Fundamental Understanding and Implementation of Al-enhanced PECVD SiN_x Hydrogenation in Silicon Ribbons

A. Rohatgi[1],V. Yelundur[1], J. Jeong[1], A. Ebong[1], M. D. Rosenblum[2], J. I. Hanoka[3]

[1]University Center of Excellence for Photovoltaics Research and Education, School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0250
[2]ASE Americas Inc., 4 Suburban Park Drive, Billerica, MA 01821
[3]Evergreen Solar, 211 Second Avenue, Waltham, MA 02154

ABSTRACT

A low-cost, manufacturable defect gettering and passivation treatment, involving simultaneous anneal of a PECVD SiN_x film and a screen-printed Al layer, is found to improve the lifetime in Si ribbon materials from 1-10 μs to over 20 μs. Our results indicate that the optimum anneal temperature for SiN_x-induced hydrogenation is 700°C for EFG and increases to 825°C when Al is present on the back of the sample. This not only improves the degree of hydrogenation, but also forms an effective back surface field. We propose a three-step physical model, based our results, in which defect passivation is governed by the release of hydrogen from the SiN_x film due to annealing, the generation of vacancies during Al-Si alloying, and the retention of hydrogen at defect sites due to rapid cooling. Controlled rapid cooling was implemented after the hydrogenation anneal to improve the retention of hydrogen at defect sites by incorporating an RTP contact firing scheme. RTP contact firing improved the performance of ribbon solar cells by 1.3-1.5% absolute when compared to slow, belt furnace contact firing. This enhancement was due to improved back surface recombination velocity, fill factor, and bulk lifetime. Enhanced hydrogenation and rapid heating and cooling resulted in screen-printed Si ribbon cell efficiencies approaching 15%.

1. Introduction

The U.S. PV Industry Roadmap has identified the development of 18% efficient thin Si solar cells as a top R&D goal to be achieved in the next 3-10 years [1]. Si ribbon materials such as Edge-defined film-fed grown (EFG), dendritic web, and String Ribbon Si may offer the substrates of choice to meet this goal because thin (~100 μm) ribbon samples can be grown directly from the melt, eliminating losses associated with wafer slicing and etching. Although the low-cost growth of Si ribbon samples makes them attractive for photovoltaic substrates, the as-grown minority carrier lifetime is typically in the range of 1-10 μs, which is not suitable for high-efficiency cells (≥15%). Several gettering and passivation techniques have been examined for the improvement in the lifetime of Si PV materials including P and Al gettering and hydrogen passivation via post-deposition anneal of PECVD SiN_x films. The aim of this study is to raise the lifetime in low-cost Si ribbon materials to over 20 μs by investigating the combination of SiN_x-induced hydrogenation and Al gettering, and to identify any synergism between the two. To evaluate the effectiveness of the passivation treatments in this study and improve the fundamental understanding of the hydrogenation process, minority carrier lifetime measurements were performed before and after the passivation treatments. A physical model is proposed which relates the high temperature (850°C) SiN_x-induced hydrogenation to the release of hydrogen into the sample, the injection of vacancies from backside Al/Si alloying, and the retention of hydrogen at defects. This model is further validated by implementing RTP for the post- deposition anneal of SiN_x and contact firing. Finally, high-efficiency solar cells are fabricated and analyzed to demonstrate the positive synergistic effects of Al-enhanced hydrogenation and RTP.

2. Fundamental Understating and Modeling of Gettering and Passivation of Defects in Si ribbon

2.1. Experimental Details of Defect Gettering and Passivation Treatments

EFG, dendritic web, and String Ribbon Si samples were grown by *ASE Americas*, *Ebara Solar Inc.*, and *Evergreen Solar*, respectively. EFG and String Ribbon samples with thickness of ~300 μm and a base resistivity of ~3 Ω-cm, and dendritic web samples with a thickness of ~100 μm and a base resistivity of ~20 Ω-cm were used in this study. Samples were etched and cleaned before and after each lifetime measurement as detailed elsewhere [2]. Lifetime measurements were made before and after each gettering and passivation treatment using the quasi-steady state photoconductance (QSSPC) technique with samples immersed in an I_2/methanol solution. Due to the variation in lifetime across these samples, several lifetime measurements were made on each sample. Average lifetime values were recorded at an injection level of 1 x 10^{15} cm^{-3} to avoid erroneously high recombination lifetimes at lower injection levels caused by shallow traps [3]. After the initial lifetime measurement, samples were cleaned and subjected to various manufacturable gettering and passivation process sequences involving P and Al gettering, and SiN_x-induced hydrogenation, individually and in combination. P gettering involved the application of a spin-on doped film (*Filmtronics P507-6% or P506 -6%*) followed by belt furnace (*Radiant Tech. Corp.*) diffusion at ~ 930°C to form a 45 Ω/sq. emitter. SiN_x-induced hydrogenation was performed by SiN_x film deposition and anneal in a belt furnace or an RTP system (*AG Assoc. 610*) at temperatures in the range of 500°C-900°C. SiN_x films were deposited in a direct-plasma PECVD reactor operating at a frequency of 13.56 MHz and plasma power of 30 W at 300°C. A film thickness of 830 Å was deposited with an index of refraction (n) of 1.98. This film densifies to 780 Å and n=2.0 after an Al-BSF anneal to give a suitable anti-reflective coating. Al gettering was performed by annealing a screen-printed Al paste (*Ferro FX 53-038*) on the back of samples.

2.2. Al-enhanced PECVD SiN_x-induced hydrogen passivation of Si ribbons

Fig. 1 shows the lifetime enhancement in EFG, dendritic web, and String Ribbon Si due to gettering and hydrogen passivation treatments. The lifetime of EFG and dendritic web Si did not increase after PECVD SiN_x film deposition and anneal at 850°C in a belt furnace, while the lifetime of String Ribbon showed a moderate increase from 8.3 µs to 12.9 µs. The ~930°C P and 850°C Al gettering treatments improved the lifetime in all three ribbon materials but were unable to raise the lifetimes over 20 µs. To identify any interaction between the Al gettering and hydrogen passivation processes, the SiN_x-induced hydrogenation and Al gettering treatments were performed simultaneously at 850°C after the P gettering. The simultaneous anneal of SiN_x and Al increased the lifetime in EFG, dendritic web, and String Ribbon Si to 25.6 µs, 20.0 µs, and 38.4 µs, respectively. The significant enhancement in lifetime achieved after the simultaneous anneal of SiN_x and Al indicates that there is a positive synergistic interaction between the SiN_x-induced hydrogenation on the front and Al-Si alloying at the back of the sample which enhances the lifetime to over 20 µs in all three materials.

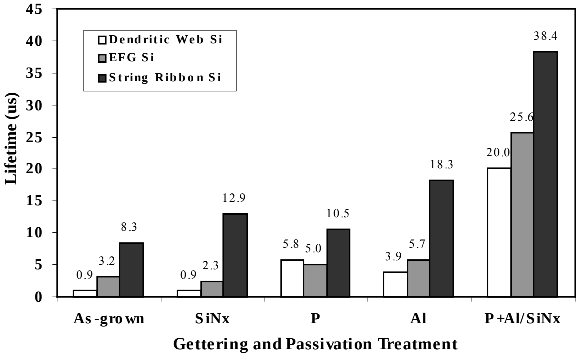

Fig. 1. Al-enhanced SiN_x-induced defect passivation in Si ribbon materials.

2.3. Optimization of the simultaneous SiN_x/Al anneal temperature in an RTP system for defect gettering and passivation

To improve the understanding of Al-enhanced SiN_x-induced hydrogenation, we have optimized the Al/SiN_x anneal temperature in an RTP system. The results of SiN_x-induced defect passivation and Al gettering in EFG Si, individually and in combination, as a function of the RTP anneal temperature are shown in Fig. 2. The as-grown lifetime of EFG samples in this study was in the range of 1.5-2.0 µs. SiN_x-induced defect passivation was ineffective at temperatures below 600°C, and improves the lifetime by only about 1 µs when the anneal temperature is raised to 700°C. FTIR measurements of annealed PECVD SiN_x films showed that the release of hydrogen from the SiN_x film increases with the anneal temperature [4]. The decrease in SiN_x-induced passivation above 700°C maybe due to a decrease in the retention of hydrogen at defect sites in Si at high temperatures. In the absence of Al on the back, the competition between the release of hydrogen from the SiN_x film and the retention of hydrogen at defect sites in Si results in an optimum anneal temperature at 700°C for the SiN_x-induced passivation of defects in EFG Si.

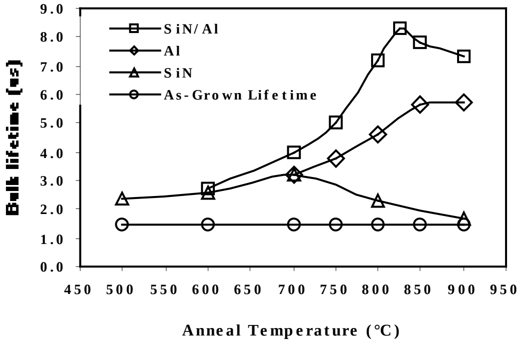

Fig. 2. Optimization of the anneal temperature for Al-enhanced SiN_x induced defect passivation.

Fig. 2 shows that the effectiveness of Al gettering of EFG Si increases with the anneal temperature resulting in a lifetime of about 5.7 µs at 850°C - 900°C. The combined effect of simultaneous SiN_x-induced defect passivation and Al gettering (Al/SiN_x) in EFG Si is shown in Fig. 2. The presence of Al on the back of the samples during the anneal shifts of the optimum anneal temperature from 700°C to 825°C and increases the maximum lifetime from 3.2 to 8.3

μs as shown in Fig. 2. This improvement in lifetime is much greater than the sum of the improvements due to the individual SiN_x and Al treatments for all temperatures above 700°C, indicating that there is a synergistic interaction between the hydrogenation process and Al/Si alloying above 700°C. The increase in the optimum anneal temperature for Al/SiN_x above 800°C for lifetime enhancement is also expected to improve the quality of the Al-BSF and hence the cell performance [5]. The absolute lifetime values shown in Fig. 2 are low partly due to the absence of prior P gettering and the use of very low as-grown lifetime samples.

2.4. Physical Model for Al-enhanced SiN_x-induced hydrogenation

We propose a three-step physical model according to 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 Si. At low temperatures, the effectiveness of the SiN_x/Al anneal is reduced by the limited release of hydrogen from the SiN_x film, the low generation of vacancies during Al alloying, and the ineffectiveness of Al gettering. When the anneal temperature is increased to 825°C, vacancies generated in Si during Al/Si alloying, increase the dissociation of molecular hydrogen into atomic hydrogen [6] and enhance the transport of hydrogen in Si. The high binding energy of hydrogen to vacancy clusters (3-4 eV) [7] provides an additional driving force for the diffusion of hydrogen enabling the passivation of defects deep in Si. At temperatures above 825°C, the retention of hydrogen at defects in Si decreases which lowers the lifetime.

2.5. Controlled rapid cooling for improved defect passivation

To support the above model, the relative improvement in the lifetime of String Ribbon samples was measured as a function of the cooling rate after the post deposition anneal of the SiN_x film with and without Al. After SiN_x deposition onto both surfaces or only the front surface (when Al is printed on the back), samples were annealed at 850°C for 2 minutes and rapidly cooled to 500°C at controlled rates followed by rapid cooling to room temperature. In another experiment, Al/SiN_x annealing was done for a very short time at a temperature below 750°C. This was followed by rapid cooling to 300°C at controlled rates and rapid cooling to room temperature in an RTP system. This anneal simulates a co-firing scheme in which Al, SiN_x, and Ag front contacts can be annealed simultaneously. Fig. 3 shows that the average relative improvement in lifetime is about 40% for all cooling rates (curve (a)) for the RTP co-firing scheme. 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. When the anneal temperature and time are increased to 850°C and 2 minutes, the average relative change in lifetime increases with the cooling rate after anneal 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 after the anneal. It is well known that hydrogen can evolve out of Si above 500°C during prolonged anneals [6]. The average relative change in lifetime increases for all cooling rates when Al is present on the back, curve (c) in Fig. 3, 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. 3 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.

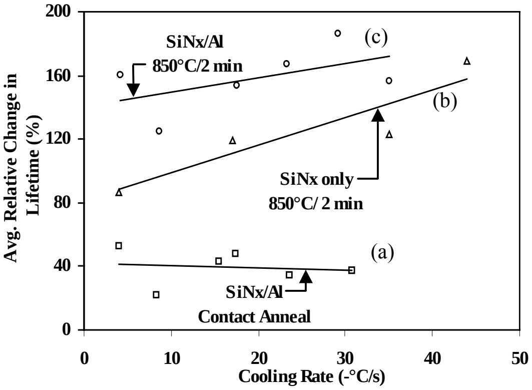

Fig. 3. Impact of the cooling rate on the effectiveness of the SiN_x induced hydrogen passivation process.

3. Fabrication and analysis of high-efficiency, screen-printed Si ribbon solar cells by enhanced hydrogenation

The results in Fig. 3 reveal that the Al-enhanced SiN_x-induced defect passivation is more effective when the anneal is performed at 850°C for 2 minutes. However, prolonged high temperature anneals are not compatible with front contact firing. Therefore, a second firing step, dedicated only to front contact firing, is necessary after the initial hydrogenation and Al-BSF formation. To investigate the stability of the Al-enhanced SiN_x-induced defect passivation during front contact firing anneals; EFG, String Ribbon, and float zone Si solar cells were fabricated with front contacts fired in a belt furnace with a low heating and cooling rate (<7°C/s), or in an RTP system having a high heating and cooling rate (>10°C/s).

After sample cleaning, n^+-emitter diffusion, PECVD SiN_x deposition, Al screen-printing and annealing at 850°C in a belt furnace (all detailed in section 2.1), Ag paste (*Ferro 3349*) was screen-printed onto the front surface of all of the samples.

After RTP or belt furnace firing of contacts, 4 cm^2 cells were isolated using a dicing saw. Table 1 shows that the average float zone cell efficiency improves by 0.5% (absolute) when the front contacts are fired in the RTP system after the SiN_x/Al simultaneous anneal at 850°C in the belt furnace. Analysis of the long wavelength IQE showed that RTP contact firing improves the back surface recombination velocity by a factor of two, due to the rapid remelting of Al which improves the uniformity of the Al-BSF [8]. Table 1 also shows that efficiency of EFG and String Ribbon solar cells increase by 1.4% and 1.7% respectively due to RTP front contact firing. Noteworthy high efficiencies of 14.7% (measured by Sandia National Labs.) and 14.6% were achieved on String Ribbon and EFG when contacts were fired in the RTP system. The efficiency enhancement from RTP contact firing of ribbon cells is reflected in improved bulk and surface passivation (J_{sc} and V_{oc}) and contact quality (FF).

Table 1. Impact of RTP front contact firing on float zone, EFG, and String Ribbon Si solar cells.

Contact Firing			V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Eff (%)
RTP	Float Zone	Average	621	34.2	0.777	16.5
		High	622	34.3	0.779	16.6
	EFG	Average	573	32.1	0.749	13.8
		High	585	32.8	0.757	14.6
	String Ribbon	Average	574	31.6	0.762	13.8
		High *	600	31.6	0.778	14.7
Belt Furnace	Float Zone	Average	614	33.7	0.770	15.9
		High	615	33.9	0.771	16.1
	EFG	Average	554	30.1	0.743	12.4
		High	566	30.9	0.751	13.1
	String Ribbon	Average	553	29.7	0.738	12.1
		High	575	31.1	0.747	13.4

* - confirmed by Sandia National Labs.

Fig. 4 shows LBIC scans, made with the *PVSCAN 5000* system using a 905 nm laser, of String Ribbon cells taken from consecutive sections of the ribbon to identify defects and their activity. Note that these samples have similar crystallographic defect structures. The LBIC response in intragrain regions improved from 0.58 A/W to 0.64 A/W with RTP contact firing as opposed to slow belt firing. Fig. 4 reveals a defect whose activity decreases as the defect extends from Cell 1-3 into Cell 16-1. The cell efficiency data in Table 1 and LBIC analysis in Fig. 4 indicate that RTP firing of screen-printed contacts is more effective in retaining the hydrogen at defects that was introduced during the 850°C Al/SiN_x anneal. Conversely, the slow ramp rates during belt furnace contact firing result in increased dehydrogenation of defects, increasing their electrical activity.

4. Conclusion

SiN_x-induced hydrogen passivation of Si ribbons has been found to be most effective when the SiN_x post-deposition anneal includes controlled rapid cooling and backside Al alloying. A three-step model is proposed and relates the hydrogen passivation to the release of hydrogen from the SiN_x film, retention of hydrogen at defect sites, and injection of vacancies generated during Al/Si alloying. Vacancies generated during Al alloying enhance the dissociation of hydrogen molecules and the flux of atomic hydrogen deep into the bulk Si to improve bulk passivation. RTP contact firing was found to be more effective in preserving the hydrogen defect passivation achieved during the initial hydrogenation step and has resulted in 4-cm^2 screen-printed cell efficiencies as high as 14.7% on 300μm thick String Ribbon Si and 14.6% on 300 μm EFG Si.

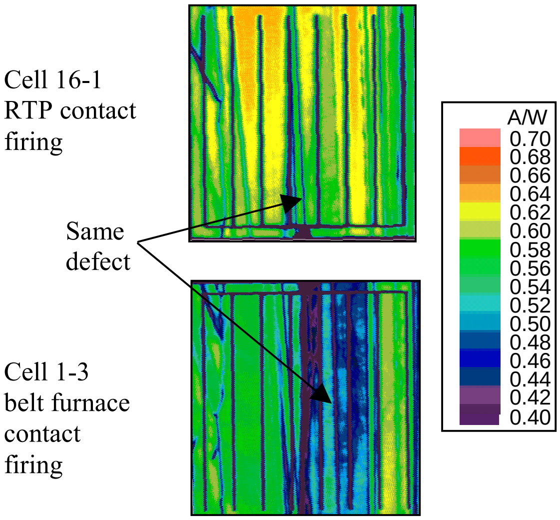

Fig. 4. Improved passivation of intergrain and intragrain defects with RTP contact firing.

Acknowledgement

This work was supported by NREL contract No. XA8-17607-5 and Evergreen Solar through NIST contract 1997-01-0257.

References

[1] NCPV, [Online document], Available HTTP: http://www.nrel.gov/ncpv/pdfs/27450.pdf, (1999).

[2] V. Yelundur, A. Rohatgi, J. Electron.Mats. **30** (5), 526 (2001).

[3] D. Macdonald, A. Cuevas, Appl, Phys. Letts., **74**, 1710 (1999).

[4] A. Ebong, P. Doshi, S. Narasimha, A. Rohatgi, J. Wang, M.A. El-Sayed, J. Electroche. Soc. **146**, 1921 (1999).

[5] S. Narasimha, A. Rohatgi, Proc. 26th IEEE PVSC, Anaheim, CA, 63 (1997).

[6] S. K. Estreicher, J. L. Hastings, Phys. Rev. B. **57**, 12663(1998)

[7] S. K. Estreicher, J. L. Hastings, P. A. Fedders, Mater. Sci. Eng. **B58**, 31 (1999).

[8] J-W. Jeong, A. Rohatgi, to be published.