PECVD SiN_X INDUCED HYDROGEN PASSIVATION IN STRING RIBBON SILICON

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ABSTRACT

To improve the bulk minority carrier lifetime in String Ribbon silicon, SiN_x induced defect passivation during a post deposition anneal is investigated. Our results indicate that SiN_x induced hydrogen passivation is very effective when the SiN_x film is annealed in conjunction with a screen-printed Al layer on the back. In addition, it is found that controlled rapid cooling can be used to enhance the defect passivation process. A model is proposed which relates the high temperature passivation to the release of hydrogen from the SiN_x film, the injection of vacancies from backside Al alloying, and the retention of hydrogen at defect sites. High efficiency screen-printed String Ribbon solar cells (>14.5%) are fabricated utilizing the simultaneous SiN_x/Al anneal in a belt furnace for hydrogenation and Al-BSF formation, followed by RTP firing of screen-printed contacts to improve the retention of hydrogen at defects.

INTRODUCTION

The String Ribbon growth process [1] can reduce the cost of substrate growth because thin ribbon substrates (100 μm) for solar cells can be grown directly from the melt, eliminating the losses associated with slicing and subsequent etching. While the growth of String Ribbon makes it an attractive material for low-cost silicon photovoltaics, the as-grown minority carrier lifetime in the material is typically in the range of 1-10 μs. Several gettering and passivation techniques have been examined for the improvement of silicon PV materials including phosphorus and Al gettering and hydrogen passivation via post deposition anneal of PECVD SiN_x films. While PECVD SiN_x induced hydrogenation has been shown to effectively passivate defects in silicon during low temperature anneals (<775°C), the hydrogenation process has been found to be ineffective at higher temperatures [2]. The aim of this study is to examine the combination of SiN_x induced hydrogenation and Al gettering to identify any synergism between the hydrogenation and Al alloying processes that may enhance the high temperature defect passivation. In addition, we study what effect, if any, the cooling rate of the post deposition anneal has on the high temperature (850°C) passivation process. To evaluate the effectiveness of the passivation treatments in this study and improve the fundamental understanding of the hydrogenation process, minority carrier lifetime measurements are performed before and after the passivation treatments using the quasi-steady state photoconductance (QSSPC) technique. Finally, a model is proposed which relates the high temperature (850°C) SiN_x induced hydrogenation of String Ribbon silicon to the release of hydrogen into the wafer, the injection of vacancies from backside Al/Si alloying, and the retention of hydrogen at defects.

DEFECT GETTERING AND PASSIVATION TREATMENTS

String Ribbon wafers were grown by *Evergreen Solar* with a thickness of ~300 μm and a base resistivity of 3 Ω-cm. Wafers were etched and cleaned before each lifetime measurement. Lifetime measurements were made with the quasi-steady state photoconductance (QSSPC) technique with samples immersed in an I_2/methanol solution before and after each gettering and passivation treatment. Four lifetime measurements were made on each 25-cm^2 sample 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 [3]. After the initial lifetime measurement, wafers were cleaned in the sequence detailed above, and subjected to various manufacturable gettering and passivation process sequences involving phosphorus and aluminum gettering, and SiN_x-induced hydrogenation, individually and in combination. Phosphorus emitter diffusion involved the application of a spin-on doped film (*Filmtronics P507 or P506 -6%*) followed by belt furnace anneal to form a 45 Ω/sq. emitter. 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 of n=1.98, which densifies to 780 Å and n=2.0 after thermal treatment, using 320 sccm of SiH_4, 6.5 sccm of NH_3 and 900 sccm of N_2. To determine the change in the hydrogen content in SiN_x films after thermal treatments, SiN_x was deposited on chemically polished (100) float zone silicon wafers. Selected float zone wafers were annealed at 400°C in a tube furnace for 20 min. in forming gas, 730°C in a belt furnace for 30 sec. in air, and

0-7803-5772-8/00/$10.00

at 850°C in a belt furnace for 2 min. in air. The hydrogen content in the as-deposited and annealed SiN_x films was determined by FTIR measurements followed by integration of Si-H and N-H absorptance peaks [4]. Al gettering was performed by annealing a screen-printed Al paste (*Ferro FX 53-038*) printed on the back of wafers at 850°C for 2 minutes, also forming an effective Al-BSF [5]. Al gettering, front contact firing, and SiN_x anneals were performed in a conveyer belt furnace (*Radiant Tech. Corp.*) or RTP system (*AG Assoc. 610*), as indicated in the forthcoming sections.

RESULTS AND DISCUSSION

Release of hydrogen from PECVD SiN_x and the induced defect passivation in String Ribbon

After initial lifetime measurement and wafer cleaning, a SiN_x film was deposited on both surfaces of several wafers. Wafers were then annealed in the temperature range of 600°C-850°C in air for 2 minutes in a belt furnace. Fig. 1 shows that at post deposition anneal temperatures between 600°C and 725°C, the relative improvement in lifetime (τ_{final} - $\tau_{as\text{-}grown}/\tau_{as\text{-}grown}$ X100) due to SiN_x induced passivation increases to about 100% at 725°C. Fig. 1 also shows that the bonded hydrogen content in the SiN_x film decreases as the anneal temperature increases indicating that more hydrogen is released as the anneal temperature is increased. When the annealed temperature is increased above 750°C, the

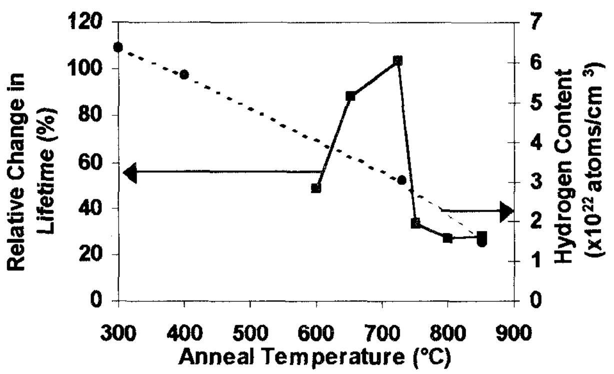

Fig. 1. Dependence of defect passivation (proportional to the relative change in lifetime) on the release of hydrogen from the SiN_x film (inversely related to the hydrogen content of the film).

relative improvement drops to about 30%. The dramatic decrease in the effectiveness of hydrogen passivation above 725°C observed in Fig. 1 may be due to the high temperature instability of hydrogen at defect sites in silicon. These results suggest that the hydrogen passivation of silicon defects may be proportional to the release of hydrogen from the SiN_x film as well the retention of hydrogen at defect sites in silicon.

Al-enhanced SiN_x induced hydrogenation of defects

To further enhance the lifetime of String Ribbon and investigate the interaction of the hydrogenation process with phosphorus and Al gettering, we examined the combinations of phosphorus and Al gettering with PECVD SiN_x hydrogenation during a post-deposition anneal at 850°C. Fig. 3 shows that the combination of phosphorus gettering and SiN_x hydrogenation at 850°C improves the lifetime by 7 μs, which is nearly equal to the sum of the enhancement provided by individual phosphorus gettering and hydrogenation treatments. A similar additive effect is observed in the combination of phosphorus and Al gettering, in which the lifetime improved by 11 μs. In contrast, a noteworthy average lifetime of 38 μs, an improvement of 30 μs, is observed when the PECVD SiN_x hydrogenation treatment and Al gettering treatment are combined in one heat treatment at 850°C for 2 minutes. This improvement in lifetime is far greater than the sum of the 850°C hydrogenation and Al treatments alone suggesting that there may be a positive synergistic interaction between the hydrogenation from the front

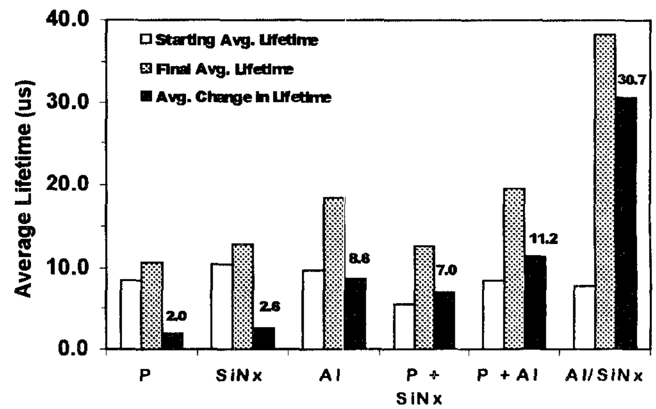

Fig. 2. Al-enhanced PECVD SiN_x induced defect passivation.

surface and the Al alloying process simultaneously occurring at the back surface of the wafer.

Enhanced SiN_x induced hydrogen passivation by controlled rapid cooling

To improve the retention of hydrogen at defect sites, the relative improvement in the bulk lifetime of String Ribbon wafers was measured as a function of the cooling rate after the post deposition anneal of the SiN_x film. 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. Another set of samples was annealed in an RTP contact firing scheme and rapidly cooled to 300°C at controlled rates followed by rapid cooling to room temperature after SiN_x deposition and Al screen-printing. Fig. 3 shows that the average relative improvement in lifetime is about 40% for all cooling rates (curve a) for the RTP contact firing scheme. The lifetime enhancement after this anneal may be limited by the release of hydrogen from the SiN_x film during this relatively short, low temperature anneal. When the anneal temperature and time are increased to 850°C and 2 minutes respectively, the average relative change in lifetime increases as the cooling rate after anneal increases even when no Al is present on the back (curve b). This result suggests that the ability to retain hydrogen at defect sites in silicon can be improved by increasing the cooling rate of the anneal. It is well known that hydrogen can evolve out of silicon above 500°C during prolonged anneals [6]. The average relative change in lifetime increases for all cooling rates

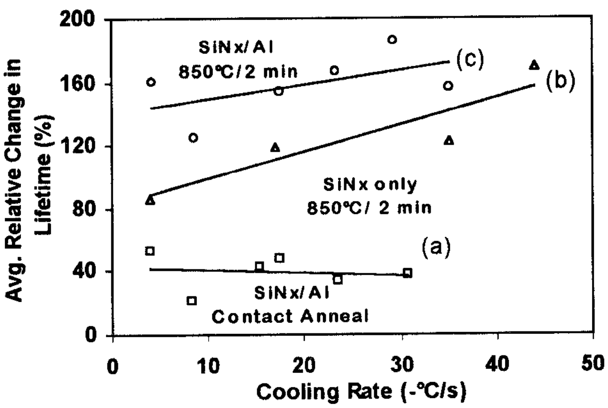

Fig. 3. Impact of the cooling rate on the effectiveness of the SiN_x induced hydrogen passivation process.

when Al is present on the back, shown 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 silicon, 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 of hydrogen in silicon reduces the dependence of the passivation process on the retention of hydrogen.

PROPOSED MODEL FOR THE HYDROGENATION OF DEFECTS IN STRING RIBBON SILICON

The data in Fig. 1 show that during high temperature anneals (>725°C), the retention of hydrogen at defect sites in silicon decreases and the SiN_x induced passivation is significantly reduced. However, the results in Fig. 2 and Fig. 3 indicate that when the SiN_x induced hydrogenation is combined with controlled rapid cooling or backside aluminum alloying, the defect passivation is improved. To describe the improved hydrogen passivation process, a three-step model is proposed based on these results and recent theoretical work [7,8]. In this model, the passivation is governed by the release of hydrogen from the SiN_x film, the retention of hydrogen at defect sites, and the injection of vacancies generated during Al/Si alloying. The effect of controlled rapid cooling is to improve the retention of hydrogen at defect sites in silicon and thus improve the passivation of defects. The role of aluminum alloying is to generate vacancies in silicon, which enhance the dissociation of hydrogen molecules and the migration of atomic hydrogen deep into the bulk Si.

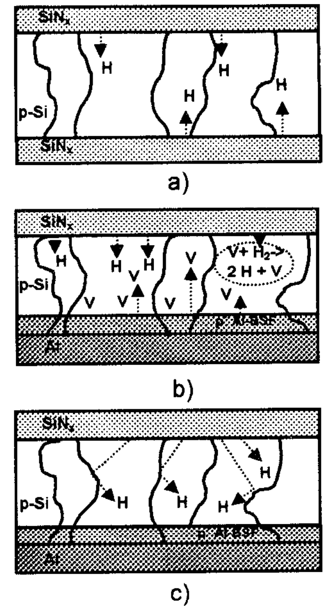

Fig. 4. Model for PECVD SiN_x induced hydrogenation in which defect passivation is governed by a) the release of hydrogen from the SiN_x film; b) the generation of vacancies during Al-Si alloying; and c) the retention of hydrogen at defect sites.

FABRICATION OF HIGH EFFICIENCY SCREEN PRINTED STRING RIBBON SOLAR CELLS

The results in Figure 3 show that the Al-enhanced SiN_x induced defect passivation is more effective when the anneal temperature is 850°C for 2 minutes. However, we have found that 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 hydrogen defect passivation during front contact firing anneals, selected String Ribbon solar cells were fabricated with front contacts fired in a conventional belt furnace with a low cooling rate, and an RTP system contact firing scheme having a high cooling rate. After wafer cleaning, phosphorus emitter diffusion, PECVD SiN_x deposition, Al screen-printing and annealing at 850°C in a belt furnace, (all detailed above) Ag paste (*Ferro 3349*) was screen-printed to the front surface of all wafers. After RTP or belt furnace firing of contacts, 4 cm^2 cells were isolated using a dicing saw. Table 1 shows that the average cell efficiency improves by 1.7% (absolute) when the front contacts are fired in the RTP furnace after the SiN_x/Al simultaneous anneal at 850°C in the belt furnace. A noteworthy high efficiency of 14.7% (measured by Sandia National Labs.) was achieved when contacts were fired in the RTP system. The results indicate that the 1.7% difference in efficiency is due to improved bulk and surface passivation (J_{sc} and V_{oc}) and contact quality (FF). It has been shown that RTP contact firing after initial Al-BSF formation in a belt furnace can improve the back surface recombination velocity by a factor of two, due to the improved uniformity of Al-BSF after RTP firing [9].

Contact Firing		V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Eff (%)
RTP	Average	574	31.6	0.762	13.8
	High	600	31.6	0.778	14.7
Belt Furnace	Average	553	29.7	0.738	12.1
	High	575	31.1	0.747	13.4

Table 1. Comparison of 4-cm^2 screen-printed String Ribbon solar cells fabricated with front contacts fired in an RTP system and belt furnace.

LBIC scans of cells were made with the *PVSCAN 5000*, system using a 905 nm laser, on cells taken from consecutive sections of the ribbon to identify differences in defect activity. Note that these samples have similar crystallographic defect structures. Figure 5 shows that the LBIC response in intragrain regions improves from 0.58 A/W to 0.64 A/W with RTP contact firing. Figure 5 shows a defect whose activity decreases as the defect extends from Cell 1-3 into Cell 16-1. The cell efficiency results in Table 1 and LBIC analysis in Figure 5 suggest that RTP firing of screen-printed contacts is more effective in retaining the hydrogenation introduced in the 850°C simultaneous Al/SiN_x anneal. In accordance with our model, these results suggest that the fast ramps associated with RTP contact firing 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.

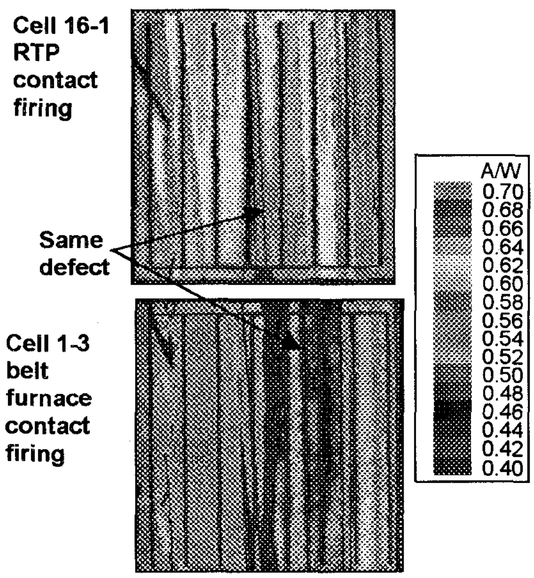

Fig. 5. Improved passivation of intergrain and intragrain defects with RTP contact firing.

CONCLUSIONS

The SiN_x induced hydrogen passivation of String Ribbon has been found to be most effective when the SiN_x post deposition anneal includes controlled rapid cooling and backside aluminum 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. The roles of controlled rapid cooling and aluminum alloying are to generate vacancies in silicon and improve in the retention of hydrogen at defect sites in silicon respectively. 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.

ACKNOWLEDGEMENT

The authors wish to acknowledge the contributions to this work of A. Ebong for the FTIR measurement of the bonded hydrogen content in PECVD SiN_x films. This work was supported by NREL contract No. XA8-17607-5 and Evergreen Solar through NIST contract 1997-01-0257.

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