

# Solar Cells on EFG and String Ribbon Silicon by rapid thermal processing

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## Abstract

Record high silicon ribbon solar cell efficiencies of 18.2 % and 17.8 % were achieved on EFG and String Ribbon silicon, respectively. These cells were fabricated with photolithography front contacts and double layer antireflection coating. Improved understanding and hydrogenation of defects in these promising low-cost ribbon materials contributed to the significant increase in bulk lifetime from 1-5  $\mu\text{s}$  to as high as 90-100  $\mu\text{s}$  during cell processing. It was found that  $\text{SiN}_x$ -induced defect hydrogenation in these ribbon materials takes place within one second at peak temperatures of 740-750  $^\circ\text{C}$ . In fact, bulk lifetime decreases with the increase in annealing temperature above 750  $^\circ\text{C}$  or annealing time in excess of one second due to the enhanced dissociation of the hydrogenated defects coupled with the decrease in hydrogen supply from the  $\text{SiN}_x$  film.

## Introduction

Silicon ribbons such as String Ribbon and Edge-defined Film-fed grown (EFG) ribbon reduce both feedstock consumption and wafering cost since they are grown directly in the form of ribbon from a silicon melt<sup>1, 2</sup>. Ribbon wafers generally contain more point defects and higher dislocation density ( $10^5$ - $10^6/\text{cm}^2$ ) due to larger temperature gradient during the growth compared to the widely used ingot materials (HEM, CZ)<sup>3</sup>. This results in much lower as-grown bulk lifetimes in the range of 1-6  $\mu\text{s}$  in ribbon materials, which are not sufficient for high efficiency cells. Therefore, quality enhancement during cell processing is necessary to compete with other materials.

In spite of low as-grown lifetime, efficiencies of ribbon solar cells are approaching 13-15 % in production and 15-16 % in the laboratory due to bulk lifetime enhancement during cell processing<sup>4</sup>. In the past, high efficiency screen-printed silicon ribbon solar cells have been fabricated by optimizing rapid thermal processing (RTP) cycles to improve  $\text{SiN}_x$ -induced hydrogenation of bulk defects and quality of back surface field<sup>5, 6</sup>. These cells were fabricated by a two step process where the first step is used to form an effective Al BSF and provide Al-enhanced defect hydrogenation. The second firing step is performed at lower temperature ( $< 800^\circ\text{C}$ ) to form screen-printed Ag grid on the front. However, the latter step could degrade hydrogen passivation achieved in step one due to evolution of hydrogen from the defects. While hydrogen is found to be introduced into silicon<sup>7</sup> due to the annealing of  $\text{SiN}_x$  AR coating, it is not clear how much and how fast

the hydrogen diffuses into the underlying defective as-grown wafer because the diffusion mechanism can be influenced by temperature, defect type and concentration, doping concentration and conductivity type<sup>8,9,10,11</sup>.

Recently, record high efficiency EFG(16.7%) and String Ribbon(17.7%) cells were reported by Hahn et. al. using photolithography contacts, thermal oxidation for front surface passivation, Al gettering for 30 min, ZnS/MgF<sub>2</sub> for double layer anti-reflection (DLAR) coating, and 60 min microwave-induced remote hydrogen plasma (MIRHP) for defect passivation<sup>12</sup>. This paper reports on further enhancement in these cell efficiencies using rapid gettering and hydrogenation, endorsing the potential of these materials for photovoltaic applications. We used industrial type SiN<sub>x</sub> for surface and bulk defect passivation in addition to the first layer of the SiN<sub>x</sub>/MgF<sub>2</sub> double layer AR coating. Furthermore, defect hydrogenation and Al BSF formation were achieved simultaneously in one second by rapid thermal annealing at ~750 °C. Front contacts were formed by evaporation and photolithography which involve no additional heat treatment to prevent any subsequent dehydrogenation of defects. Record high efficiencies achieved in this study on ribbon materials are attributed to improved understanding and effective hydrogenation of defects by minimizing their dehydrogenation.

In this study, an RTP system was used for annealing the SiN<sub>x</sub> coated samples with screen printed Al paste on the back because it can control (a) temperature ramp-up rate, (b) annealing time and temperature, and (c) cool-down rate, independently and accurately. It is shown that these features are important because hydrogenation is a very rapid process and shorter the hydrogenation cycle at ~750°C more effective it gets.

## Experimental

String Ribbon and EFG samples used in this study had an average thickness of 300 μm and resistivity of 3 Ωcm. P-type EFG ribbon was grown at ASE Americas while String Ribbon was grown at Evergreen Solar, respectively. The phosphorus diffusion was performed using a liquid POCl<sub>3</sub> source in a tube furnace to obtain an 85 Ω/□ n<sup>+</sup>-emitter. SiN<sub>x</sub> film with a thickness of 78 nm and index of 2.0 was deposited in a commercial low-frequency PECVD reactor on the phosphorus-diffused emitter. Aluminum paste (Ferro FX 53-038) was screen-printed on the back surface of the wafers. The SiN<sub>x</sub> on the front and the Al on the rear were fired simultaneously in an RTP chamber to enhance hydrogen passivation. The ramp-up and cooling rates were set to greater than 50 °C/sec to achieve a uniform Al-BSF layer and provide good hydrogenation. The firing temperatures were varied from 700 to 800 °C<sup>13,14</sup> and firing time from 1 to 60 seconds to understand and optimize the hydrogenation of defects and quality of BSF simultaneously. The front metal grid was defined by a photolithography process involving etching of the SiN<sub>x</sub> film in BOE (buffered oxide etchant). Front contacts were then formed by evaporating 60 nm Ti, 40 nm Pd and 60 nm Ag followed by a lift-off process. Additional Ag was plated to increase the grid thickness to ~8 μm and reduce the series resistance to ~ 0.5 Ω-cm<sup>2</sup>. Nine 4 cm<sup>2</sup> cells were fabricated on each wafer and isolated using a dicing saw followed by a 30 min forming gas anneal at 400 °C. In order to minimize the reflectance, the SiN<sub>x</sub> thickness was adjusted to 67.8 nm and capped with 99.5 nm magnesium fluoride film by

vacuum evaporation to form a DLAR, which reduced the integrated front surface reflectance to ~ 6.19 %.

## Results and Discussion

Fig.1 shows the progress in efficiency of ribbon solar cells with photolithography contacts. Data for Dendritic Web and EFG cells with photolithography (PL) contacts is limited. Cell efficiencies of ~17 % have been reported on Dendritic Web Si in the past whereas relatively steady progress has been made on String Ribbon cells with PL contacts with maximum efficiency of 16.2 % in 2001. This paper reports on record high efficiencies of 18.2 % on EFG and 17.8 % on String Ribbon. These 4 cm<sup>2</sup> cells were tested and verified by NREL, demonstrating the potential of these ribbon materials.

Fig. 2 shows the process-induced lifetime enhancement in these materials. The as-grown bulk lifetime was in the range of 2-5 μs, which increased to 4-15 μs range after the 85 Ω/□ phosphorus emitter diffusion. The bulk lifetime improved significantly after the SiN<sub>x</sub> /Al co-firing in the RTP chamber without the need for any additional or extra gettering step. In this study, lifetime enhancement was found to be very sensitive to the co-firing time and temperature. Average bulk lifetime increased from 4.5 μs to 73.7 μs in String Ribbon and from 3 μs to 95 μs in EFG with only one second RTP firing at ~ 750 °C. One second firing maintained bulk lifetime over 50 μs even at 800 °C whereas bulk lifetime dropped rapidly to 33 μs at 750 °C for 60 second firing. This indicates that hydrogen diffusion into silicon and bulk defect passivation by the hydrogen take place in a very short time. Optimum co-firing condition was found to ~750°C/1s. Fig.2 clearly shows that defect passivation or bulk lifetime enhancement degrades at higher co-firing temperature (>750 °C) or longer time (>1 second). The low starting lifetime in String Ribbon and EFG Si is the result of high dislocation density and metal impurities<sup>15</sup>. It has been reported that hydrogenated metal defects dissociate during high temperature annealing with activation energies in the range of 2.2~2.5 eV<sup>16</sup>. This can give rise to deep levels. The dissociation energy for the hydrogenated dislocation related Si-H bonds reported to be 2.6~3.5 eV<sup>17</sup>. Therefore, if hydrogen diffusion or supply into the silicon stops, the fraction of reactivated defects (N/N<sub>0</sub>) can be described by the equation<sup>18</sup>

$$\frac{N}{N_0} = 1 - \exp[-t\nu \exp(-E_d / kT)] \quad (1)$$

where t is the annealing time, ν is attempt frequency (10<sup>13</sup>~10<sup>14</sup> /s), E<sub>d</sub> is the activation energy for the reactivation process and T is the temperature. Calculations reveal that 63 % of passivated metal defects can re-activated in just 0.055 second at 740 °C assuming ν = 5x10<sup>13</sup> /s and E<sub>d</sub> = 2.5 eV. In contrast, it should take 53 second to re-activate 63 % of the hydrogenated dislocations, using an activation energy of ~3.1 eV and ν = 5x10<sup>13</sup> /s. In order to maximize the bulk lifetime, the dehydrogenation process should be quenched after the defects are saturated with hydrogen. It has been shown that the Si-H concentration in the SiN<sub>x</sub> film decreases rapidly within 20 seconds down to the detection limit at temperatures above 700 °C<sup>19</sup> while the N-H concentration decreases rapidly followed by a slower decrease. This suggests that the supply of hydrogen from the SiN<sub>x</sub>

film or the hydrogen flux into the silicon decreases rapidly within the first 20 seconds and then decrease slowly. However, the activation of defect continues with time and it's rate increases with temperature (equation 1). This explains the observed decrease in bulk lifetime with the increase in firing time or temperature (Fig.2). In order to support the rapid activation rate, we removed the SiN<sub>x</sub> film after the hydrogenation at 740°C/1s to stop the hydrogen supply and then re-annealed the sample at 740 °C. We found that in the absence of hydrogen supply it only took 2 seconds to activate the defects and the lifetime dropped from 74 μs to 9 μs.

Hydrogen diffusion into a defective silicon can be influenced by defects type and concentration, in addition to temperature, doping density and conductivity type. For example, it has been shown that hydrogen can diffuse rapidly via dislocations<sup>20</sup>. On the other hand, the hindrances to hydrogen diffusion have been reported in single crystalline silicon at low temperature. In p-type Si, most of the hydrogen diffuses by rapid interstitial motion at high temperature over 500 °C, without any retardation by either acceptor trapping or molecule formation<sup>21</sup>. Van Weirengen and Warmoltz measured the interstitial hydrogen diffusivity in the temperature range of 1090 ~ 1200 °C<sup>22</sup> given by

$$D_H = 9.4 \times 10^{-3} \exp\left(\frac{-0.48 eV}{kT}\right) \text{ cm}^2 / \text{s} \quad (2)$$

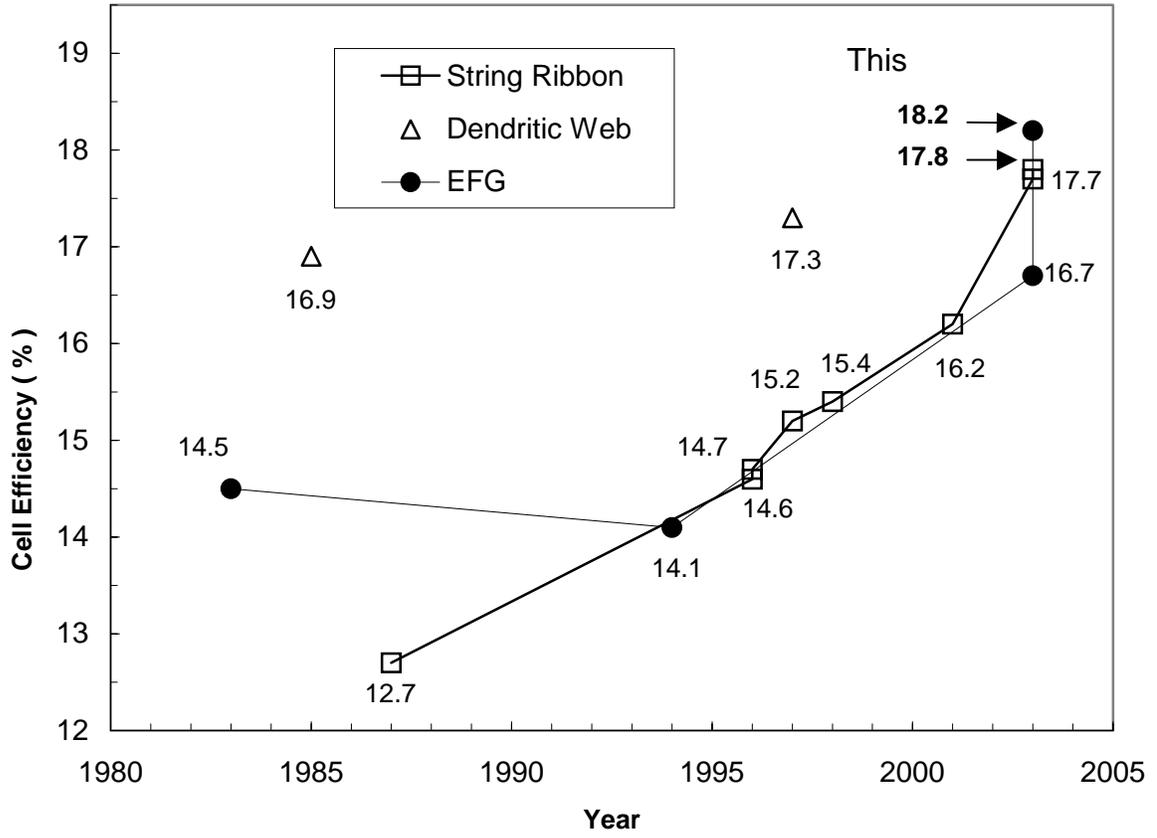
However, the experimental results on diffusivity measurements at lower temperature have given smaller values<sup>23,24</sup> than the extrapolated VWW data<sup>25,26</sup>. The extrapolation of the VWW data yields a diffusivity of 4.0582x10<sup>-5</sup> cm<sup>2</sup>/s at 750 °C. Substantial improvement in the bulk lifetime (85~95μs) coupled with significant increases in the long IQE response for the EFG and String Ribbon cells after one second firing indicates that the defect passivation by hydrogen is accomplished throughout entire 300 μm thick wafers within one second. A Simple  $x = (Dt)^{1/2}$  approximation gives 9x10<sup>-4</sup> cm<sup>2</sup>/s, assuming that hydrogen diffuses through a 300 μm thick wafer in 1 second at 750 °C. This is a factor of twenty times higher than the extrapolated interstitial diffusivity from VWW data. Using 5 second thermal budget above 500 °C associated with the ramp-up and ramp-down gives a diffusivity of 1.8x10<sup>-4</sup> cm<sup>2</sup>/s which is still 4 times higher than the VWW's diffusivity at 750 °C. This suggests that effective hydrogen diffusion may be enhanced by mechanisms other than interstitial diffusion. Ribbon materials contain high dislocation concentration (10<sup>5</sup>~10<sup>6</sup> /cm<sup>2</sup>) which could accelerate the movement of hydrogen through the bulk. It was shown by Dube<sup>27</sup> that hydrogen diffuses more rapidly along the dislocations than grain boundaries or intragrain single crystal regions. Furthermore, it has been suggested that the dislocations and vacancies can increase the hydrogen solubility by dissociating H<sub>2</sub> molecules into atomic hydrogen<sup>28,29</sup>. Ribbon materials have high concentration of vacancies which are introduced into the bulk during the ribbon growth or cell processing steps such as Al-BSF formation and SiN<sub>x</sub> deposition. It has been suggested that vacancies can enhance hydrogen diffusion and defect passivation by providing additional driving force for diffusion or by dissociating H<sub>2</sub> molecules<sup>30,31,32,33</sup>. In addition, light-enhanced<sup>34</sup> hydrogen release from Si-H bonds or strain-enhanced H<sub>2</sub> molecule dissociation<sup>35</sup> has been suggested which could increase the hydrogen diffusion in our experiment since intense illumination is used in RTP to heat the wafers and stress is introduced during the Al-BSF process. Sopori et. al. used

computer simulation to show that hydrogen can diffuse through a 100  $\mu\text{m}$  thick wafer after 10 second annealing of  $\text{SiN}_x$  coated wafers at 800  $^\circ\text{C}$  in an RTP chamber<sup>36</sup>. Thus, very rapid and effective hydrogenation of defects observed in ribbon materials seems to be the result of multiple effects that tend to enhance hydrogen diffusion or concentration.

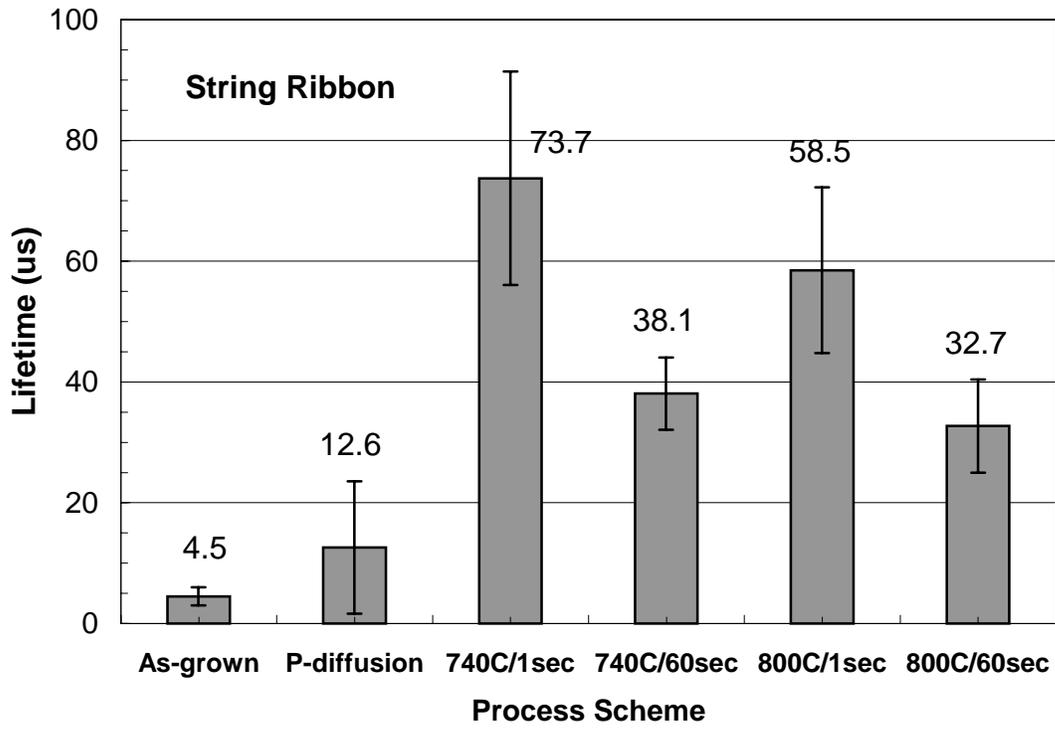
Based on the above understanding and experimental data, optimum hydrogenation conditions ( $\sim 750^\circ\text{C}/1\text{s}$ ) were used (Fig.2) to fabricate ribbon cells. Fig.3 shows the light I-V characteristics of the record high efficiency cells achieved on EFG and String Ribbon silicon. The 18.2 % cell on EFG and 17.8 % cell on String Ribbon were tested and verified by NREL. The cells had  $V_{oc}$  of  $\sim 620$  mV and FF of 0.78. The  $J_{sc}$  for EFG and String Ribbon were of  $\sim 37$   $\text{mA}/\text{cm}^2$  and  $36.8$   $\text{mA}/\text{cm}^2$ , respectively. These results are consistent with very high bulk lifetimes approaching 100  $\mu\text{s}$  and double layer AR coating.

In conclusion, ribbon silicon solar cells with efficiency of 18.2 % on EFG and 17.8 % on String Ribbon were achieved, supporting the potential of ribbon materials. It was found that effective defect hydrogenation in ribbon materials takes place within 1 second at 740~750  $^\circ\text{C}$ . Bulk lifetimes approaching 100  $\mu\text{s}$  were achieved. The bulk lifetime was found to decrease with the increase in annealing temperature above 750  $^\circ\text{C}$  and annealing time over 1second due to the decrease in hydrogen supply from the  $\text{SiN}_x$  film and continued dissociation of the hydrogenated defects. These cell results with photolithography contacts and double layer AR coating suggest that 16-17 % efficient manufacturable ribbon cells can be realized with screen printed Ag contacts and single layer  $\text{SiN}_x$  AR coating.

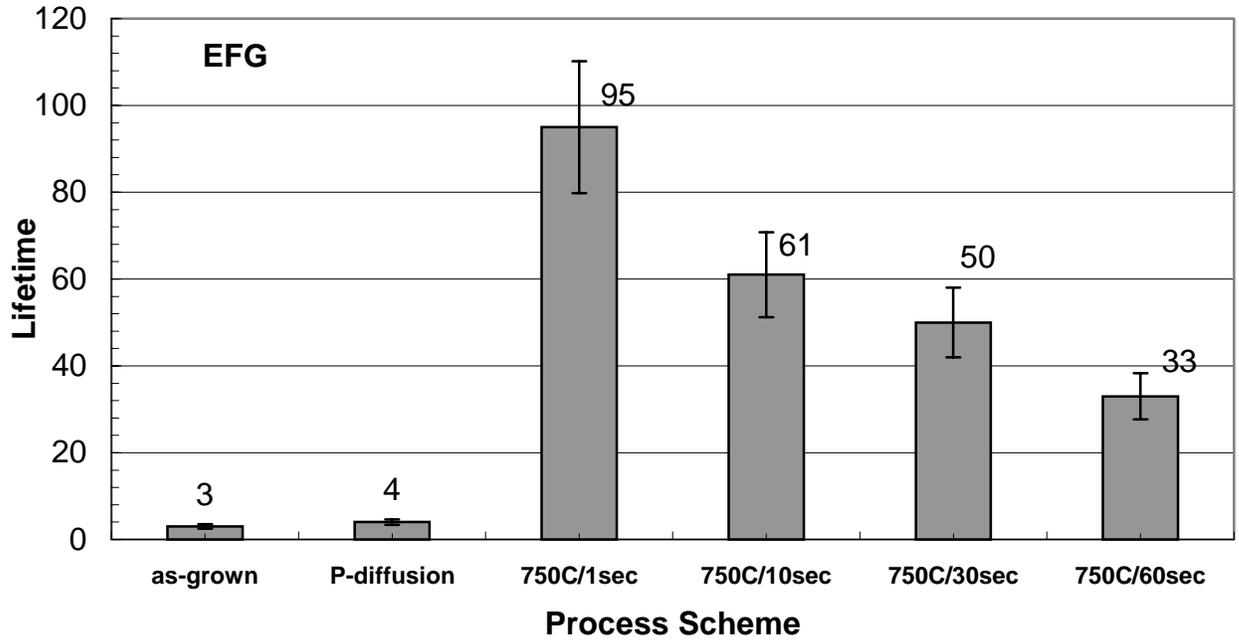
The author would like to thank T.Moriarty of NREL for the cell characterizations



**Fig. 1** Progress in efficiency of laboratory scale ribbon solar cells with photolithography contacts.

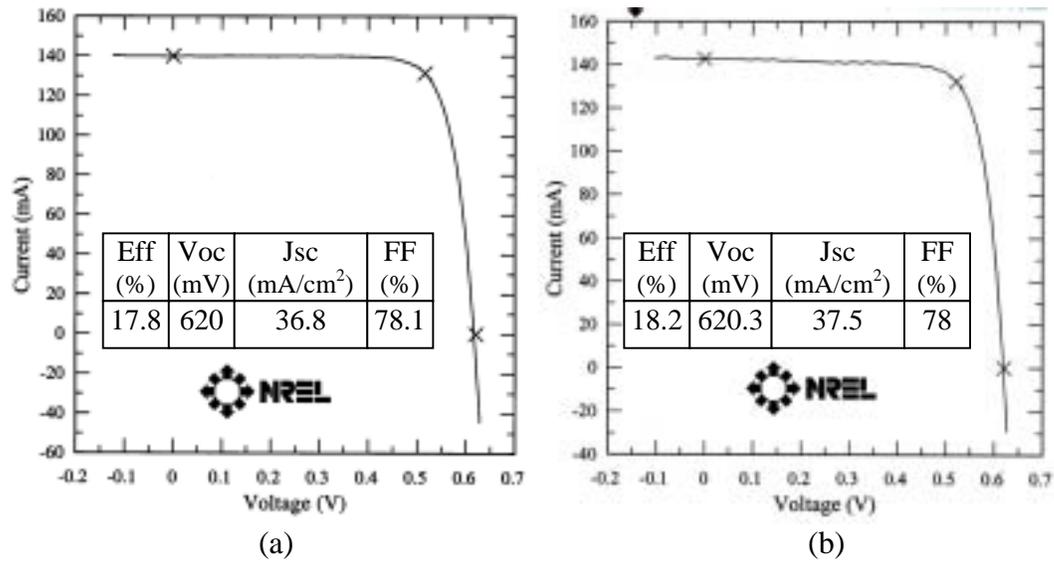


(a)



(b)

**Fig. 2** Process induced lifetime enhancement in String Ribbon (a) and EFG Si (b). Lifetime is shown as a function of P-diffusion and SiN<sub>x</sub>/Al co-firing at different condition.



**Fig. 3** Light I-V characteristics of ribbon silicon solar cells on String Ribbon(a) and EFG(b) measured by NREL.

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