INDUSTRIAL PECVD SILICON NITRIDE: SURFACE AND BULK PASSIVATION OF SILICON WAFERS

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ABSTRACT: Plasma-Enhanced Chemical-Vapour-Deposited silicon nitride films created in an industrial reactor are characterised here in terms of their capacity to passivate the surface of crystalline silicon wafers and hydrogenate defects in multicrystalline silicon. The temperature behaviour of the surface passivation is investigated for a broad range of deposition conditions, and experimental evidence of SiN-induced hydrogenation of mc-Si is presented. An excellent surface passivation, similar to the best reported in the literature, has been obtained with low refractive index SiN films ($n \approx 2$). Upon annealing, such films also result in effective hydrogenation of cast mc-Si, globally improving the carrier lifetime by 56%.

Keywords: Silicon-Nitride, Passivation, PECVD

1. INTRODUCTION

The use of PECVD SiN (Plasma-enhanced chemical-vapour-deposited silicon nitride) technology in the fabrication of mc-Si (multicrystalline silicon) solar cells is becoming pervasive. The main driving force for the expansion of this new technology is the improvement in solar cell efficiency that results when SiN is applied in conjunction with fire-through techniques for the metallisation step [1, 2]. This 1-1.5% (absolute) improvement is attributed to hydrogenation of defects in the volume of the mc-Si wafers. A second driving force is surface passivation, a property that the majority of today's industrial solar cells do not exploit as much as they could due to their simplistic design and to fabrication constraints. Surface passivation is, nevertheless, a must in order to enable advanced devices having an optimized emitter, a thin base and a locally contacted rear surface. PECVD SiN has been shown to give very low surface recombination velocities both on phosphorus diffused regions [3] and on p-type and n-type wafers [4-7].

This paper aims at contributing to the development of PECVD SiN technology by addressing both fronts, surface and bulk passivation. To make it relevant to the PV industry, the experimental work focuses on a specific class of commercial PECVD reactors. This is significant, because the properties of SiN films are usually strongly dependent on the type of machine used to deposit them. The Roth and Rau SINA reactor used in this study is capable of coating up to 1200 wafers per hour with excellent uniformity. The plasma is excited by a microwave antenna operated at a frequency of 2.45GHz, remote from the silicon wafers. A distinctive feature of this large reactor is that the plasma source is pulsating, rather than continuous, as is common in many laboratory sized machines. The latter have already been shown to produce SiN films with excellent surface and bulk passivation (see ref. [8] for a review). In this study we explore a broad range of deposition and thermal annealing conditions to better understand the physics of the passivation and to determine the optimal conditions for a given application. We separate the investigation in two parts, the first using single crystalline wafers to characterise surface passivation and the second using mc-Si wafers to learn about bulk hydrogenation.

2. EXPERIMENTAL DETAILS

In order to cover a broad range of processing variables we have used a design of experiments approach to define nine different PECVD SiN deposition conditions. By modifying the ratio between ammonia and silane, as well as the pressure in the chamber, we obtained a range of refractive indices between 1.97 and 2.34. The deposition temperature set point was 400^oC for all the experiments, but a lower actual wafer temperature cannot be excluded. In our experiments the plasma power, optimised to obtain good uniformity across this meter-wide reactor, and the carrier transport speed were slightly adjusted from run to run to obtain a product of the film thickness by its refractive index of 155nm, which is optimal for antireflection properties.

The nine different SiN layers were deposited on 4-inch, FZ, 1.4 Ωcm, <100>, 300-micron thick, p-type silicon wafers. The refractive index and thickness of the SiN layers were measured by ellipsometry. For the bulk hydrogenation studies, the same SiN films were deposited on crystallographically matched 12.5cmx12.5cm cast multicrystalline silicon wafers with a nominal resistivity of 1-1.5 Ωcm.

To investigate the thermal behaviour of the nine different SiN layers from the point of view of their ability to passivate the surface of crystalline silicon wafers, the effective carrier lifetime was measured using the QSSPC technique [9] after annealing the wafers at different temperatures for increasing periods of time. For this, the FZ Si wafers were cut into quarter pieces and each of them was annealed at a different temperature: 390^oC, 500^oC, 600^oC, 650^oC, and 700^oC. The first three anneals were conducted in a conventional quartz tube furnace in forming gas ambient. Above 650^oC the experiments were performed in a rapid thermal annealing (RTA) furnace, also in forming gas. In addition, another set of quarter wafers was subjected to a typical fire-trough cycle in an industrial conveyor belt furnace.

3. SURFACE PASSIVATION OF MONOCRYSTALLINE SILICON

The first finding of our investigation was that the surface passivation of the as-deposited SiN layers was poor and that an anneal was necessary to improve it. This does not have to be necessarily the case; in fact, almost all the research laboratories have reported good as-deposited passivation. The latter is usually the result of a thorough optimisation of the deposition conditions. Our view is that this optimisation is not essential, since common solar cell fabrication processes include a subsequent thermal step, particularly the firing of the screen-printed metallization. It is possible that a better control of wafer cleaning and surface preparation would have resulted in a better as-deposited passivation in our experiments. But this does not really matter, since in all cases the surface passivation improved drastically after a moderate annealing treatment.

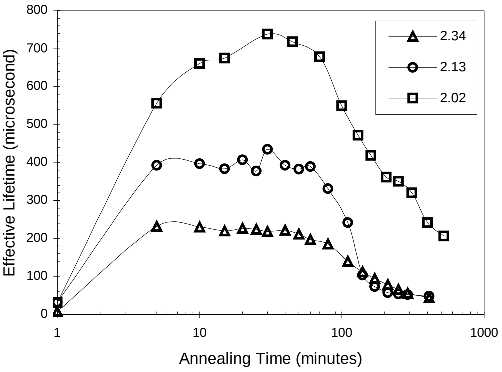

Figure 1. Effective lifetime of 1.4 Ωcm FZ silicon wafers passivated with industrial PECVD SiN as a function of annealing time at 390 °C. Three SiN layers with refractive indices of 2.02, 2.13 and 2.34.

The effective lifetime of three different SiN layers as a function of annealing time at 390°C is shown in Figure 1, where the "1 min" point indicates the as-deposited condition. Note that a high effective lifetime is synonymous with a low surface recombination velocity. The sample with refractive index of 2.02 follows the type of thermal behaviour that one would logically expect: the lifetime increases first with anneal time, reaches a peak value, and then drops-off. The decay can be approximated by an exponential function. For this low annealing temperature, a plateau where the lifetime remains approximately constant for a relatively long period of time is clearly observed for most of the samples. Nevertheless, different SiN layers behave quite differently in terms of electronic quality. The results in Fig. 1 indicate that the level of surface passivation achievable with the different layers used in this study varies considerably. In particular, the high refractive layer (n=2.34) is incapable of the same good passivation as the other two layers shown.

Figure 2 gives an overview of the lengthy experiments to which every one of the nine different samples were subjected to. This particular sample S2 had an as-deposited refractive index of 2.02. The effective minority carrier lifetime, which is dominated by recombination at the surface, was measured as a function of annealing time at five different temperatures. The "0.01 min" data point indicates the as-deposited condition. For all the temperatures, the effective lifetime followed the same qualitative behaviour mentioned above: it increased to reach a maximum and then decreased with time. For this particular sample the maxima at 400°C, 500°C and 650°C are very similar, in the range 600µs-820µs. We obviously missed the peak at 600°C and 700°C. As can be noticed in Fig.2, the commencement of the degradation occurs earlier with increasing anneal temperature. At 400°C the surface passivation starts degrading after approximately 30 minutes, while at 650°C it only takes six seconds.

Similar annealing experiments were performed for all the SiN layers, revealing peculiar features that will be described in more detail elsewhere. We consistently observed that the best surface passivation that may be achieved with every one of those layers is quite different.

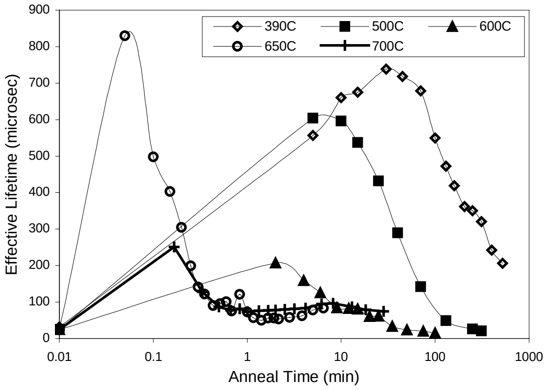

Figure 2. Effective lifetime of 1.4Ωcm FZ silicon wafers passivated with PECVD SiN of refractive index 2.02 as a function of annealing time. Five different curves are shown for the annealing temperatures of 390°C, 500°C, 600°C, 650°C and 700°C.

The best lifetimes measured for every SiN layer at any annealing temperature are collected in Figure 3. In some cases the best passivation was obtained after annealing at 390°C in a conventional furnace, while in other samples a short RTA gave the best results. A second set of data points in Fig. 3 correspond to a typical industrial firing process using a conveyor belt furnace.

The highest lifetime measured in this study was 1.27ms (equivalent to a surface recombination velocity of 7.5cm/s), for a SiN layer with n=1.97, after a 10-second anneal at 700°C. This is similar to the best values for SiN passivated silicon wafers of the same resistivity reported to date [7]. Although this was a one-off occurrence, several samples repeatedly reached peak effective lifetimes in the vicinity of 800µs (that is, a surface recombination velocity of 15cm/s). These results prove that the industrial size PECVD reactor used for this study is capable of producing a surface passivation quality that matches that of laboratory size machines.

As can be noted in Fig. 3, the peak effective lifetime observed for the different SiN layers increases as their refractive index decreases. Our study therefore indicates that the best surface passivation is obtained with low refractive index, nearly stoichiometric, SiN layers. This trend is similar to laboratory results obtained using a direct HF plasma machine [10], but it contradicts the prevalent belief that high refractive index layers are better [6, 11].

The results corresponding to a typical industrial firing process, also plotted in Fig. 3, show a similar trend, that is, better passivation for low refractive indices, even if the trend is much less accentuated. This similarity is not surprising, since all the data points shown in Fig. 3 correspond to some kind of post annealing conditions. Obviously, the industrial firing is not optimal in terms of surface passivation, but it is quite acceptable. Even after the industrial firing process most of the SiN layers in this study still achieved a surface recombination velocity in the vicinity of 75cm/s (effective lifetime of about 200µs), which is sufficient for most solar cell applications.

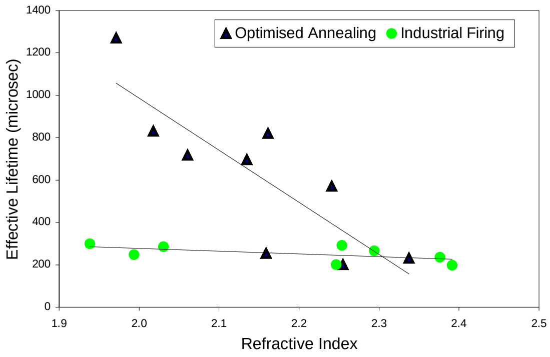

Figure 3. Effective lifetime as a function of the refractive index corresponding to nine different PECVD SiN deposition conditions. The lifetimes after a firing cycle in a belt furnace are given by the lower curve.

The trend observed for the industrial anneal case agrees well with a similar experiment reported by Lenkeit[12] for SiN layers in the range n=2-2.4, which concluded that the most thermally stable layers (that is, in terms of maintaining good surface passivation after annealing in a conveyor belt furnace) were those with a refractive index of approximately 2.0. Recent experiments at ISFH [13] have shown that the surface passivation is more stable thermally for SiN layers having moderate Si content (n=2.1) than for Si-rich layers (n-2.4).

4. BULK HYDROGENATION OF MC-SI

Although several researchers have reported that the efficiency of mc-Si solar cells and the lifetime of mc-Si wafers improve significantly after firing the screen-printed metal contacts or annealing the wafers in the presence of a PECVD SiN layer, the experimental evidence of the effect is still somewhat incomplete. The prevalent physical explanation is that hydrogen is released by the SiN_x:H film, diffuses deep into the wafer and subsequently passivates defects that abound in mc-Si.

It is conceivable that different SiN layers may possess different hydrogenation qualities. Some researchers have observed that different plasma machines and deposition methods lead to different results. For example, Dekkers et al.[14] have found that to achieve a similar level of hydrogenation with high-frequency SiN as with low-frequency SiN it is necessary to add hydrogen to the gas mixture in the HF machine. Rohatgi et al. [15] have found LF nitride deposition to be more effective than HF nitride for ribbon materials. Interestingly, the latter have found that an extremely short, 1 second, anneal at 750°C is sufficient to obtain hydrogenation. Hong et al.[16] have found that the hydrogenation properties of SiN deposited by an Expanding Thermal Plasma technique could be practically as good as those of SiN deposited in industrial microwave-excited plasma reactors. These researchers have found that the mass density of the SiN film is a key factor for bulk passivation of mc-Si, with higher density films being more effective. They also measured a higher mass density for N-rich (nearly stoichiometric films) than for as-deposited Si-rich films. Hence, the former, they concluded, is preferable in terms of bulk passivation.

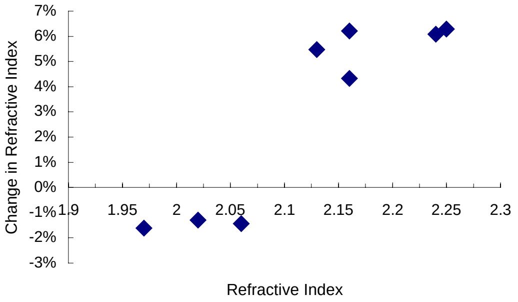

Figure 4. Change of the refractive index of the nine PECVD SiN after atypical firing cycle.

Fig.4 shows the change of the refractive index of the nine different SiN layers used in this paper after industrial annealing. The change was negligible for n<2.1, but quite noticeable (5.7%) for the silicon rich SiN layers. This is in agreement with the results of Hong et al.[16], and may be considered to be an indication that the Si-rich layers are less thermally stable than the nearly stoichiometric ones.

To assess possible differences in the bulk hydrogenation resulting from the different SiN layers we used matched 1-1.5Ωcm p-type cast mc-Si wafers and subjected them to a typical 40-50Ω/sq industrial phosphorus diffusion, followed by deglazing and PECVD SiN deposition on both sides. Every one of the nine SiN layers described in Section 3 was deposited on two mc-Si wafers. One of the two wafers was annealed in an industrial conveyor belt furnace, while the other was kept as reference.

The lifetime was then measured at nine different locations of each wafer. Although the effective lifetime that can be measured at this stage is capped by the presence of the phosphorus emitter[17] we were able to observe a significant improvement of the lifetime upon annealing. The average of all nine SiN layers and nine wafer positions was 13µs before anneal and 22µs after anneal. The impact of this 1.7 times lifetime improvement is that the implied V_{oc} increases from 595mV to 610mV. This is in agreement with voltage gains typically achieved in industrial fabrication thanks to PECVD SiN.

To evaluate the true impact of the hydrogenation treatment on the bulk lifetime of the mc-Si wafers, we etched the n^+diffused and re-passivated their surfaces with fresh PECVD SiN layers. The latter were deposited at 400°C, and should not produce additional bulk hydrogenation effects. The new lifetime measurements, shown in Fig.5, can confidently be interpreted to reflect the bulk lifetime of the mc-Si material, given that the surface passivation typically achieved with these stoichiometric SiN layers is in the millisecond range.

The lower curve in Fig.5, labelled “non fired”, corresponds to the lifetime measured before annealing at nine positions across each wafer (A to I). We have

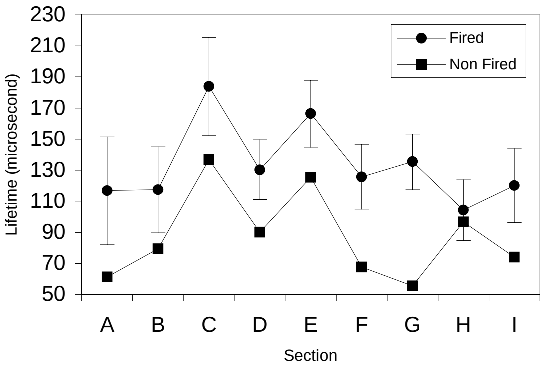

Figure 5. Improvement of the effective lifetime of mc-Si wafers after industrial annealing. The average values of all the SiN layers are plotted as a function of position across the wafer.

averaged the lifetimes measured for the nine wafers used in the experiment, since no post-deposition anneal of the SiN layers had been performed on them and they should be identical. As can be noted, the lifetime varies considerably across the surface of the wafer, between 55µs and 136µs; the average value being 86µs. The second curve in Fig.5, labelled "fired", manifests a general improvement of the lifetime after annealing the SiN layers. The variability of the lifetime is now less pronounced, between 104µs and 184µs, with an average value of 131µs. Note, in particular, that the lowest values of the lifetime (about 90µs) are considerably higher than the lowest observed before firing. The error bars in this curve represent the standard deviation of the lifetime for the nine different SiN layers investigated. It is also interesting to note that the very worst regions before firing (sections A and G) improved drastically, while region H, the only exception, did not improve much. The lifetime improvement of these mc-Si wafers attributable to the annealing of the SiN layers is, globally, a 56%. This result is consistent with the 145% reported by IMEC [2], the 75% reported by ISFH [18], and the 24% reported by ECN[1].

Even if the QSSPC instrument used in this study does not have enough resolution to reveal grain boundaries and localised high recombination points (every data point in our study represents an average lifetime value over an area of about 3cm^2), it appears that the benefits of SiN-induced hydrogenation are more significant the lower the initial lifetime of the material is. This is further shown in Fig.6, where the relative improvement can be seen to be much higher for the low lifetime regions (30% - 180%), than for the high lifetime regions (20% to 60%). Also plotted in Fig.6 are the trend lines for three different SiN layers having refractive indices of 2, 2.16 and 2.29. The best results were obtained for the layer having the lowest refractive index, but the scatter of the data points is, in general, very large. A definite conclusion as to which SiN deposition condition and refractive index is preferable from the point of view of bulk hydrogenation cannot be confidently extracted from this experiment.

5. CONCLUSIONS

The experimental results presented in this paper prove that the state-of-the-art industrial PECVD SiN reactors are capable of yielding outstanding surface passivation. Effective bulk hydrogenation of multicrystalline silicon is manifested by a 56% average improvement of the minority carrier lifetime. Our experiments show that SiN layers with relatively low refractive indices (lower than 2.1) are preferable from both the surface passivation and bulk hydrogenation points of view. In addition, they have low optical absorption and good antireflection properties. Globally they are, therefore, ideal for solar cell applications.

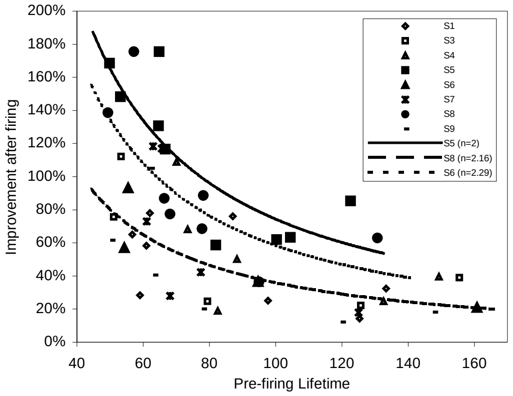

Figure 6. Increase of the effective lifetime of mc-Si as a function of the initial lifetime of the specific region of the wafer. Data are given for nine different PECVD SiN layers

Acknowledgement: This work has been funded by the Australian Research Council.

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