STUDY OF DIRECT PECVD SIN$_X$-INDUCED SURFACE EMITTER AND BULK DEFECT PASSIVATION IN P-TYPE SILICON SOLAR CELLS

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ABSTRACT

This paper shows that direct low-frequency (LF) deposition of SiN films at 425 °C by PECVD followed by a conventional screen-printed contact firing cycle is more effective than a high-frequency (HF) SiN film deposited at 300 °C in passivating both bulk defects and the emitter surface. The emitter saturation current density (J_{oe}), was found to be higher for LF SiN compared to the HF SiN just after deposition. J_{oe} values for LF SiN reduced dramatically after contact firing to 100-200 fA/cm^2, well below the J_{oe} for HF SiN passivated emitters. Solar cells fabricated on float zone (FZ) Si and mc-Si grown by the Heat Exchanger Method (HEM) yielded efficiencies as high as 17.2% and 16.8%, respectively, when coated with LF SiN. The enhanced cell performance is corroborated by a higher short wavelength IQE response in FZ and HEM cells and a higher post hydrogenation lifetime in HEM mc-Si cells coated with LF SiN.

INTRODUCTION

Bulk lifetime enhancement and good surface passivation are becoming increasingly important for high-efficiency solar cells as we move toward cheaper and thinner Si substrates. It has been shown that Plasma-Enhanced Chemical Vapor Deposition (PECVD) of silicon nitride (SiN) can accomplish both [1-4], but the degree of enhancement is a function of deposition and annealing conditions. Recently, we reported 16.9% efficient solar cells on cast mc-Si [5] with a high current density (J_{sc}~35 mA/cm^2). These cells had a single-layer SiN antireflection coating (ARC) deposited at 425 °C in a direct low-frequency PECVD reactor. Moreover, the average processed bulk lifetime in some of these cells was in the range of 250 to 300 µs. Since starting lifetime was below 50 µs, these results are indicative of very effective bulk passivation provided by the low-frequency SiN ARC. In this paper, the quality of emitter surface passivation is quantified by J_{oe} measurements for two types of SiN films suitable for cell manufacturing: a low-frequency (LF) SiN film deposited at 425 °C in a horizontal tube reactor, and a high-frequency (HF) film deposited in a parallel plate reactor at 300 °C. Note that this study includes the effect of three variables: frequency, temperature, and reactor. Various values of J_{oe} have been reported in the literature for different sheet resistivity emitters passivated with SiN films [3,6,7-9]. Si-rich SiN films (index >2.3) are known to give a lower J_{oe} [6]. However, nearly stoichiometric SiN films (index ~2.0, measured at 633 nm), which are more suitable for solar cells because of low absorption, were analyzed in this study. J_{oe} was measured for LF and HF SiN passivated phosphorous-doped n$^+$ emitters. In addition, solar cells were fabricated and analyzed by IV and IQE measurements to study the impact of surface and bulk defect passivation from LF and HF direct SiN films. The bulk lifetime in HEM mc-Si was monitored in sister wafers to characterize the bulk lifetime enhancement resulting from hydrogenation from LF and HF SiN films during the contact anneal cycle.

EXPERIMENT

For the J_{oe} measurements, symmetric n$^+$-n-n$^+$ structures were prepared on ~ 700 Ω-cm n-type FZ Si wafers. The wafers were chemically etched in acid before a standard RCA clean. Phosphorus diffusions were performed at various temperatures in the range of 835 °C to 915 °C using liquid $POCl_3$ as the dopant source. The sheet resistivity was measured on each wafer with a four-point probe after removing the phosphorous glass layer in dilute HF. By varying the temperature from 835 °C to 915 °C, sheet resistivities in the range of 30 Ω/□ to 120 Ω/□ were obtained. Silicon nitride was deposited on both sides of each wafer using direct LF and HF PECVD reactors. The HF PECVD SiN film was deposited at a frequency of 13.56 MHz and a temperature of 300 °C while, the deposition of LF PECVD SiN was performed at a frequency of 50 kHz and a temperature of 425 °C. J_{oe} was measured on each wafer before and after a heat treatment in an IR-heated belt furnace using the same profile as that for contact anneal during solar cell processing. J_{oe} was measured by the transient photoconductance decay technique (tcpd) from the slope of inverse effective lifetime ($1/\tau_{eff}$) vs. excess carrier concentration (Δn) [10]. Solar cells were fabricated on 1 Ω-cm p-type FZ and ~1.5 Ω-cm p-type HEM mc-Si wafers. All the wafers were first chemically etched in acid to remove the saw damage, followed by a standard RCA clean. Subsequently $POCl_3$ diffusion to form a ~45 Ω/□ emitter, followed by deposition of SiN AR coating on the front (in LF or HF reactors), Al screen-printing on the back, and Ag grid printing on the front, was performed using commercial pastes. Cells were then co-fired using an optimized process in a lamp-heated IR belt furnace, resulting in the simultaneous formation of an Al-doped back surface field (BSF) and the front Ag grid metallization. Cells were mechanically isolated with a dicing saw to define an active cell area of 4 cm^2. Finally, cells were annealed at 400 °C for 15 min. in forming gas before testing and analysis. The bulk lifetime in HEM mc-Si was monitored in sister wafers to characterize the bulk lifetime enhancement resulting from hydrogenation from LF and HF SiN films during the contact anneal cycle Lifetimes

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were measured on as-grown wafers and post-hydrogenated HEM mc-Si wafers after firing in the belt furnace. Lifetimes in HEM mc-Si were measured by the quasi steady-state photoconductance technique (QSSPC) [11] with surfaces passivated by an iodine-methanol solution.

RESULTS AND DISCUSSIONS

Comparison of SiN films for emitter surface passivation

J_{oe} values obtained for the LF SiN film deposited at 425 °C and HF SiN_x deposited at 300 °C before and after annealing are shown in Fig. 1. The as-deposited J_{oe} values for LF SiN were very high (~480 fA/cm^2) and did not vary much with sheet resistivity. On the other hand, the as-deposited J_{oe} values for the HF SiN were much lower and decreased from 368 to 199 fA/cm^2 as the sheet resistance increased from 30 to 120 Ω/□. Note that the trend line in Fig. 1 is a guide for the eye. This indicates that as-deposited HF SiN is more effective for emitter surface passivation than LF SiN. However, after firing in the belt furnace, the J_{oe} values for LF SiN decreased substantially, even below the values for HF SiN. For example, for a 45 Ω/□ emitter passivated by LF SiN, the J_{oe} dropped from 480 fA/cm^2 to 244 fA/cm^2 after firing, while the J_{oe} for the HF SiN passivated emitter decreased from 308 fA/cm^2 to 254 fA/cm^2 after firing. A similar but stronger pattern was seen for higher sheet resistances. For 95 Ω/□ emitter passivated with LF SiN, the J_{oe} dropped from 484 fA/cm^2 to 147 fA/cm^2 after firing. However, J_{oe} dropped from 198 fA/cm^2 to only 150 fA/cm^2 for the HF SiN passivated emitter after firing. Note that the J_{oe} values for the LF SiN decrease as the sheet resistivity increases, consistent with the literature [12]. The J_{oe} values reported here may not be the lowest that could be attained by these films. Nevertheless, they are comparable to those reported in the literature, given that the SiN films in this work were optimized for optimal overall solar cell performance rather than surface passivation.

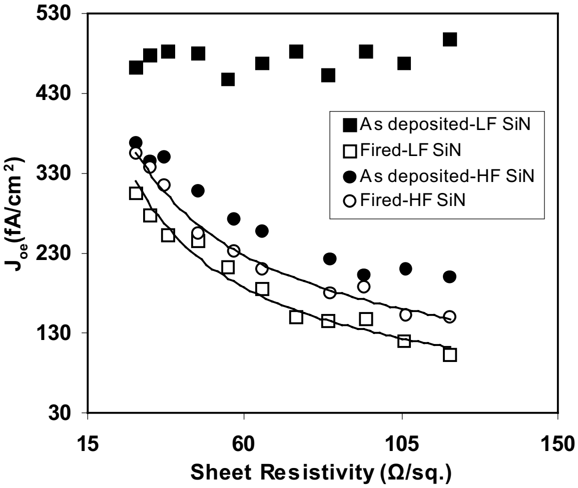

Fig. 1. J_{oe} comparison for phosphorous diffused n$^+$ emitters with different sheet resistivities for LF and HF SiN.

The dramatic decrease of J_{oe} for LF SiN passivated emitters after firing could be explained by a greater degree of surface damage caused by the plasma ions in the low-frequency reactor that impact the Si surface and trap atomic hydrogen. During the subsequent firing, the damage is annealed and the trapped hydrogen is released [13] to passivate the emitter surface.

Impact of two different PECVD SiN films on FZ and mc-Si solar cell performance

Solar cells were fabricated on FZ Si and HEM cast mc-S to determine the effect of emitter surface and bulk defect passivation from LF and HF SiN films. The solar cell data in Table 1 shows that LF SiN enhances the J_{sc} and V_{oc} and hence the overall solar cell performance. It should be noted that the difference in V_{oc} between FZ cells with HF and LF SiN is 2 mV, while in the case of the HEM mc-Si cells the difference is 4 mV. Table 1 also shows that the difference in J_{sc} between FZ cells with LF and HF SiN is 0.75 mA/cm^2. IQE and diffuse reflectance measurements were performed on FZ and mc-Si cells with HF and LF SiN films to determine if the difference in J_{sc} and V_{oc} is due to surface reflectance, surface recombination, or bulk recombination. Figure 2 shows that the reflectance for FZ solar cells with LF and HF SiN AR coatings is very similar, indicating that the difference between FZ cells is not due to reflectance. Figure 2 also shows that the short wavelength (350-650 nm) IQE of the FZ cell with the LF SiN coating is greater than that of the FZ cell with the HF SiN coating. For example, there is a 6% enhancement in the IQE response for LF SiN at 450 nm, relative to the HF SiN at the same wavelength.

Table 1. IV data for 4 cm^2 solar cells on FZ and mc-Si wafers for LF and HF coated SiN.

System	Eff (%)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)
FZ LF	**17.2**	**34.64**	**632**	**78.4**
FZ HF	**16.8**	**33.89**	**630**	**78.8**
HEM LF	**16.8**	**34.24**	**627**	**78.0**
HEM HF	**16.1**	**33.22**	**623**	**77.6**

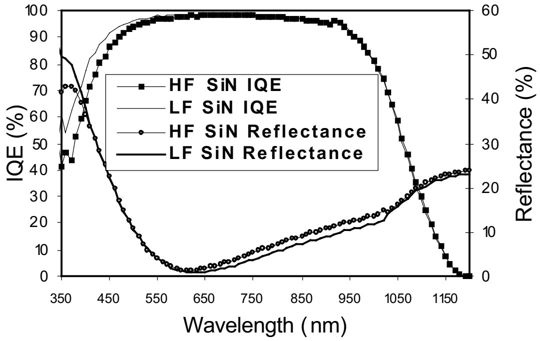

Fig. 2. IQE response and reflectance for LF and HF SiN coated FZ wafers.

Figure 2 also shows that the choice of the SiN film did not affect the long wavelength IQE response of FZ cells, indicating that these nitride films did not affect the carrier lifetime in the base, which was >250 µs, even before cell processing. Figure 3 shows the IQE response of two HEM mc-Si cells with HF and LF SiN. As in the case of FZ cells, the short wavelength response is greater for the HEM mc-Si cell with the LF SiN coating. In this case, the relative difference in the short wavelength IQE response is 7% at 450 nm. In contrast to the FZ cells, the HEM mc-Si cells with the LF SiN coating show superior long wavelength response as well, indicative of more effective bulk defect passivation relative to high-frequency SiN deposition at 300 °C. This is further supported by Fig. 4, which shows the average as-grown lifetime, post-processing lifetime, and corresponding solar cell efficiencies for high- and a low-lifetime HEM wafers.

In Fig. 4, for experiment 1 the ending lifetime is the lifetime after processing, including phosphorus diffusion, SiN coating, and Al printing and firing. For experiment 2 the ending lifetime includes the effect of phosphorus diffusion, SiN coating, and firing only. The carrier lifetime for the HF SiN deposition at 300 °C improved from 1 µs to 30 µs for the low-lifetime HEM mc-Si wafer (experiment 1) and from 35 µs to 179 µs for the high-lifetime HEM mc-Si, (experiment 2), resulting in cell efficiencies of 14.8% and 16.1%, respectively. The LF SiN deposited at 425 °C improved the bulk lifetime from 1 to 110 µs in the low-lifetime wafer (experiment 1) and from 36 µs to 279 µs in the high-lifetime wafer (experiment 2) with corresponding cell efficiencies of 15.9% and 16.8%, respectively. The data in Fig. 4 shows that the defect passivation from the LF SiN is more effective and also reduces the efficiency gap between the cells made on low- and high-lifetime HEM mc-Si wafers. Thus, the LF SiN film deposited at 425 °C results in higher cell efficiency in both materials because of better emitter surface passivation in FZ and HEM mc-Si cells and improved bulk defect passivation in HEM mc-Si cells.

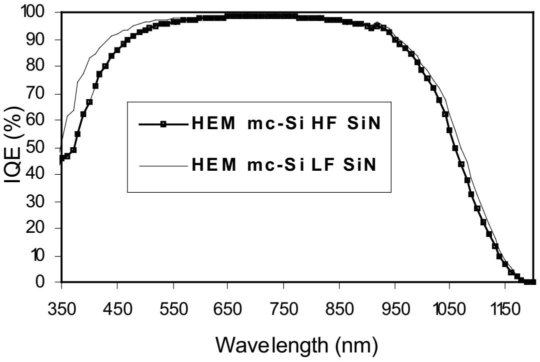

Fig. 3. IQE response for LF and HF SiN coated HEM wafers.

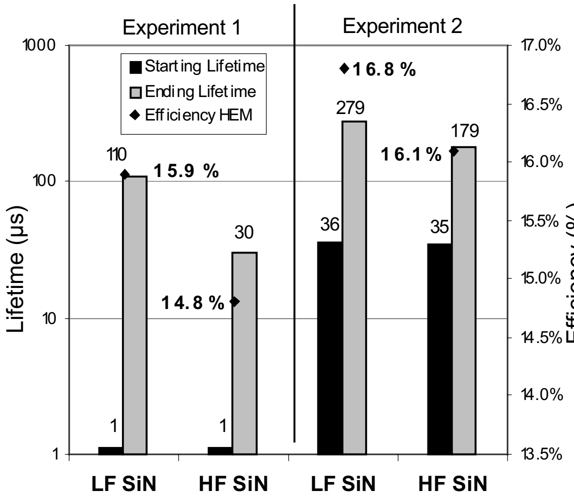

Fig. 4. Average as-grown and post-processing lifetime in HEM mc-Si wafers with LF and HF SiN and the corresponding cell efficiencies.

CONCLUSION

The emitter surface and bulk passivation provided by the LF SiN film deposited at 425 °C was found to be superior to that provided by a HF SiN film deposited at 300 °C. The contact formation cycle is found to induce a significant decrease in the J_{oe} of the LF SiN passivated phosphorus-doped emitter. This is attributed to the annealing of the damage at the emitter surface caused by the deposition of SiN at low frequency. During the post-deposition firing, hydrogen is released from the SiN film and improves the passivation of the emitter surface and defects in the bulk. Solar cells fabricated on FZ Si and HEM mc-Si gave efficiencies of 17.2% and 16.8%, respectively with a LF SiN ARC and 16.8% and 16.1% with a HF SiN ARC. Carrier lifetime measurements showed that the LF SiN film deposited at 425 °C increased the bulk lifetime in HEM mc-Si wafers from 35 µs to 279 µs, while the HF SiN film deposited at 300 °C enhanced the lifetime in a similar quality wafer to an average value to 179 µs. Thus, the combined effect of SiN deposition, frequency, temperature, and reactor on the surface and bulk defect passivation can be very significant. The LF SiN film employed in this study gave significant improvement in bulk lifetime and J_{oe} and reduced the performance gap between cells made on low- and high-lifetime HEM mc-Si wafers to less than 1% absolute.

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