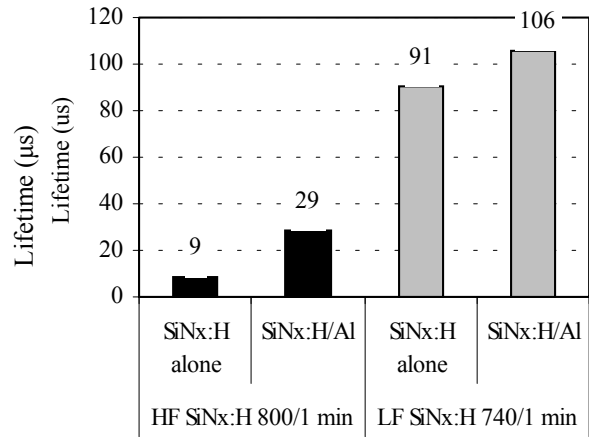
#### 3.1 Lifetime enhancement due to in-situ NH<sub>3</sub> plasma pretreatment and deposition of SiN<sub>x</sub> film

The effect of an in-situ NH<sub>3</sub> plasma pretreatment before SiN<sub>x</sub> deposition was investigated to increase the supply of H and provide further enhancement of lifetime using String Ribbon Si. Lifetime measurements were performed after SiN<sub>x</sub> deposition, Al screen-printing on the back surface, and heat treatment in RTP at 800°C for high-frequency SiN<sub>x</sub> and 740°C for low-frequency SiN<sub>x</sub> deposition. The results in Fig. 2 indicate that the deposition and annealing of low-frequency SiN<sub>x</sub> is more effective than high-frequency SiN<sub>x</sub> in providing hydrogen passivation of bulk defects. Fig. 2 also shows that low-frequency SiN<sub>x</sub>-induced hydrogenation increases the average lifetime in String Ribbon to 63 μs, without the NH<sub>3</sub> pretreatment, after an RTP anneal at 740°C



**Fig. 2** Effect of in-situ NH<sub>3</sub> plasma pretreatment before LF and HF SiN<sub>x</sub> deposition on lifetime enhancement in String Ribbon Si.

for one minute. When the NH<sub>3</sub> pretreatment is performed before low-frequency SiN<sub>x</sub> deposition, the average lifetime



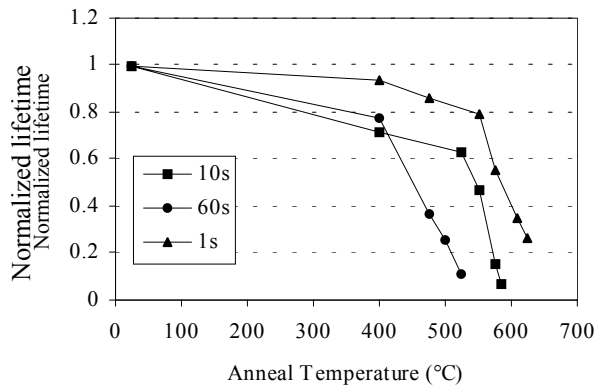
**Fig. 3** Impact of Al on hydrogenation from high and low frequency PECVD SiN<sub>x</sub>.

after RTP at 740°C anneal increases to 92 μs. High-frequency SiN<sub>x</sub>-induced hydrogenation results in an average lifetime of only 20 μs without in-situ NH<sub>3</sub> pretreatment and 27 μs with pretreatment. The effectiveness of low-frequency hydrogenation may be due to an increased supply of hydrogen in SiN<sub>x</sub> film or hydrogen incorporation in the damage region near the Si surface during SiN<sub>x</sub> deposition.

Fig. 3 shows that when Al is present on the back during high-frequency SiN<sub>x</sub>-induced hydrogenation, the average lifetime in String Ribbon increases from 9 μs to 29 μs. This is consistent with the results shown in Ref. [2]. However, Fig. 3 shows that the effect of Al alloying during low-frequency SiN<sub>x</sub>-induced hydrogenation is less significant. When Al is present during low-frequency SiN<sub>x</sub>-induced hydrogenation, the average lifetime in String Ribbon increases from 91 μs to 106 μs. This result can be explained by enhanced hydrogenation by vacancies introduced during Al-alloying or the high solubility of hydrogen in the Al-Si melt compared to Si [3]. During low-frequency SiN<sub>x</sub>-induced hydrogenation, the supply of H may be governed by the H incorporation in Si near the surface during SiN<sub>x</sub> deposition, and may only be marginally increased by the presence of Al. In this case, hydrogenation is limited by the retention of H at defects which improves by rapid cooling and shorter anneal time as shown in the section 3.2.

#### 3.2 Lifetime enhancement due to rapid annealing of contacts and SiN<sub>x</sub> film

This section shows the merit of rapid firing. It shows that the hydrogenation time must be reduced from minutes to one to five seconds in order to achieve effective defect passivation, Al-BSF, and good ohmic contacts. The retention of H at defects sites in Si is enhanced by a short hydrogenation step. The degree of hydrogen passivation is the result of competition between the supply and dissociation of hydrogen to and from defect sites, which happen simultaneously at the hydrogenation temperature. In order to investigate the dehydrogenation of defects, the hydrogenated String Ribbon samples were annealed in RTP for 1, 10, and 60 s at temperatures in the range of 400-650°C. The SiN<sub>x</sub> film, Al, n<sup>+</sup>, and p<sup>+</sup> regions were removed by chemical etching before annealing. Fig. 4 shows the change in normalized carrier lifetime ( $\tau_p/\tau_{p0}$ ) after annealing. It should be noted that SiN<sub>x</sub> layer on the front and Al back contact might prevent the out diffusion of H during the heat treatment. The data for 1 and 10 s annealing in Fig. 4 indicate that dehydrogenation starts to occur at low temperature (400-500°C), but does not become severe until temperature above 525°C when no SiN<sub>x</sub> is present on the wafer. The data also shows that the onset temperature for severe dehydrogenation increases from 525°C to 550°C when the annealing time is reduced from 10 to 1 s. This indicates that hydrogenated defects can tolerate higher temperatures if the anneal time is reduced. Finally, 1 s firing at 625°C in the absence of SiN<sub>x</sub> coating results in 80% reduction in hydrogenated bulk lifetime. This result could

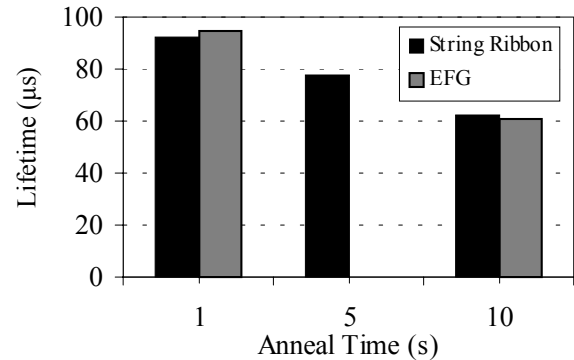


**Fig. 4** Decrease of the lifetime in hydrogenated String Ribbon during RTA at 400°C to 650° for 1s, 10s, and 60s.

prove to be very important in designing the appropriate contact firing cycle [3].

Fig. 5 shows the effect of RTA time during LF SiN<sub>x</sub>:H-induced hydrogenation in EFG and String Ribbon samples performed at 750°C and 740°C, respectively. Fig. 5 shows that the lifetime in String Ribbon and EFG Si increases as the anneal time is reduced from ten seconds to one second. When the anneal time is reduced to one second, the lifetime increases to 78  $\mu$ s in String Ribbon and 92  $\mu$ s in EFG. This suggests that when the anneal time is reduced, the retention

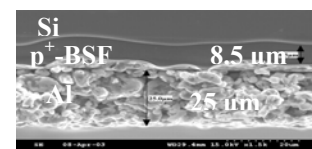
of H at defects increases, resulting in very significant lifetime enhancement (3-6  $\mu$ s to 78-92  $\mu$ s) even though the supply of H may decrease during the short RTA. Next section shows that fast and short firing does not compromise the quality of Al-BSF.



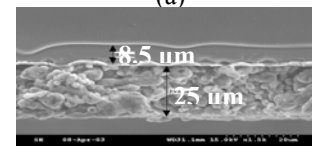
**Fig. 5** Effect of anneal time on lifetime enhancement from SiN<sub>x</sub>:H-induced hydrogenation.

### 3.3 Effective back surface field formation during short RTA

Fig. 5 revealed that the short time firing can enhance the retention of hydrogen at defect sites. However, the V<sub>OC</sub> depends not only on carrier lifetime but also on the quality of Al-BSF. In order to study the effect of firing temperature and time on the properties of Al-BSF quality, float zone (FZ) samples were annealed in RTP system at 750°C for 1 and 60 s. Fig. 6 shows the cross-sectional SEM micrographs of FZ wafers subjected to 1 and 60 s firing at 750°C. In both cases, Al-BSF regions were continuous with thickness of 8.5  $\mu$ m. These two pictures indicate that the quality and



(a)



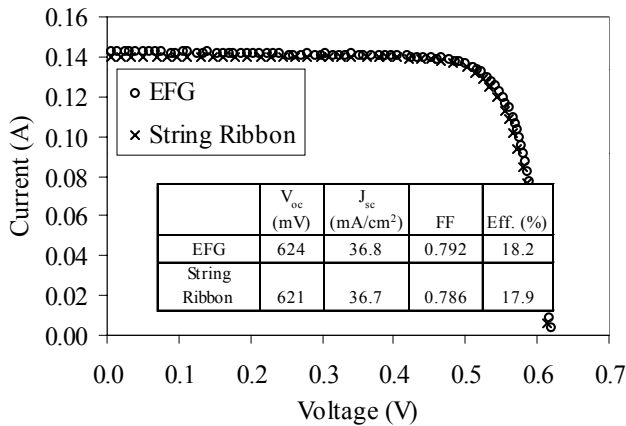
(b)

**Fig. 6** Cross-sectional SEM micrographs of the Al-BSF region in float zone Si fired at 750°C for (a) 1 s and (b) 60 s.

thickness of Al-BSF region is not a strong function of firing time in the range of 1-60 s. The V<sub>OC</sub> of both cells were very similar. This supports the merit of short firing cycle without compromising the BSF quality.

### 3.4 High-efficiency photolithography cells on EFG (18.2%) and String Ribbon (17.9%) Si

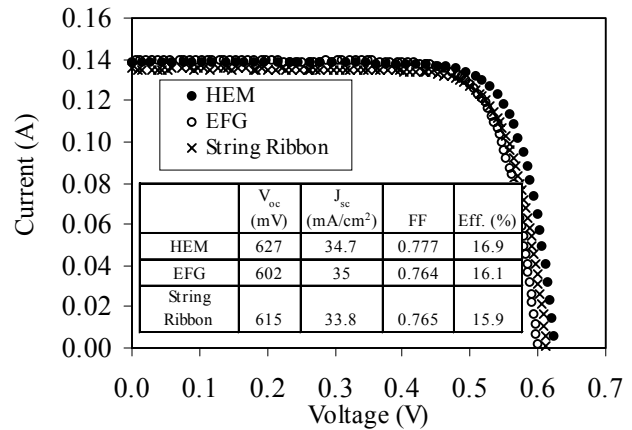
Above understanding was implemented in cell fabrication. Low-frequency  $\text{SiN}_x$  films were deposited with  $\text{NH}_3$  pretreatment and fired rapidly with fast ramp-up and cooling rates with very short hold time. Photolithography cells were fabricated using 3  $\Omega$ -cm EFG and String Ribbon Si. The fabrication process involved  $\text{POCl}_3$  diffusion, low frequency PECVD  $\text{SiN}_x$  deposition with  $\text{NH}_3$  pretreatment, Al screen-printing on the back, metal grid definition by photolithography process, and  $\text{MgF}_2$  deposition on top of  $\text{SiN}_x$  for double layer AR coating. Fig. 7 shows the efficiencies and cell performance parameters of these cells, confirmed by NREL. The  $\text{SiN}_x$  on the front and Al on the back were fired simultaneously in RTP system at 740-750°C for 1 s with ramp-up and cooling rates set to greater than 50°C/s. The open-circuit voltage ( $V_{OC}$ ) of >620 mV and efficiencies of ~18% were achieved on these materials, indicating that the hydrogenation occurs very rapidly and shorter firing cycle are very effective.



**Fig. 7** I-V characteristics of 18.2% EFG and 17.9% String Ribbon solar cells with photolithography contacts and double-layer AR coating (confirmed by NREL).

### 3.5 High-efficiency screen-printed cells on cast mc-Si (16.9%), EFG (16.1%) and String Ribbon (15.9%) Si

Based on the hydrogenation and Al-BSF formation studies, belt furnace processing was tailored to achieve high efficiencies with manufacturable process. The fabrication process involved  $\text{POCl}_3$  diffusion, low-frequency PECVD  $\text{SiN}_x$  deposition with  $\text{NH}_3$  pretreatment, and co-firing of screen-printed metals in the belt furnace. In the case of HEM and String Ribbon cells, the emitter was 45  $\Omega$ /sq. and a 100  $\Omega$ /sq. emitter was formed for EFG cells. Fig. 8 shows the efficiencies and cell performance parameters, verified by NREL. Average bulk lifetime in HEM, EFG and String Ribbon cells was 200  $\mu\text{s}$ , 100  $\mu\text{s}$ , and 77  $\mu\text{s}$ , respectively, with fill factors approaching or exceeding 0.77. Screen-printed cell efficiencies as high as 16.9%, 16.1%, and 15.9% were achieved on HEM, EFG, and String Ribbon Si.



**Fig. 8** I-V characteristics of 16.9% HEM, 16.1% EFG and 15.9% String Ribbon cells with screen-printed contacts and a single layer AR coating (confirmed by NREL).

## 4. Conclusion

This paper shows five record efficiency 4 cm<sup>2</sup> cells on three different mc-Si materials through effective hydrogenation of defects during contact firing. Record-high silicon ribbon solar cell efficiencies of 18.2% and 17.9% were achieved on EFG and String Ribbon Si cells fabricated with PL front contacts, screen-printed Al-BSF, and double layer AR coating. In addition, record-high screen-printed manufacturable cells were achieved on HEM (16.9%), EFG (16.1%), and String Ribbon (15.9%) Si. These cells were fabricated using  $\text{POCl}_3$  diffusion, single layer AR coating, and rapid co-firing of Ag grid and Al-BSF in a belt furnace. Improved understanding and hydrogenation of defects in these promising low-cost ribbon materials contributed to the significant increase in bulk lifetime from 1-10  $\mu\text{s}$  to as high as 100  $\mu\text{s}$  during cell processing. It was found that  $\text{SiN}_x$ -induced defect hydrogenation in these materials takes place within one second at peak temperature of 740-750°C. A combination of low-frequency deposition of  $\text{SiN}_x$  film, in-situ  $\text{NH}_3$  plasma pretreatment and simultaneous and rapid firing of contacts and  $\text{SiN}_x$  played a major role in lifetime and cell performance enhancement.

## REFERENCES

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