COMPARISON OF HIGH QUALITY SURFACE PASSIVATION SCHEMES FOR PHOSPHORUS DIFFUSED EMITTERS

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ABSTRACT: The emitter saturation current density (J_{oe}) of various high quality passivation schemes on phosphorus diffused emitters has been measured and compared. The passivation schemes investigated were: (i) stoichiometric PECVD silicon nitride (SiN), (ii) forming gas annealed and alnealed thin thermal silicon oxides and (iii) double layers of thin thermal oxide and PECVD SiN. Optimised deposition parameters for our PECVD SiN layers have been determined. The resulting J_{oe} values ranged from 20-120fA/cm^2 (47-105fA/cm^2) as the sheet resistance decreased from 400-30Ω/☐ (380-50Ω/☐) on planar surfaces (textured surfaces). The best passivation schemes, for all sheet resistances, were an alnealed thin oxide or a thin oxide/PECVD SiN stack with J_{oe} values as low as 5fA/cm^2 being measured. The optimised PECVD SiN is, nevertheless, sufficiently good for most silicon solar cells.
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1. INTRODUCTION

Emitter passivation is an important aspect of high efficiency solar cells [1, 2]. Not only must the passivating layer reduce the surface recombination at the n^+ diffused surface to acceptably low levels, it must also be compatible with antireflection coatings to maximise the photogenerated current within the silicon substrate.

In the highest efficiency laboratory cells, this is achieved by appropriately annealing a thin, high temperature thermal oxide, and subsequently depositing ZnS/MgF_2 antireflection coatings [3]. For commercial solar cells, a promising technology to simultaneously provide surface passivation and an effective antireflection coating is the plasma enhanced chemical vapor deposition (PECVD) of silicon nitride (SiN) [4]. PECVD SiN films have the additional benefits that they are deposited at low temperature (<400°C) and are thus compatible with many other commercial fabrication processes like screenprinted metal contacts [5].

In this work, we present a systematic comparison of phosphorus-diffused emitter passivation achieved with thin, high temperature thermal oxides and optimised PECVD SiN layers. Both planar and textured surfaces have been investigated with emitters suitable for both laboratory and commercial solar cells (sheet resistivities ranging from ≈40-400Ω/☐). Double layers of thin thermal oxide and PECVD SiN were also investigated.

2. EXPERIMENTAL DETAILS

The n^+pn^+ test structures used to investigate the emitter passivation were prepared using shiny etched 50Ωcm p-type FZ wafers. Texturing was performed in a mixture of KOH and isopropanol to produce random pyramids which are ≈10μm in size. All diffusions were performed in a quartz tube at temperatures between 840°C and 925°C using liquid $POCl_3$ as the dopant source. After stripping the phosphorus glass, the samples were oxidised at 900°C for 30mins. This produced a thin oxide layer (≈13nm) and simultaneously drove-in the diffusion. The samples were then divided into four batches:

- Batch 1 – The thin oxide was stripped in HF, optimised SiN layers deposited on both sides and J_{oe} measured (planar and textured surfaces).
- Batch 2 – J_{oe} measurements made for the as-oxidised samples, forming gas annealed (FGA) samples and alnealed samples (planar and textured surfaces).
- Batch 3 – Optimised SiN layers were deposited on top of the thin oxide layers (both sides) and J_{oe} measured (planar and textured surfaces).
- Batch 4 – Si-rich SiN layers were deposited on top of the thin oxide layers (both sides) and J_{oe} measured (planar surfaces only).

The SiN films were fabricated in a high frequency (13.56MHz), direct PECVD reactor. Ammonia (NH_3) and 4.5% silane ($SiH_4:N_2$) in nitrogen were used as the process gases. Optimised deposition parameters were determined using planar samples with a sheet resistance of 120Ω/☐.

The emitter saturation current density (J_{oe}) was determined using the quasi-steady-state photoconductance method [2, 6] with the samples in high injection ($\Delta n > 1 \times 10^{15}$cm^{-3}). Following J_{oe} measurements, the thin oxide and SiN layers were etched and the emitter sheet resistance determined using a four-point probe.

3. PECVD SiN DEPOSITION PARAMETERS

The deposition parameters optimised were the substrate temperature, the gas flows, the silane to ammonia gas flow ratio $[SiH_4:N_2]/[NH_3]$, the total gas pressure and the plasma power. Only main effects were studied with interactions assumed to be small.

Substrate temperature and gas flow ratio were found to be the most important parameters with their effects shown in Figures 1 and 2. A minimum in J_{oe} occurs for high ammonia flows with a gas flow ratio between 7 and 9. Also, higher substrate temperature leads to lower J_{oe}.

The refractive index (n) of some of the SiN films, determined at 630nm from reflectance data, are included in

Figure 1. The optimised SiN films have a refractive index of ≈1.9, which indicates they are nearly stoichiometric in composition. They are also suitable as a single layer anti-reflection coating (SLARC) for non-encapsulated solar cells. Further, the high hydrogen content of the stoichiometric films allows them to be patterned using standard photolithography and wet chemical etching.

It is important to note that for this work we consider the optimal films to be those with the lowest J_{oe}. These are not necessarily the best films for solar cell applications. While the high refractive index films do not offer quite as good a J_{oe}, they are suitable for the first layer of a DLARC or as a SLARC for glass encapsulated solar cells. High refractive index SiN films may result in a nett increase in cell efficiency due to increased photogeneration when compared to the lowest J_{oe} films. We do not consider this trade off any further in this work.

It is interesting to compare our optimisation results with those of Lenkeit et al [7]. In contrast to our results, they found that SiN films with higher refractive index provided better surface passivation. Also, for near stoichiometric SiN films (n≈1.9), Lenkeit et al found the optimal deposition temperature to be 300-350°C, with higher temperatures reducing the surface passivation. We attribute the differences in the results to the fact that we used 4.5% silane in nitrogen while Lenkeit et al used pure silane.

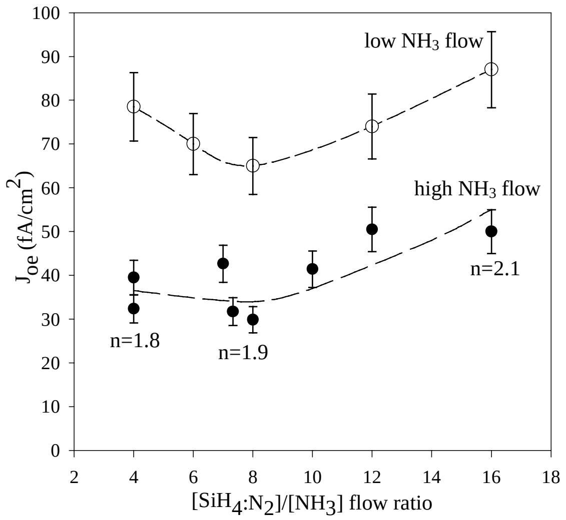

Figure 1: Effect of silane/nitrogen to ammonia gas flow ratio on the J_{oe} of SiN passivated emitters. The refractive index (n) of some samples is indicated.

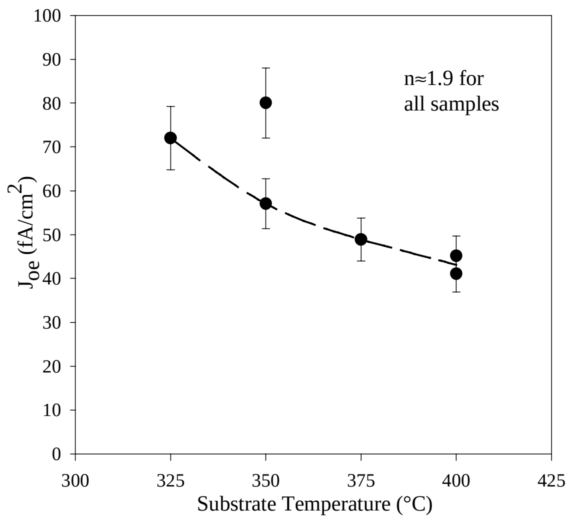

Figure 2: Effect of SiN deposition temperature on the J_{oe} of SiN passivated emitters.

These results suggest it is possible to vary the silane carrier gas composition to achieve the lowest J_{oe} at any desired refractive index between n≈1.9 (dilute silane in nitrogen) to n≥2.4 (pure silane). This ability to independently optimise the passivation quality and the optical properties of SiN films is of importance to the commercial application of PECVD SiN films to solar cells. Clearly, an optimisation study of the emitter passivation as a function of carrier gas composition is warranted.

4. RESULTS AND DISCUSSION

4.1 SiN Passivated Planar Samples

The effect of sheet resistance on the J_{oe} of SiN passivated, phosphorus diffused emitters is shown in Figure 3. The range of sheet resistances covered is from 30-430Ω/☐. This covers: i) emitters which can accommodate screen printed contacts (≈40Ω/☐); ii) high efficiency homogenous emitters suitable for evaporated contacts (≈100Ω/☐); and iii) transparent, lightly doped emitters as would occur at uncontacted sections of a selective emitter structure (>150Ω/☐). The error bars in the figure represent an estimated error of ±10% in the J_{oe} value. The dashed line is included as a visual guide.

As expected, the J_{oe} increases as the sheet resistance decreases. J_{oe} values as low as ≈20fA/cm^2 have been measured for lightly doped emitters and ≈100fA/cm^2 for industrial like emitters. Assuming a short circuit current density of 41mA/cm^2, these J_{oe} values limit the open circuit voltage of a solar cell to 728mV and 687mV respectively (not including recombination at the contacts). The surface passivation of these PECVD SiN films is clearly very good.

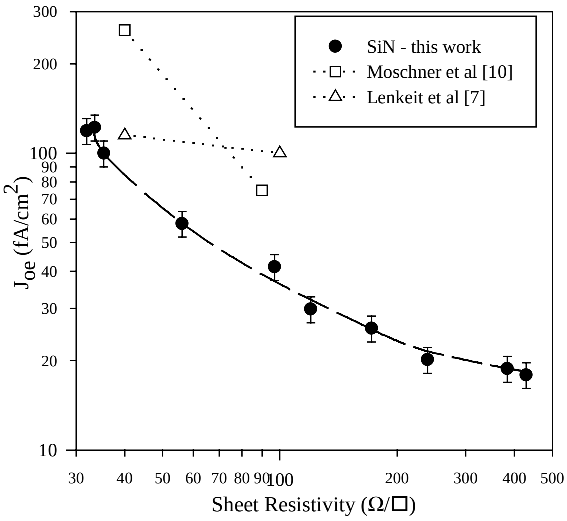

Figure 3: Effect of sheet resistance on the J_{oe} of SiN passivated phosphorus diffused emitters with a planar surface.

Included in Figure 3 are data for other PECVD SiN systems obtained from the literature. While the diffusion profiles, PECVD deposition parameters, mode of plasma excitation and method for measuring J_{oe} may be different for some of these data, the J_{oe} values of our optimised films compare favourably with other SiN films.

To confirm the excellent emitter passivation of our SiN films, we have fabricated all SiN passivated simplified PERC cells with a planar front surface and homogenous emitter (see [8] for details). The emitter of these cells was fabricated in the same way as for the n^+pn^+ test structures and had a sheet resistance of approximately 100Ω/☐. The internal quantum efficiency (IQE) for one of these cells is shown in Figure 4. The IQE is approximately 100% between the wavelengths of 350-650nm demonstrating the excellent passivation provided by the front SiN layer.

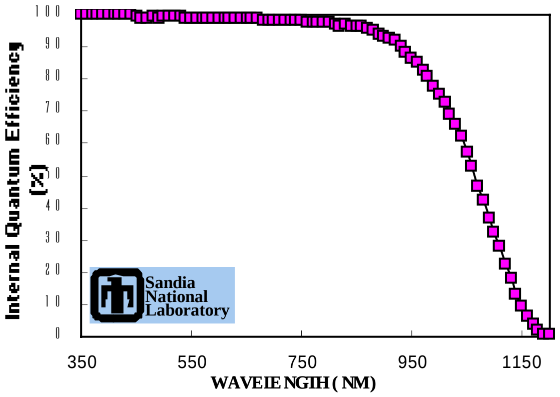

Figure 4: Internal quantum efficiency of an all SiN passivated PERC cell. The front surface was planar with a homogenous emitter.

4.2 Thin Oxide Passivated Planar Samples

The J_{oe} for planar, thin oxide samples is compared to the SiN passivated samples in Figure 5. While the SiN films offer very good passivation, it can be seen that a thin oxide offers superior passivation, particularly when the oxide is FGA or alnealed. Indeed, for the alnealed oxides, J_{oe} as low as ≈5fA/cm^2 have been measured for sheet resistances above 200Ω/☐. The very low J_{oe} values measured for lightly doped emitters with an alnealed thin oxide are comparable with the values published by King et al [1] and Cuevas et al [9].

At lower sheet resistances, where the emitters are more opaque, there is minimal difference in the passivation quality of the SiN films compared to any of the oxide films. This is a significant result, as it indicates that on industrial like emitters, PECVD SiN films are capable of passivating the surface as well as the best solid film passivation schemes available.

Another highly effective passivation scheme is the oxide/SiN stack as used by Moschner et al [10]. Figure 6 compares the J_{oe} of alnealed thin oxides with oxide/SiN stacks. Data for both optimal SiN (n≈1.9) and Si-rich SiN (n≥2.1) have been included. It can be seen that the three passivation schemes are all outstandingly good and essentially equivalent. For these oxide/SiN stacks, the Si-rich SiN stack would be superior due to the potentially better antireflection properties mentioned previously.

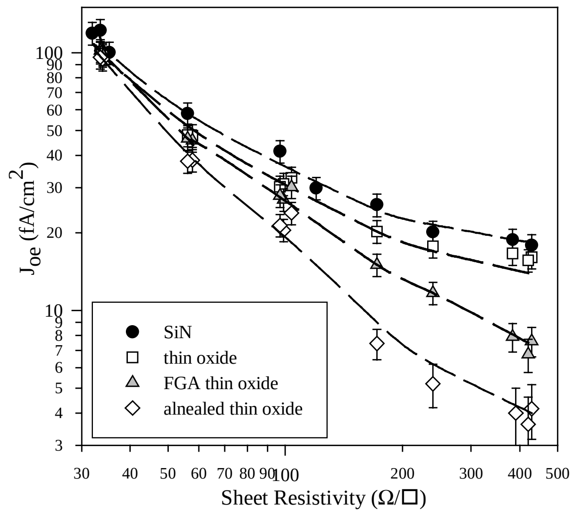

Figure 5: Comparison of the J_{oe} of phosphorus diffused emitters passivated with PECVD SiN and thin thermal oxides.

It is worth mentioning that for emitters passivated with SiN and thin oxide/optimal SiN stack, we tested if the passivation was stable against a short anneal (30mins) at 400°C as would normally be used to sinter evaporated contacts. No change in the measured J_{oe} values was found. This is different to alnealed thin oxide passivation, where a short anneal degrades the passivation quality.

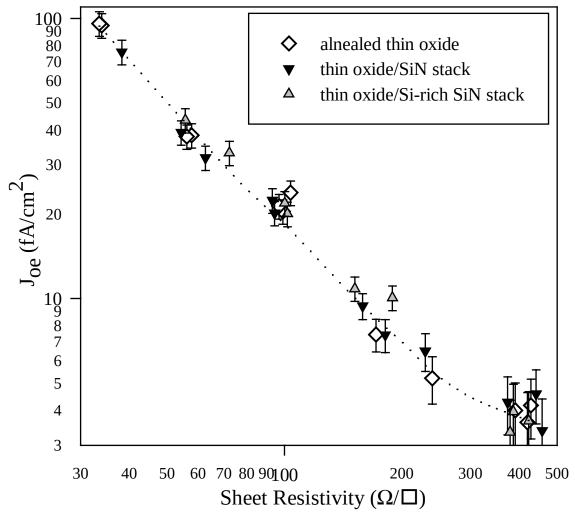

Figure 6: Comparison of the J_{oe} of phosphorus diffused emitters passivated with alnealed thin thermal oxides and oxide/SiN stacks.

It is interesting to compare the relative passivation quality of PECVD SiN layers and thermal oxides on p-type and n-type surfaces. The results above show that thin oxides (with no annealing) and FGA oxides both offer better passivation of the n^+ diffused surface than SiN layers. However, on undiffused p-type surfaces, SiN layers offer significantly better surface passivation than FGA oxides [11]. Assuming that doped and diffused surfaces are similar, it follows that there should be a doping level where the passivation qualities, under low injection conditions, are similar.

Further, on the heavily diffused samples (N_{surf} > $2x10^{20}cm^{-3}$), the SiN films still passivate the surface reasonably well ($J_{oe,pass}$≈120fA/cm^2 c.f. $J_{oe,unpass}$≈400fA/cm^2). It is thus unlikely that SiN films rely solely on fixed positive charges at the Si/SiN interface for surface passivation.

4.3 Textured Samples

The measured J_{oe} values for textured samples passivated with SiN layers and thin thermal oxides are shown in Figure 7. For the SiN passivated emitters, the J_{oe} values range from 47-105fA/cm^2 as the sheet resistance decreases from 380-50Ω/☐. Again, this emitter passivation is very acceptable with the open circuit voltage limited to between 685-706mV depending on the emitter sheet resistance.

Comparison of the data in Figure 3 and Figure 7 for SiN passivated emitters indicates that the J_{oe} increases by a factor of 1.5-2.5 when going from a planar to a textured surface. This is similar to the increase measured by Moschner et al and is consistent with the increase in surface area of the emitter and the possibility of increased surface recombination of the <111> silicon planes.

The data in Figure 7 for oxide passivated emitters again shows that thin oxide passivation is superior to SiN passivation. Similarly, an alnealed oxide is superior to a FGA oxide, which is superior to the as-oxidised samples. Also, the thin oxide/SiN stack gave comparable passivation to the alnealed oxide samples. The lowest J_{oe} measured for textured samples (either the alnealed oxide or oxide/SiN stack samples) was ≈12fA/cm^2 for sheet resistances above 300Ω/☐. The increase in J_{oe} when comparing textured and planar oxide passivated samples was a factor of 1.5-2.5, the same as for the SiN samples.

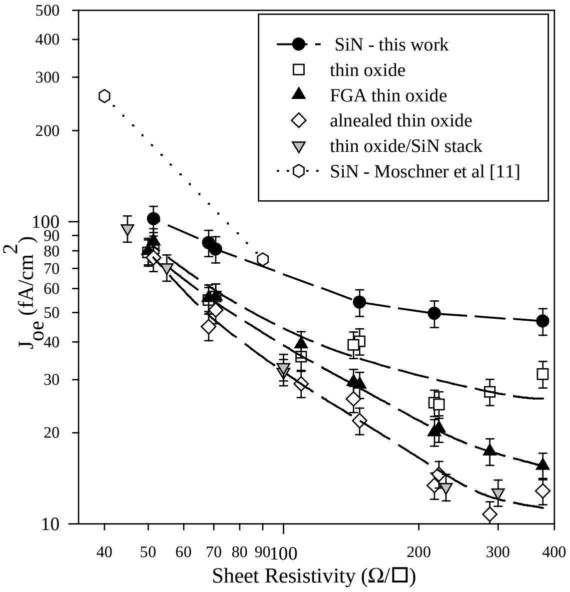

Figure 7: Comparison of the J_{oe} of phosphorus diffused, textured emitters passivated with PECVD SiN and thin thermal oxides.

5. CONCLUSION

A systematic comparison of phosphorus-diffused emitter passivation achieved with thin, high temperature thermal oxides and optimised PECVD SiN layers has been made. Optimised deposition parameters for our PECVD SiN layers have been identified, resulting in low J_{oe} values ranging from 20-120fA/cm^2 (47-105fA/cm^2) as the sheet resistance decreased from 400-30Ω/☐ (380-50Ω/☐) on planar surfaces (textured surfaces).

Thin oxide passivation was found to be superior to SiN passivation, with an alnealed oxide superior to a FGA oxide, which is superior to the as-oxidised samples. J_{oe} values as low as 5fA/cm^2 (12fA/cm^2) were measured for alnealed passivated emitters with a high sheet resistivity on a planar (textured) surface. The passivation quality of emitters passivated with an alnealed, thin oxide or a thin oxide/SiN stack was equivalent.

For industrial like emitters (~40Ω/☐), the J_{oe} values for SiN passivated and the various oxide passivated emitters are very similar. The J_{oe} values for textured surfaces was a factor of 1.5-2.5 times greater than for planar surfaces.

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