Improved String Ribbon Silicon Solar Cell Performance by Rapid Thermal Firing of Screen-Printed Contacts

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***Abstract*—Al-enhanced SiN_x-induced hydrogenation is implemented to improve the minority carrier lifetime in String Ribbon Si. Rapid cooling after the hydrogenation anneal is found to increase the spatially averaged relative lifetime enhancement by over 160% for String Ribbon Si samples with a spatially averaged as-grown lifetime of 2.9 μs. Partial coverage of back surface by Al eliminates wafer bowing in 100 μm thick substrates, but reduces the spatially averaged lifetime enhancement to below 100% because vacancy generation at the back surface is decreased. Rapid thermal firing (RTF) of screen-printed contacts, with high heating and cooling rates, is found to improve String Ribbon solar cell efficiency by an average of 1.2% absolute over lamp heated belt furnace contact firing. Light beam-induced current (LBIC) mapping and light biased or differential internal quantum efficiency (IQE) analysis show that the enhancement in cell performance is primarily due to an improved effective diffusion length and diffusion length uniformity, which are both a result of the improved retention of hydrogen at defects achieved during rapid cooling after contact firing. Screen-printed String Ribbon cells with independently confirmed efficiencies as high as 14.7% are achieved through an understanding and implementation of hydrogen passivation of defects.**

***Index Terms*—Hydrogen passivation, multicrystalline silicon (mc-Si), rapid thermal processing (RTP), ribbon silicon, silicon nitride.**

I. INTRODUCTION

THE U.S. Photovoltaics Industry Roadmap calls for the development of 18% manufacturable cells on low-cost crystalline silicon materials within the next eight to ten years [1]. To meet this target, the as-grown minority carrier lifetime in low-cost Si materials must be increased to over 20 μs, and integrated with a high-quality surface passivation scheme, light trapping, a selective emitter, and high quality metallization, all achieved with manufacturable processing technologies. The prevalent low-cost Si materials used by the photovoltaics industry today are cast or directionally solidified multicrystalline Si, which have carbon and oxygen concentrations in the range of 10^{16}-10^{17} cm^{-3} and a dislocation density of approximately 10^{-5} cm^{-2}[2]. The String Ribbon Si growth process [3] can reduce the cost of solar cell substrates because thin ribbons (100 μm) can be grown directly from the melt, eliminating the losses associated with slicing and subsequent etching of wafers. The central regions of String Ribbon Si contain mostly coherent twin boundaries and an intragranular dislocation density of 5×10^5 cm^{-2}[2], as a result of thermal gradients produced during high-speed growth. String ribbon Si is grown in a graphite crucible, which results in a carbon concentration of 4×10^{17} cm^{-3} and a low oxygen concentration ($< 5 \times 10^{16}$ cm^{-3}) [2]. While the growth of String Ribbon makes it an attractive material for low-cost silicon photovoltaics, crystallographic defects and impurities limit the minority carrier lifetime and solar cell performance. Our previous work [4] has shown that the simultaneous anneal of a screen-printed Al layer on the back and a PECVD silicon nitride (SiN_x) film on the front after phosphorus gettering, can improve the spatially averaged lifetime in String Ribbon to over 30 μs, which is required to achieve $> 16\%$ efficient cells. During this anneal, hydrogen is released from the SiN_x film and passivates defects in the String Ribbon substrate. The role of Al in this process is to generate vacancies in Si as a result of Al-Si alloying. Vacancies dissociate molecular hydrogen into atomic hydrogen [5] and may enhance the diffusion of hydrogen in silicon [4]. Other researchers have reported an enhanced diffusion of H in silicon, mediated by vacancies generated by surface damage [6]. To describe the Al-enhanced SiN_x-induced hydrogenation, we have proposed a three-step physical model [4] in which defect passivation is governed by the release of hydrogen from the SiN_x film, the generation of vacancies, and the retention of hydrogen at defect sites. In this paper, we investigate the impact of improved hydrogen retention by rapid cooling after the hydrogenation anneal for increased bulk defect passivation. While beneficial for lifetime enhancement, we have found that full Al rear coverage causes thin (100 μm) String Ribbon Si wafers to bow during alloying at 850 °C. The bowing of thin wafers can be avoided by depositing Al in a grid pattern on the back. Partial coverage of the rear also permits bifacial cell designs where the surface between the Al grid may be passivated with a dielectric. The effect of reduced Al area

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rear coverage on Al-enhanced SiN_x-induced hydrogenation is investigated to eliminate bowing of thin wafers while achieving defect passivation.

Rapid thermal processing (RTP) has been investigated to reduce the thermal budget of solar cell processing and hence reduce processing costs. It has been shown that firing of screen-printed contacts in an RTP system can result in a contact resistance as low as 10^{-5} Ω-cm^2[7], though the resulting fill factor (FF) was only 0.724 on multicrystalline silicon, presumably due to junction leakage. Recently, the Design of Experiment technique has been implemented to optimize a rapid thermal firing (RTF) process resulting in FF as high as 0.782 on Cz Si and 0.774 on multicrystalline Si [8]. However, the influence of RTF on the bulk defect passivation of mc-Si solar cells, if any, was not identified. In this study, the impact of RTF, with fast heating and cooling rates, performed after the simultaneous screen-printed aluminum back surface field (Al-BSF) formation and SiN_x hydrogenation anneal is investigated for improved defect passivation and contact quality in String Ribbon Si solar cells. For comparison, cells are also fabricated with a lamp heated belt furnace contact firing scheme, characterized by slow heating and cooling rates. String ribbon solar cells are analyzed by illuminated current–voltage I–V) measurement, light beam-induced current (LBIC) mapping of spectral response, and light biased or differential internal quantum efficiency (IQE).

II. Experimental

A. Minority Carrier Lifetime Measurements

String ribbon samples with a thickness and resistivity of approximately 300 μm and 3 Ω-cm are selected for lifetime studies on the impact of partial Al coverage and cooling rate on SiN_x-induced hydrogen passivation. Because there is some variability in the lifetime in String Ribbon samples, the lifetime of each sample is measured before and after the defect passivation treatments. Prior to initial lifetime measurement, samples are cleaned using a sequence of solutions detailed in [4]. Silicon nitride films are deposited on all samples in a direct, parallel plate PECVD reactor operating at a frequency of 13.56 MHz and a temperature of 300 °C. A film thickness of 850 Å is deposited either on both surfaces or only the front surface (when Al is to be printed on the back) with an index of refraction of 1.95 using gas flow rates of 6.0 sccm for NH_3, 320 sccm for SiH_4 (2% in N_2) and 900 sccm for N_2 at a total pressure of 900 mtorr. After SiN_x deposition, Al paste (Ferro 53–038) is screen-printed on the back of selected samples. Selected samples are annealed at 850 °C for 2 min in an RTP system (AG Assoc. Heatpulse 610) and rapidly cooled to 500 °C at controlled rates, followed by natural cooling to room temperature. Selected samples are annealed for one second at 700 °C, followed by rapid cooling to 300 °C at controlled rates and natural cooling to room temperature in an RTP system. This 700°C/1 s anneal, referred to as RTF, simulates a co-firing scheme in which Al, SiN_x, and Ag front contacts are annealed simultaneously. The RTP system uses tungsten-halogen lamps to heat the sample and a thermocouple to monitor sample temperature as well as the heating and cooling rates, in a responsive closed-loop system.

To investigate the impact of partial Al coverage of the back surface on hydrogenation, Al paste is screen-printed onto to the back surface after SiN_x deposition on the front. Six different screens are used to print Al in a grid pattern and vary the Al area coverage fraction from 15 to 100% by increasing the density of lines in the screen pattern. The dimensions of the longitudinal and transverse lines are 4.7 cm and 7.4 cm, respectively. All samples are annealed in a belt furnace at a setpoint temperature of 850 °C for 2 min. The Al and SiN_x layers are removed by chemical etching and the samples are cleaned in the above series of solutions before final lifetime measurement. Lifetime measurements are made using the QSSPC technique [9] with samples immersed in an I_2/methanol solution that has been shown to effectively passivate silicon surfaces [10]. The QSSPC technique is based on the quasi-steady-state measurement of the average excess carrier concentration through the thickness of the sample as well as a lateral area of approximately 4 cm^2. Lifetime values are recorded at an injection level of 1×10^{15} cm^{-3} to avoid recording erroneously high recombination lifetimes at lower injection levels caused by shallow traps [11]. Because String Ribbon is a spatially nonuniform material, four lifetime measurements are made on each $\sim$ 25 cm^2 sample and the average lifetime value is used to characterize the entire substrate.

B. Solar Cell Fabrication

Samples for solar cell fabrication are cleaned in the series of solutions detailed in [4]. Following sample cleaning, phosphorus emitter diffusion is performed at a temperature of $\sim$ 960°C in a belt furnace using a spin-on liquid dopant to achieve a sheet resistance of 35-45 Ω/sq. A SiN_x film is deposited on the front surface and serves as an antireflective coating (ARC), a surface passivation dielectric, and a source of hydrogen for bulk defect passivation. After SiN_x deposition, Al is screen-printed to the back surface of all samples, baked, and annealed in a belt furnace at a set-point temperature of 850 °C for 2 min, forming an Al-BSF. During the anneal, the SiN_x film thickness and index change to approximately $t = 725$ Å and $n = 1.98$, which results in an effective single layer ARC. A silver paste (*Ferro 3349*) is screen-printed in a grid pattern onto the front surface of all samples and baked. Front contacts are fired by RTF at 700 °C for 1 s followed by rapid cooling at a rate of -40 °C/s. For comparison, the front contacts of selected solar cells are fired in a belt furnace (Radiant Tech. LA-310) at a setpoint temperature of 700 °C for 30 s in air followed by slow cooling at a rate of -4 °C/s. Finally, cells are isolated using a dicing saw to define an active area of 4 cm^2 per cell and annealed in forming gas (10% H_2) at 400 °C for 15 min.

III. Results and Discussion

A. Effect of the Cooling Rate on SiN_x-Induced Hydrogenation

The spatially averaged relative improvement in the lifetime of String Ribbon samples, with a spatially averaged as-grown lifetime of 2.9 μs, is measured as a function of the cooling rate after the post deposition anneal of the SiN_x film with and without Al. Samples shown in Fig. 1 were processed according

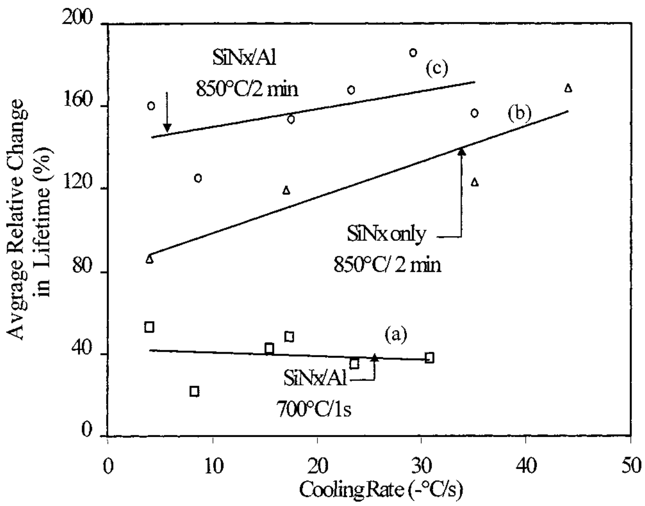

Fig. 1. Impact of rapid cooling on SiN_x-induced hydrogenation. The spatially averaged as-grown lifetime was 2.9 μs.

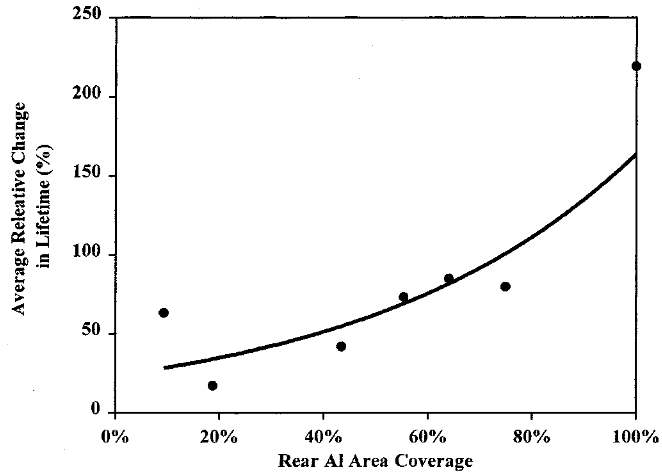

Fig. 2. Impact of Al area coverage on Al-enhanced SiN_x-induced hydrogenation at 850 °C/2 min with a cooling rate of -6°C/s. The spatially averaged as-grown lifetime was in the range of 2.0-3.8 μs.

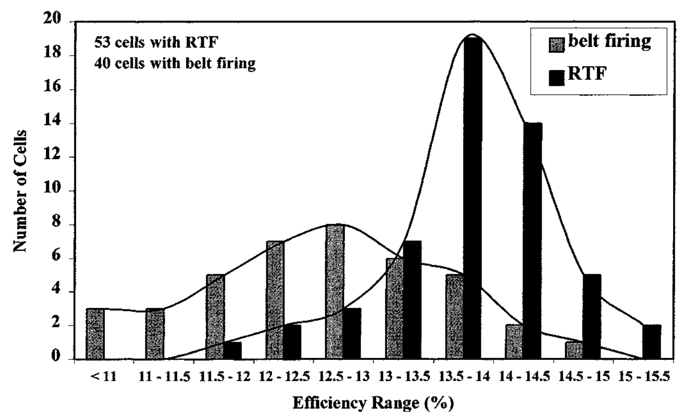

Fig. 3. Efficiency distribution of String Ribbon cells with RTF and belt furnace front contact firing.

to Section II-A. The cooling rate plotted in Fig. 1 is determined by measuring the time required for the sample temperature to decrease to 300 °C from 850 °C [curves (b) and c)] or 700 °C [curve (a)]. Fig. 1 shows that the spatially averaged relative improvement in lifetime is about 40% for all cooling rates for RTF [curve (a)]. In this process, the lifetime enhancement is limited by the release of hydrogen from the SiN_x due to the relatively short, low temperature anneal (1 s, 700 °C). When the anneal temperature and time are increased to 850 °C and 2 min, the spatially averaged relative change in lifetime increases with the cooling rate even when no Al is present on the back [curve (b)]. This suggests that the ability to retain hydrogen at defect sites in Si can be improved by increasing the cooling rate. It is well known that hydrogen can evolve out of Si above 500 °C during prolonged anneals [12]. The spatially averaged relative change in lifetime increases for all cooling rates when Al is present on the back [curve (c)] due to vacancy generation during Al–Si alloying. When Al is present on the back, vacancies generated during Al-Si alloying increase the flux of hydrogen in Si, which results in significant defect passivation. Fig. 1 also shows that the Al-enhanced hydrogenation process is less sensitive to the cooling rate [curve (c)]. The increased flux, or supply, of hydrogen in Si due to vacancy generation reduces the dependence of the passivation process on the retention of hydrogen.

B. Impact of Partial Al Coverage on Al-Enhanced SiN_x-Induced Defect Passivation

Fig. 2 shows the lifetime enhancement as a function of rear Al coverage after SiN_x/Al anneal at 850 °C/2 min followed by cooling at a rate of -6 °C/s. Samples shown in Fig. 2 had a spatially averaged as-grown lifetime in the range of 2.0–3.8 μs and were processed according to Section II-A. Full coverage (100%) of the rear surface by Al results in a spatially averaged relative change in lifetime of 219%. This lifetime enhancement is larger than expected based on the exponential fit of the data points in Fig. 2 and the data in Fig. 1. This discrepancy in the lifetime enhancement is likely due to differences in the spatially averaged as-grown lifetime and the defect distribution among the samples of the two experiments. The lifetime enhancement drops dramatically to 80% when the Al area coverage is reduced to 75%, which illustrates the importance of Al in the hydrogenation process. According to our model for Al-enhanced hydrogenation [4], the reduction in Al coverage reduces the amount of Al-Si alloying and thus the generation of vacancies, which enhance the dissociation and migration of atomic hydrogen. The lifetime enhancement decreases monotonically as the Al coverage decreases from 75% to 0%. While partial Al coverage reduces hydrogenation, 100-μm-thick String Ribbon samples do not bow during Al-Si alloying when the Al coverage is reduced to 75% or below. Preliminary results have shown that rapid cooling can improve the retention of hydrogen and increase the lifetime enhancement achieved with 55% Al coverage to 159%.

C. Solar Cell Results and Analysis

Fig. 3 shows the efficiency distribution of 93 String Ribbon cells with RTF with a cooling rate of -40 °C/s and belt furnace contact firing with a cooling rate of -4 °C/s. The solar cell efficiencies shown in Fig. 3 were measured using a calibrated String Ribbon Si solar cell measured at Sandia National Labs. While there is a wide distribution in the cell performance in both

TABLE I
AVERAGE STRING RIBBON CELL EFFICIENCY FOR BELT FURNACE CONTACT FIRING AND RTF

Contact Firing	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Eff (%)
RTF	576	31.42	0.763	13.8
belt furnace	562	30.12	0.746	12.6

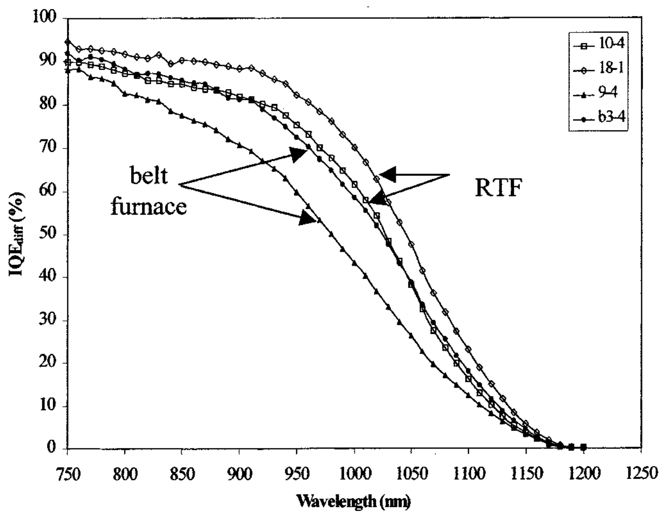

Fig. 4. Long wavelength differential IQE of cells with RTF and belt furnace contact firing.

schemes, RTF is clearly superior with an average cell efficiency of 13.8%, an improvement of 1.2% absolute higher than conventional belt furnace contact firing. This difference in efficiency is the result of differences in J_{sc}, V_{oc}, and FF, shown Table I, indicating that RTF improves the contact quality, minority carrier diffusion length, and possibly the rear surface passivation in String Ribbon devices.

LBIC and light biased or differential IQE analysis were performed on selected cells in order to evaluate the effective diffusion length in the bulk region of RTF and belt furnace fired cells. LBIC scans were performed using the PVSCAN 5000 system with a 905-nm laser to scan each cell. LBIC maps and average spectral responsivities (not shown) demonstrated that cells with RTF are more uniform and have a higher spatially averaged spectral response than those fired in the belt furnace. Hemispherical reflectance and differential spectral response measurements were performed by focusing the chopped monochromatic beam on the areas of the solar cell identified by LBIC analysis. The response in these areas was approximately equal to the average response for the entire cell. Differential spectral response measurements were biased by steady illumination with white light. The long wavelength differential IQE of four cells, shown in Fig. 4, indicates that cells with RTF have a higher response than those fired in the belt furnace, supporting the theory that RTF improves bulk and possibly rear surface passivation in String Ribbon solar cells. The effective diffusion length L_{eff} in these four cells was determined by the well-known relation

TABLE II
RESULTS OF L_{eff} ANALYSIS AND L_{bulk} ESTIMATE FOR CELLS FIRED IN THE BELT FURNACE AND BY RTF

Cell	Firing	Efficiency (%)	L_{eff} (μm)	Minimum L_{bulk}* (μm)
9-4	belt furnace	12.6	99	99
b3-4	belt furnace	12.8	212	197
10-4	RTF	13.8	281	247
18-1	RTF	13.8	544	411

* - Denotes estimate value

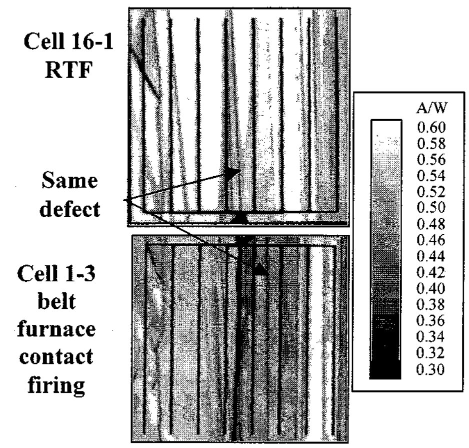

Fig. 5. Improved passivation of intergrain and intragrain defects by RTF.

shown below using tabulated absorption coefficient, α, data and measured IQE data in the wavelength range of 800-900 nm.

$$\frac{1}{IQE} = 1 + \frac{1}{\alpha L_{eff}}. \quad (1)$$

L_{eff} values for the four cells analyzed, shown in Table II, indicate that cells with RTF have a higher effective diffusion length, as expected based on the IQE data in Fig. 4. An estimate of the minimum bulk diffusion length (L_{bulk}) in these cells was determined by assuming a low rear surface recombination velocity ($S = 200$ cm/s), which has been measured on 2.3 Ω-cm float zone silicon solar cells with a similar screen-printed Al-BSF [13]. Table II show that the minimum bulk diffusion length in average regions of String Ribbon cells is in the range of 99-197 μm for belt furnace firing and 247-411 μm for RTF. Though cell b3-4, fired in the belt furnace, and cell 10-4 have similar diffusion lengths, their efficiency differs by 1.0% absolute. The large difference in the efficiency of these two cells is attributed mainly to the difference in spectral response uniformity (hence, diffusion length uniformity) identified by the LBIC analysis.

LBIC scans were made on cells taken from consecutive sections of the ribbon to identify differences in defect activity due to contact firing. Fig. 5 shows that these samples have similar crystallographic defect structures and the LBIC response in intragrain regions improves from 0.58 A/W to 0.64 A/W due to RTF. Fig. 5 also shows a defect whose activity decreases as the defect extends from cell 1–3 into cell 16–1. The reduced electrical activity of defects along with the cell efficiency results in

Table I suggest that RTF is more effective in retaining the hydrogen introduced in the 850 °C simultaneous Al/SiN_x anneal. In accordance with our model, these results suggest that the fast ramps associated with RTF improve the retention of hydrogen after the initial Al-enhanced SiN_x induced hydrogenation. The slow ramp rates in belt furnace contact firing result in dehydrogenation of defects, increasing their electrical activity.

IV. Conclusion

The results of this study indicate that the Al-enhanced SiN_x induced defect passivation can be improved by rapidly cooling samples after the hydrogenation anneal. Rapid cooling increases the retention of hydrogen at defects, improving defect passivation. Full Al coverage of the backside of samples results in the maximum spatially averaged lifetime enhancement of 219%, but causes 100-μm–thick substrates to bow during Al-Si alloying. Partial Al coverage eliminates wafer bowing, but decreases the spatially averaged lifetime enhancement to 80%. RTF improves String Ribbon cell efficiency by 1.2%, on average, over belt furnace contact firing. We have also found that the performance of EFG Si solar cells improves by 1.4% absolute due to RTF [14]. The relative improvement due to RTF is expected to be material dependent. Materials that benefit most from hydrogenation should show greater improvement in cell efficiency due to RTF. The efficiency improvement is the result of improved $J_{\rm sc}$, $V_{\rm oc}$, and FF. Based on our model for Al-enhanced hydrogenation, the improved bulk defect passivation during RTF is due to the fast cooling rate after the firing, which improves the retention of hydrogen at defects in the material. LBIC mapping and L_{eff} analysis of long wavelength differential IQE data confirm that RTF improves bulk and possibly surface passivation. An estimate of the minimum bulk diffusion length ranges from 99 to 197 μm in belt furnace fired cells to 247 to 411 μm in RTP fired cells. LBIC analysis also identifies reduced electrical activity of defects suggesting that RTF is more effective in retaining the hydrogenation introduced in the 850 °C simultaneous Al/SiN_x anneal.

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