LIFETIME ENHANCEMENT IN EFG MULTICRYSTALLINE SILICON

J.-W. Jeong, A. Rohatgi
University Center of Excellence for Photovoltaics Research and Education
School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

M. D. Rosenblum, J. P. Kalejs
ASE Americas, Inc. 4 Suburban Park Drive Billerica, MA 01821, U.S.A.

ABSTRACT

P and Al gettering and SiN-induced hydrogenation of EFG Si have been investigated using manufacturable process techniques. Annealing of SiN coated EFG, without Al on the back, shows very little defect passivation with maximum lifetime enhancement at 700°C. However, annealing of the SiN film, in the presence of Al, significantly increases the defect passivation and moves the optimum temperature to above 800°C. This increase in the optimum temperature is the result of tradeoff between the increase in the release of hydrogen from the SiN film and the decrease in the retention of hydrogen at defects at high temperatures. A higher annealing temperature (>800°C) is desirable because it produces a superior Al-BSF without sacrificing defect passivation. Finally, it is shown that the efficacy of the gettering and hydrogenation process is a strong function of the as-grown lifetime, which dictates the final lifetime as well as cell efficiency.

INTRODUCTION

The cost of silicon (Si) photovoltaic (PV) modules must decrease by at least a factor of two for large-scale applications. Si material accounts for about one-third or more of the cost of the current Si PV modules. Sheet or ribbon Si technologies can significantly reduce the cost of Si PV by providing the efficient use of Si feedstock with no mechanical sawing steps, no deep surface damage etching, and the ability to grow thin Si substrates.

EFG Si ribbon is one of the most promising candidates to achieve both low cost and high efficiency. EFG Si ribbon is pulled through a graphite die via capillary action. Due to the direct contact with the die and thermal stresses, EFG Si ribbon has a high density of crystallographic defects such as dislocations, twins, and grain boundaries, and relatively high concentrations of impurities such as carbon, oxygen, and transition metals [1]. These defects and impurities act as carrier recombination sites. As a result, the minority carrier lifetime is typically in the range of 1 to 5 μs, which is not enough for high efficient cells (≥15 %).

Fig. 1 shows the result of a PC1D calculations for a 300 μm thick EFG Si ribbon as a function of carrier lifetime for three different back surface recombination velocities (BSRV). The calculations reveal that the carrier lifetime limits the screen-printed (SP) EFG Si cell efficiency for lifetimes below ~30 μs. For a 300 μm thick device, the carrier lifetime should be greater than 30 μs to realize the full benefit of a low BSRV. Therefore, lifetime enhancement is essential for achieving high efficiency solar cells on low cost Si ribbon materials.

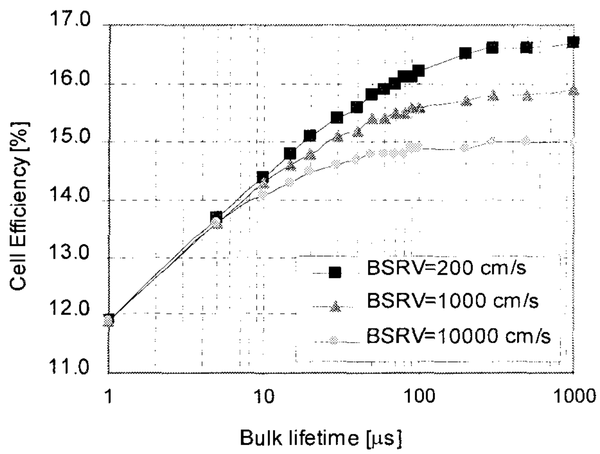

Fig. 1. PC1D calculation for EFG ribbon solar cell showing cell efficiency as a function of carrier lifetime for three different back surface recombination velocity (BSRV) values.

Gettering of impurities and hydrogen passivation of defects have been shown to be very effective in improving the electrical properties of PV grade multicrystalline silicon (mc-Si) materials [2-3]. However, further understanding is necessary to maximize their impact during rapid manufacturing techniques, such as belt-line processing (BLP) and rapid thermal processing (RTP).

In this paper, the effects of low cost gettering and hydrogen passivation techniques have been investigated to improve the bulk lifetime in EFG Si ribbon. Spin-on doped P diffusion and SP Al back surface field (BSF) formation were used for gettering of impurities. For defect passivation, a plasma enhanced chemical vapor deposited (PECVD) SiN film was annealed, with and without the presence of SP Al, to understand the role of Al in the

0-7803-5772-8/00/$10.00 © 2000 IEEE

hydrogenation process. All heat treatments were performed in either a conveyor belt furnace or a single-wafer RTP system. Retention of hydrogen in the hydrogenated EFG Si ribbon was also studied to understand the reason for optimum annealing conditions. Finally, the effect of as-grown lifetime on the response to gettering and hydrogenation treatments was studied to explain the cell efficiency distribution in EFG Si solar cells.

RESULTS AND DISCUSSION

1. Al-enhanced PECVD SiN hydrogen passivation of EFG Si ribbon

Fig. 2 shows the lifetime enhancement in EFG Si ribbon due to gettering and hydrogenation processes. Spin-on doped P diffusion at 930 °C / 6 min in the BLP and at 925 °C / 1 min in the RTP increased the lifetime from 1.2 to 3.1 μs and from 1.5 to 2.9 μs, respectively. These conditions were selected to form an n^+ emitter with a sheet resistance of ~40 Ω/ , which is suitable for SP contacts. The P diffusion at 930 °C / 1 min in the BLP did not improve the lifetime. After the P diffusion, SP Al paste was applied to the backside of the wafer and alloyed at 850 °C / 2 min in the BLP and the RTP. This treatment increased the lifetime from 3.1 to 7.5 μs in the BLP and from 2.9 to 9.5 μs in the RTP, respectively. Although short gettering treatments by P and Al were effective for lifetime enhancement in EFG Si ribbon, the lifetime is still not high enough to achieve high efficiency (≥15 %). Therefore, In order to improve the lifetime further, PECVD SiN-induced hydrogen passivation of defects was implemented by post-deposition anneal of a SiN film at 850 °C / 2 min, with and without the SP Al layer on the backside.

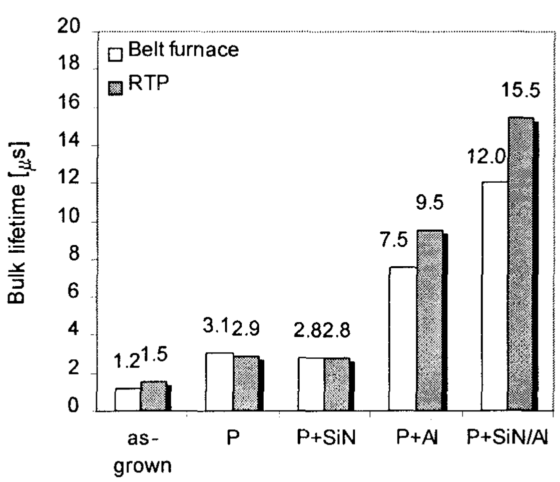

Fig. 2. Bulk lifetime response of EFG silicon to gettering and hydrogenation treatments in conveyor belt and RTP.

As shown in Fig. 2, post-deposition anneal of a SiN film, without the Al on the back, did not produce appreciable lifetime improvement for the BLP and the RTP. This suggests that either annealing of SiN at 850 °C / 2 min is not effective for passivation of defects, or the lifetime is dictated by other mechanisms. However, annealing of the SiN film, in the presence of Al, at 850 °C / 2 min significantly enhanced the hydrogenation ability of the SiN film for both the BLP and the RTP. Recall that the combined effect of the P and Al gettering treatments raised the lifetime from 1.2 to 7.5 μs in the BLP and from 1.5 to 9.5 μs in the RTP, respectively. Therefore, the additional 4.5 μs and 6.0 μs increases obtained here in the BLP and the RTP, respectively, must come from a positive synergistic effect of the simultaneous anneal of SiN and Al. This can be explained on the basis of vacancies generated at the back surface due to the Al/Si alloying. These vacancies increase the chemical potential gradient for the hydrogen diffusion from the SiN film. In addition, vacancies can also dissociate molecular hydrogen, resulting in a higher atomic hydrogen concentration available for defect passivation.

The above hypothesis is supported by the data in Table 1, which shows that a sequential process where Al and SiN heat treatments are performed separately gives lower bulk lifetime compared to the simultaneous process. In the sequential process, an Al-Si eutectic layer, initially formed during the Al alloying, melts during the SiN anneal at 850 °C. This eutectic layer already contains 12 at.% Si. Therefore, less Si is dissolved in this molten alloy and fewer vacancies are generated during the subsequent SiN hydrogenation step. As a result, we observe less defect passivation or low bulk lifetime for sequential annealing.

Table 1. Effect of simultaneous and sequential annealing of SiN and Al on SiN-induced hydrogen passivation of defects in EFG Si.

Process Scheme	Process Sequence	Final lifetime
Simultaneous	P+SiN/Al (850°C)	14.5 μs
Sequential	P+Al(850°C)+SiN(850°C)	7.5 μs

No appreciable difference was observed between the BLP and the RTP for P gettering and SiN-induced hydrogenation steps, Fig. 2, in the absence of Al. However, the P gettering time in the RTP was only 1 min, much shorter than 6 min in the BLP, suggesting that the RTP may be more efficient in gettering impurities. In addition, Fig. 2 reveals that the RTP is also more effective, than the BLP, for SiN-induced hydrogenation when the SiN and Al are annealed simultaneously. This is probably due to the fact that RTP delivers much higher energy photons to the wafer, which may enhance the release of hydrogen from the SiN film, diffusion of hydrogen in Si, or the vacancy generation at the Si/Al interface during the simultaneous processing.

2. Optimization of SiN-induced hydrogen passivation via a simultaneous annealing of SiN and Al in EFG Si ribbon

Since a simultaneous annealing of SiN and Al increased the lifetime more than the sum of improvement due to individual treatments, a systematic study was performed to further optimize the simultaneous processing of SiN and Al for EFG Si ribbon. In this experiment, EFG Si ribbon samples with fairly low as-grown lifetimes of ~ 1.5 μs were selected. Annealing of PECVD SiN film and SP Al were performed in the RTP at different temperatures. The bulk lifetime was measured before and after the treatments to quantify the effect.

Post-deposition anneal of SiN film in the RTP, without the presence of Al, showed very little defect passivation with maximum lifetime enhancement at 700 °C. As the annealing temperature increased above 700 °C, lifetime enhancement began decreasing as shown in Fig. 3. This result indicates that retention of hydrogen at defect decreases at higher temperatures (> 700 °C). On the other hand, Al-enhanced hydrogenation due to vacancy generation, release of hydrogen from the SiN film, and gettering efficacy of Al increases with the increase in alloying temperature above 700 °C. The tradeoff between these processes result in a higher optimum annealing temperature in the presence of Al, Fig. 3. It is important to recognize that a higher annealing temperature (≥ 800 °C as opposed to 700 °C) is desirable because it can produce a superior Al-BSF without sacrificing hydrogenation.

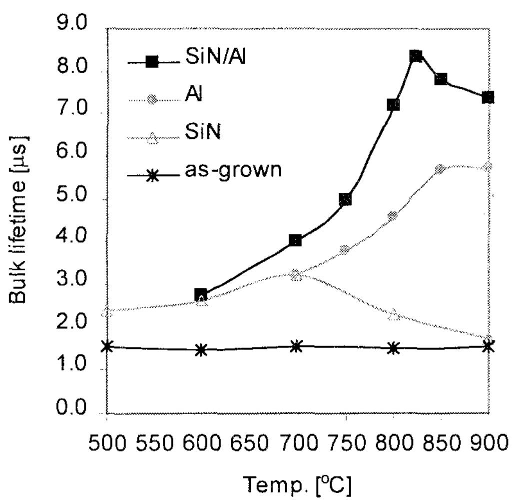

Fig. 3. Optimization of SP Al gettering and PECVD SiN-induced hydrogen passivation in EFG Si ribbon.

Fig. 3 also shows that the improvement in lifetime due to the simultaneous annealing is much greater than the sum of the improvements due to the individual SiN and Al treatments for all temperatures above 700 °C, indicating a positive synergistic interaction between the hydrogenation process and Al/Si alloying. At low temperatures below 700 °C, the effect of the simultaneous annealing of SiN and Al is limited by the release of hydrogen from the SiN film, the low generation of vacancies during heat treatment, and the ineffectiveness of Al gettering. As the temperature increases to 700 °C, the release of hydrogen increases, but vacancy generation remains low due to the low solubility of Si (~20 at.%) in the Al melt, and there is no positive synergistic effect as shown in Fig. 3. As the solubility of Si in Al increases to ~30 at.% at 825 °C, vacancy generation at the Al/Si interface increases significantly, enhancing the defect passivation. Finally, at temperatures above 850 °C, lifetime drops due to lower retention of hydrogen at defects. This is supported by the observation in the following section. The absolute lifetime values shown in Fig. 3 are low due to the absence of prior phosphorus gettering.

Similar to the RTP, an optimum temperature for the simultaneous annealing of SiN and Al in the BLP was found at ~850 °C. Decrease in lifetime enhancement at higher annealing temperature above 850 °C was also observed.

3. Annealing-induced dehydrogenation of hydrogenated EFG Si ribbon

For further understanding of the retention of atomic hydrogen at defects, an experiment was designed and performed using hydrogenated EFG Si ribbon samples. The hydrogenated EFG samples were annealed at temperatures in the range of 400 ~ 700 °C in the RTP in N_2 ambient. The bulk lifetime was measured after each re-annealing treatment.

Fig. 4 shows that the hydrogenated bulk lifetime did not change due to re-annealing until about 500 °C. The lifetime decreased by ~20 % at 600 °C and by another ~45% at 700 °C. The lifetime degradation shown in Fig. 4 indicates that passivated defects become reactivated above 500 °C due to dissociation of hydrogen. This is the reason for the decrease in lifetime above 850 °C during simultaneous anneal in Fig. 3.

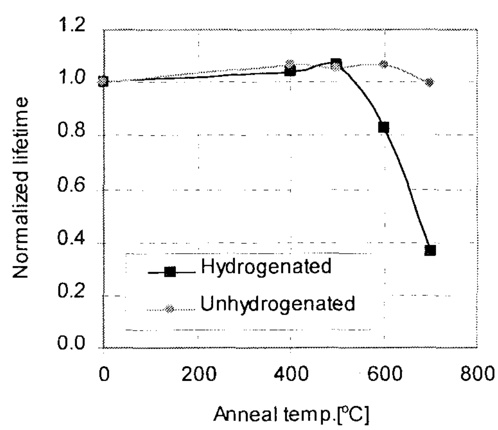

Fig. 4. Lifetime change in hydrogenated and unhydrogenated EFG Si ribbon due to 5 s re-annealing in the RTP.

4. Effect of as-grown lifetime on final lifetime and solar cell performance in EFG Si ribbon

The effect of hydrogen passivation of defects on minority carrier lifetime in low cost mc-Si materials is generally material specific [5]. Some investigators have shown that hydrogen passivation of defects produces greater diffusion length improvement in lower quality regions [5-6]. Since bulk lifetime in the as-grown EFG Si ribbon can vary from ~1 to 5 μs over a 10 × 10 cm^2 wafer, the impact of as-grown lifetime on solar cell performance and efficacy of lifetime enhancing techniques was investigated.

Fig. 5 shows the correlation between as-grown lifetime and processed lifetime after the gettering and hydrogenation processes in the BLP. Results reveal that the final lifetime after the gettering and hydrogenation treatments strongly depends on the as-grown lifetime. The production-worthy gettering and hydrogenation techniques used in this study are more effective if the as-grown lifetime is greater than ~3 μs. For example, the as-grown lifetime of 5 μs increases to ~50 μs while the as-grown lifetime of 2 μs goes to only ~10 μs after the same gettering and hydrogenation treatments. The corresponding cell efficiencies are ~10% and ~13.5%. Thus in order to achieve high efficiency (≥15%) in SP EFG Si solar cells, either as-grown lifetimes should be higher than 3μs, or more intense and effective lifetime enhancement techniques should be developed.

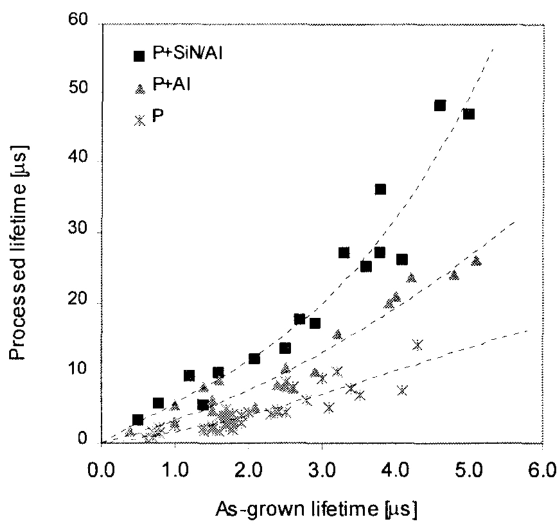

Fig. 5. Measured bulk lifetime as a function of as-grown lifetime after gettering and hydrogenation treatments in EFG Si ribbon.

CONCLUSION

Cost effective gettering and hydrogenation techniques have been successfully applied to improve the bulk lifetime in EFG Si ribbon during cell processing. RTP produced greater improvement in bulk lifetime compared to BLP. Annealing of SiN, in the absence of Al, does not provide much defect passivation in EFG Si and shows a weak maximum at 700 °C. However, a simultaneous annealing of PECVD SiN and SP Al has been found to enhance the bulk lifetime much more than the sum of enhancement due to individual SiN and Al treatments. Simultaneous annealing of SiN and Al also increases the optimum hydrogenation temperature from 700 °C to above 800 °C for both the RTP and the BLP techniques. Finally, lifetime improvement due to the gettering and hydrogenation techniques and cell performance were found to be a strong function of the starting lifetime in EFG Si ribbon.

ACKNOWLEDGMENT

This work was supported in part by a subcontract via ASE Americas from DOE/NREL Subcontract No. ZAX-8-17647-10 and in part by the NREL Subcontract No. XA8-17607-05.

REFERENCES

[1] R. O. Bell et al., "Growth of silicon sheets for photovoltaic applications", *J. Mater. Res.* **13** (10), 1998, pp. 2732-2739.

[2] P. Sana et al., "Gettering and hydrogen passivation of edge-defined film-fed grown multicrystalline silicon solar cells by Al diffusion and forming gas anneal", *Appl. Phys. Lett.* **64** (1), 1994, pp. 97-99, 1994.

[3] B. Sopori et al., "A comparison of gettering in single- and multicrystalline silicon for solar cells", *Proc. of 25th IEEE Photovoltaic Specialists Conference*, 1996, pp. 625-628.

[4] M. Spiegel et al., "Investigation of hydrogen diffusion, effusion and passivation in solar cells using different multicrystalline silicon base materials", *Proc. of 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, 1998, pp. 1685-1688.

[5] R. Lüdemann et al., "Hydrogen passivation of low-and high-quality mc-Silicon for high-efficiency solar cells", *Proc. of 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, 1998, pp. 1638-1641.

[6] J. Bailey et al., "Material electronic quality specification factors for polycrystalline silicon wafers", *Proc. of 1st World Conference of Photovoltaic Energy Conversion*, 1994, pp. 1356-1359.