BENEFICIAL IMPACT OF LOW FREQUENCY PECVD SIN$_X$:H-INDUCED HYDROGENATION IN HIGH-EFFICIENCY STRING RIBBON SILICON SOLAR CELLS

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ABSTRACT: PECVD SiN$_x$:H-induced hydrogenation of bulk defects in String Ribbon Si during RTP anneal is investigated in this study to enhance the carrier lifetime and understand the role of the plasma excitation frequency and an in-situ NH$_3$ plasma pretreatment before SiN$_x$:H deposition. The results show that a low frequency SiN$_x$:H film with a NH$_3$ plasma pretreatment annealed in RTP at 740°C for 60 seconds enhances the lifetime in String Ribbon Si from 5-6 µs to 90-100 µs. Secondary ion mass spectroscopy underneath SiN$_x$:H films deposited with deuterated ammonia (ND$_3$) and silane shows greater deuterium incorporation in Si under the low frequency SiN$_x$:H film. Thus, hydrogen incorporated in Si during SiN$_x$:H deposition may act as an additional source that enhances hydrogen defect passivation during subsequent RTP treatments. In addition, the effect of the anneal time during RTA for hydrogenation is studied in an effort to reduce the hydrogenation time and improve the retention of hydrogen at defects in Si. The RTA time for hydrogenation is reduced to one second without loss of lifetime enhancement and leads to the fabrication of high-efficiency String Ribbon solar cells (17.9%) with photolithography-defined contacts. A rapid belt furnace contact co-firing scheme is developed based on the short RTA and produces screen-printed 4-cm^2 String Ribbon solar cells with efficiencies as high as 15.9%.
Keywords: Hydrogen passivation – 1: String Ribbon Si – 2: Screen Printing – 3

1 INTRODUCTION

Hydrogen passivation of bulk defects via the deposition and anneal of PECVD SiN$_x$:H films provides the bulk lifetime enhancement necessary to achieve high solar cell efficiencies on ribbon silicon materials. In our previous work, we developed a hydrogenation treatment that relies on the simultaneous anneal of a high-frequency (HF) SiN$_x$:H film and an Al layer. This treatment results in a spatially averaged lifetime of 30-40 µs in String Ribbon with solar cell efficiencies approaching 15% [1,2]. A three-step physical model was proposed to explain the Al-enhanced hydrogenation in which the degree of defect passivation is governed by the supply of hydrogen released from the SiN$_x$:H film, Al-Si alloying, and the retention of hydrogen at defects in Si. While this is a noteworthy result, the efficiency remained below the targeted cell efficiencies of 16-17%, which is achievable with further lifetime improvement up to 75 µs and a reduction of the back surface recombination velocity to the range of 100 to 300 cm/s. One component of the model that has not yet been fully explored is the supply of hydrogen from the deposition and anneal of the PECVD SiN$_x$:H film. During low frequency (LF) PECVD film deposition, the oscillation of the RF field is slow enough that ions are accelerated in one direction for a longer time and bombard the substrate with high energy. Of importance to Si solar cells is the ion bombardment and damage during low frequency PECVD, which may increase H incorporation in Si during SiN$_x$:H deposition and improve the hydrogenation of defects in Si. A theoretical model to fit experimental diffusion profiles of H in Si has been developed by Sopori et al. [3]. This model considers the capture of hydrogen at processing-induced traps created during SiN$_x$:H deposition and the release of hydrogen from traps during heat treatment [3]. Sopori's simulations show that the post-deposition anneal of a SiN$_x$:H film in RTP at 800°C can drive hydrogen through the thickness of a Si wafer that has a trap density of 10^{16} cm^{-3} in only 10 s [3]. In this paper, the hydrogenation of defects in String

Ribbon Si from the deposition and anneal of LF and HF SiN$_x$:H films is studied through spatially averaged quasi-steady-state photoconductance (QSSPC) measurements of the carrier lifetime. To understand the mechanisms during hydrogenation from the two types of nitride films, the hydrogen content in LF and HF nitride films before and after heat treatments is measured by FTIR. In addition, secondary ion mass spectroscopy (SIMS) is used to measure the depth profile of deuterium in Si substrates after nitride deposition from SiH$_4$ and deuterated ammonia (ND$_3$) gases. Finally, the RTA time for hydrogenation is reduced to improve the retention of hydrogen at defects. High-efficiency String Ribbon solar cells with photolithography contacts are fabricated using the RTA for hydrogenation. Based on this RTA, a rapid belt furnace contact co-firing scheme is developed to achieve high-efficiency String Ribbon solar cells with co-fired screen-printed contacts.

2 EXPERIMENT

To assess the degree of hydrogen defect passivation, 300-µm-thick, 3 Ω-cm p-type String Ribbon samples were cleaned using the solutions listed in [1]. Phosphorus diffusion was performed at 893°C in a tube furnace using a POCl$_3$ liquid source to achieve an emitter sheet resistance of 40-45 Ω/sq. Samples were cleaned again after the P glass removal and a PECVD SiN$_x$:H film was deposited on the String Ribbon samples using a parallel plate direct PECVD reactor operating at high frequency (13.56 MHz) and a temperature of 300°C, or a horizontal tube direct PECVD system operating at low frequency (50 kHz) and a temperature of 430°C. Selected samples were subjected to a NH$_3$ plasma pretreatment performed in low- and high-frequency reactors before SiN$_x$:H deposition to increase hydrogen incorporation in Si. After SiN$_x$:H deposition, samples were annealed in RTP at optimum hydrogenation temperatures of 740°C and 800°C for LF and HF nitride films, respectively. The identification of the optimum hydrogenation anneal

temperatures for LF and HF SiN$_x$:H films is described [4]. To investigate Al-enhanced hydrogenation with LF and HF SiN$_x$:H, an Al paste (*Ferro 53-038*) was screen-printed on the back of selected String Ribbon wafers before RTP heat treatment. After heat treatment, the Al, n$^+$, and p$^+$ layers were removed by chemical etching and samples were cleaned before post-processing lifetime measurement using the solutions listed in [1]. Lifetime measurements were made using the QSSPC technique with samples immersed in and I$_2$/methanol solution for surface passivation.

3 RESULTS AND DISCUSSION

3.1 Beneficial effect of low frequency SiN$_x$:H film deposition and in-situ NH$_3$ plasma pretreatment on lifetime enhancement

Fig. 1 shows that without pretreatment, the deposition and anneal of the LF SiN$_x$:H film with Al present on the back increased the average lifetime from 5 to 63 μs. The figure also shows that the anneal of HF SiN$_x$:H with Al on the back increased the average lifetime to only 20 μs. This result indicates that the deposition and anneal of LF SiN$_x$:H are more effective in passivating defects in String Ribbon. It has been shown that LF SiN$_x$:H is more effective than HF SiN$_x$:H in reducing the recombination activity of defects in cast mc-Si solar cells as well [5]. The effectiveness of the LF SiN$_x$:H hydrogenation may be due to an increased supply of hydrogen in the SiN$_x$:H film or greater hydrogen incorporation in Si during SiN$_x$:H deposition. These topics are addressed in Sections 3.3 and 3.4. Fig. 1 also shows that the addition of a NH$_3$ plasma pretreatment step improves the SiN$_x$:H-induced lifetime enhancement for both LF and HF SiN$_x$:H films, but is more beneficial for LF SiN$_x$:H-induced hydrogenation. The pretreatment step before LF SiN$_x$:H deposition improved the lifetime by 29 μs, resulting in a final average lifetime of 92 μs. The HF pretreatment was not as effective and provided a lifetime increase of only 7 μs, with a final average lifetime of 27 μs.
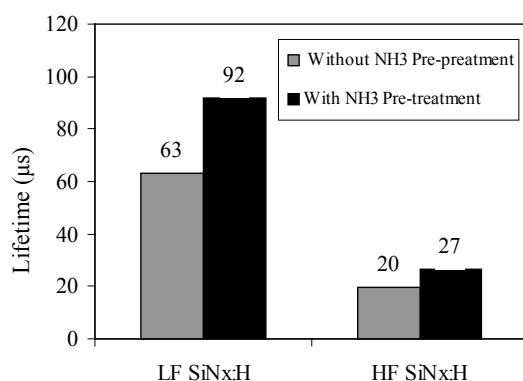

Figure 1: Effect of in-situ NH$_3$ plasma pretreatment before LF and HF SiN$_x$:H deposition on lifetime enhancement. The average as-grown lifetime was 5 μs

3.2 Impact of simultaneous Al alloying on low frequency and high frequency SiN$_x$:H-induced hydrogenation

In this section, LF SiN$_x$:H-induced hydrogenation with an NH$_3$ pretreatment is studied to determine if Al plays a significant role in hydrogenation. Fig. 2 shows

that the lifetime after HF SiN$_x$:H-induced hydrogenation at 800°C without Al was only 9 μs and is consistent with the results in [1]. When Al was present on the back during HF SiN$_x$:H-induced hydrogenation without NH$_3$ pretreatment, the lifetime reached 29 μs, once again demonstrating Al-enhanced hydrogenation. Fig. 2 shows that hydrogenation from a LF SiN$_x$:H film with a NH$_3$ pretreatment followed by a 740°C anneal for 60 seconds increased the lifetime to 91 μs even when no Al was present on the back. When Al is present on the back of the wafer during LF SiN$_x$:H-induced hydrogenation, the lifetime increased to 106 μs. The relatively small
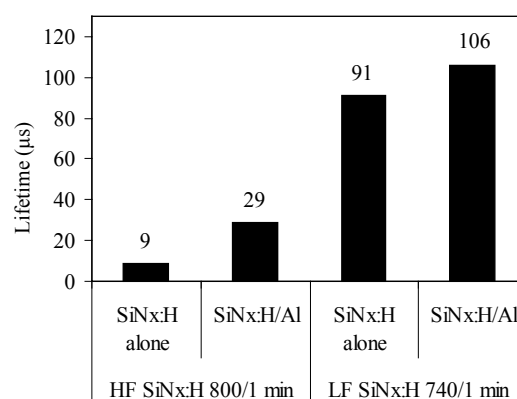

Figure 2: Impact of Al on hydrogenation of String Ribbon Si from low- and high-frequency PECVD SiN$_x$:H. The as-grown lifetime was 5 μs

difference in the average lifetime of samples with and without Al (15 μs) indicates that Al does not play as significant a role in hydrogenation from LF SiN$_x$:H as it does in the case of HF SiN$_x$:H-induced hydrogenation. The role of Al in hydrogenation may be diminished if there is a large supply of hydrogen from an additional source that is available for passivation. The results in this section demonstrate that hydrogenation from the LF SiN$_x$:H film provides an additional lifetime enhancement and is less dependent on the presence of Al, presumably because of an increased supply of hydrogen.

3.3 Quantitative assessment of the release of bonded hydrogen from low- and high-frequency SiN$_x$:H films

To determine if the enhanced hydrogenation from LF SiN$_x$:H films is due to a greater supply of hydrogen from SiN$_x$:H, the release of hydrogen from LF and HF SiN$_x$:H films deposited on float zone Si wafers was measured by FTIR. The total bonded hydrogen content in SiN$_x$:H films was determined by calculating the sum of the Si-H and N-H bond densities, as described in [6]. After film deposition, the hydrogen content in HF and LF SiN$_x$:H films was found to be 2.0×10^{22} cm^{-3} and 4.1×10^{21} cm^{-3}, respectively. The bonded hydrogen content in HF SiN$_x$:H films drops to 3.6×10^{21} cm-3 after anneal at 600°C, a decrease of 82% when compared to the as-deposited film. This result indicates that most of the hydrogen in HF SiN$_x$:H films is released at or below 600°C. As the anneal temperature is increased further, the hydrogen content in HF SiN$_x$:H films decreases at a rate of 1×10^{21} cm^{-3} per 100°C. After anneal at 600°C, the hydrogen content in LF SiN$_x$:H films is essentially unchanged from the as-deposited state. A further increase in the anneal temperature releases hydrogen at a rate of 9×10^{20} cm^{-3} for every 100°C increase in the anneal temperature.

These results show that there is more hydrogen in HF SiN_x:H after deposition, and that hydrogen is easily released from this film during heat treatment. This does not support the carrier lifetime study in Section 3.1, which showed that the LF SiN_x:H film deposited after an NH_3 pretreatment is more effective for hydrogen defect passivation.

3.4 Demonstration of hydrogen incorporation near the Si surface during PECVD SiN_x:H deposition

In this section, hydrogen incorporation in Si is measured after LF and HF SiN_x:H deposition by SIMS depth profiling. Deuterated ammonia (ND_3) was substituted for NH_3 during LF and HF SiN_x:H deposition to detect deuterium incorporation. SiN_x:H was deposited using LF and HF PECVD on mirror polished, 8- Ω-cm p-type Czochralski Si wafers after a P diffusion described in Section 2. SiN_x:H films were removed after deposition in dilute hydrofluoric acid and SIMS depth profiles of deuterium in Si were measured by the Surface Analysis Group at the National Renewable Energy Laboratory. Fig. 3 shows that the deuterium profile in Si under HF SiN_x:H without an NH_3 pretreatment has a peak concentration of 4.2×10^{16} cm-3 and a depth of 0.06 μm. The deuterium profile in Si under the LF SiN_x:H film with an NH_3 pretreatment has a peak concentration of 7.7
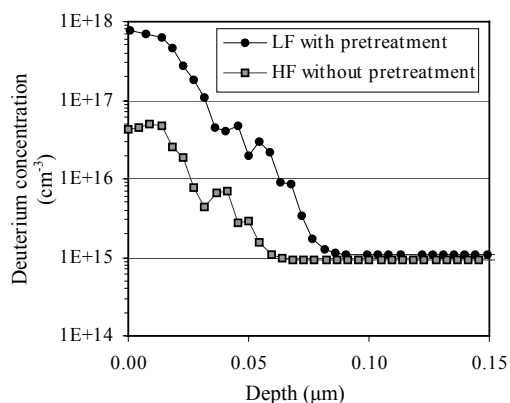

Figure 3: SIMS depth profiles of deuterium in Si after deposition of LF SiN_x:H with in-situ ND_3 plasma pretreatment and HF SiN_x:H deposition

x 10^{17}cm-3 and a depth of 0.09 μm. The detection limit for deuterium in these SIMS measurements is approximately 10^{15} cm^{-3}. We have also found that a 740°C/60-second anneal releases the hydrogen trapped in Si, which may also aid in defect passivation. Thus, the lifetime enhancement provided by LF SiN_x:H-induced hydrogenation with pretreatment shown in Fig. 1 may be partly explained by the higher dose of hydrogen during LF SiN_x:H deposition. Also contributing to LF SiN_x:H-induced hydrogenation is the deeper hydrogen incorporation that is expected during LF SiN_x:H because deposition is performed at a higher temperature (430°C).

3.5 Effect of RTA on the dehydrogenation of defects and lifetime degradation in String Ribbon silicon in the absence of a supply of hydrogen

To investigate the thermal stability of hydrogen passivation of defects in String Ribbon in the **absence** of H supply, hydrogenated samples were annealed successively for 1 second, 10 seconds, and 60 seconds at

RTA temperatures in the range of 400°C to 650°C after removal of the SiN_x:H film, n$^+$ layer, p$^+$ layer, and Al. It should be noted that the SiN_x:H layer on the front and Al layer on the rear of a solar cell may prevent the out diffusion of H during heat treatment. Fig. 4 shows the change of the normalized carrier lifetime (τ_f/τ_o) in String Ribbon samples after dehydrogenation anneals. The lifetime degradation in String Ribbon samples during the 1 second, 10 second, and 60 second anneals is attributed to the dehydrogenation of defects. In the case of the 60 second RTA, the normalized lifetime decreases to 0.76 after anneal at 400°C, and falls to 0.10 after anneal at 525°C. This indicates that the hydrogen passivation of defects is not stable above 400°C when the RTA time is 60 seconds. Fig. 4 shows that when the anneal time is reduced to 10 seconds and 1 second, two phases of lifetime degradation appear in the range of 400°C to 600°C. Moderate degradation of the lifetime occurs up to 525°C during the 10 second anneals, where the normalized lifetime drops to 0.63. When the RTA temperature is increased from 525°C to 550°C during 10 second anneals, the normalized lifetime drops to 0.47, and the dramatic decrease continues to 585°C, where the normalized lifetime falls to 0.07. For the 1-second anneals, moderate dehydrogenation was observed up to 550°C, where the normalized lifetime was 0.79, followed by a dramatic dehydrogenation up to 625°C, where the normalized lifetime falls to 0.27. The results for the 10 second and 1 second anneals shown in Fig. 4 indicate that dehydrogenation occurs at low temperatures (400-500°C), but does not become severe until temperatures above 525°C when no SiN_x:H is present on the wafer. The data also shows that the onset temperature for severe dehydrogenation increases from 525°C to 550°C when the anneal time is reduced from 10 seconds to 1 second. This indicates that hydrogenated defects can tolerate
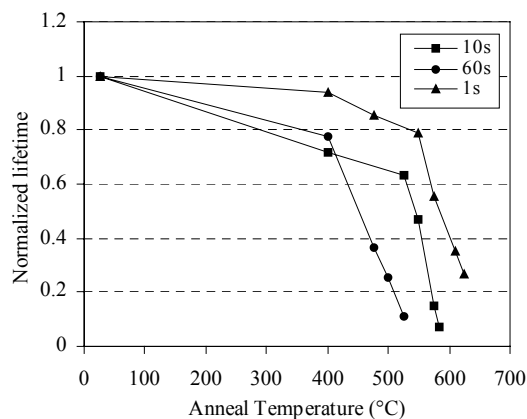

Figure 4: Decrease of the lifetime in hydrogenated String Ribbon during RTA for 1s, 10s, and 60s

higher temperatures if the anneal time is reduced. This result could prove to be very important in designing the appropriate contact firing cycle for String Ribbon solar cells.

3.6 Effect of RTA time on the lifetime enhancement from LF SiN_x:H-induced hydrogenation

The effect of RTA time during LF SiN_x:H-induced hydrogenation at 740°C was investigated using samples with an average as-grown lifetime of 6 μs. After LF

SiN_x:H deposition with a NH_3 pretreatment, followed by RTA for 60 s at 740°C, the average lifetime reached 106 μs. As the anneal time was reduced to 30 seconds, 20 seconds, and 15 seconds, the average lifetime decreased to 81 μs, 67 μs, and 63 μs, respectively. When the anneal time was reduced further to 1 second, the average lifetime increased to 93 μs. This may suggest that the retention of H at defects may increase when the anneal time is reduced below 5 seconds. This results in very effective lifetime enhancement because H retention is high, even though the supply of H may be reduced during the short RTA (1 to 5 seconds).

String Ribbon solar cells with photolithography-defined contacts were fabricated to confirm that a short (1 second) RTA can result in effective LF SiN_x:H-induced hydrogenation. The use of photolithography-defined front contacts avoids the need for post-hydrogenation heat treatments that may be associated with solar cells made with screen-printed Ag contacts. The highest efficiency String Ribbon Si solar cell fabricated with a 1 second RTA at 740°C for hydrogenation had an efficiency of 17.9 % (verified by NREL). This cell had a two-layer SiN_x:H/MgF_2 antireflection (AR) coating and an area of 4-cm^2. In the next section, rapid firing of screen-printed contacts is investigated in a belt furnace to achieve high-efficiency screen-printed String Ribbon solar cells.

3.7 Fabrication of high-efficiency String Ribbon solar cells with screen-printed contacts co-fired in a belt furnace

In this section, screen-printed String Ribbon solar cells are fabricated using a rapid conveyer belt furnace firing cycle. Solar cell fabrication began with sample cleaning and P diffusion, described in Section 2. A LF SiN_x:H film was deposited by PECVD with in-situ NH_3 plasma pretreatment on the n^+-emitter. A commercially available Al paste (*Ferro FX53-038*) was printed on the entire back surface and a commercially available Ag paste (*DuPont 4948*) was printed in a grid pattern on the front. Front and back contacts were co-fired in a conveyer belt furnace (*RTC LA-310*) using a firing cycle with a dwell time of 4 seconds near the peak temperature, and high heating and cooling rates. The average lifetime of String Ribbon samples after hydrogenation in this firing cycle was 77 μs, demonstrating that effective hydrogenation can be achieved in an industrial-type conveyer belt furnace in only one very short heat treatment. Cells were isolated using a dicing saw to define an active area of 4-cm^2 and annealed in forming gas for 15 minutes. The average efficiency of these cells was 15.2%, and the highest efficiency was 15.9% (verified by NREL). This represents the highest efficiency achieved to date on String Ribbon silicon using screen-printed contacts and a single-layer AR-coating. This cell benefited from LF SiN_x:H-induced hydrogenation with NH_3 plasma pretreatment and a short anneal in a belt furnace for hydrogenation of bulk defects and co-firing of screen-printed contacts.

4   CONCLUSIONS

The deposition and appropriate anneal of a LF SiN_x:H film with a NH_3 pretreatment increases the spatially averaged lifetime in String Ribbon Si from 3 μs to 92 μs after a 60 s RTA. This lifetime enhancement is greater than that which can be achieved using a HF SiN_x:H film, even though there is more hydrogen in the HF SiN_x:H film. SIMS analysis revealed that the addition of a NH_3 plasma pretreatment before LF SiN_x film deposition increases the incorporation of hydrogen in Si, which may act as an additional source of hydrogen for defect passivation. It was also found that hydrogenation from the LF SiN_x:H film is less dependent on the presence of Al than hydrogenation from the HF SiN_x:H film. The lifetime of hydrogenated String Ribbon samples decreased significantly after subsequent RTP treatments above 550°C during 1 second anneals. A short (1 second) RTP firing process was found to provide lifetime enhancement to 93 μs and solar cell efficiencies as high as 17.9% in cells with photolithography-defined contacts. String Ribbon samples annealed using a rapid belt furnace firing scheme had an average lifetime of 77 μs, with an average efficiency of 15.2% and a maximum efficiency of 15.9%, which is the highest efficiency to date for String Ribbon solar cells with screen-printed contacts and a single layer AR-coating.

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