

AN EARLY DEPOSITED LPCVD SILICON NITRIDE: ALLOWING THE POSSIBILITY OF NOVEL CELL DESIGNS

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ABSTRACT

An LPCVD silicon nitride layer deposited in the early stages of cell fabrication has many properties that allow for increased processing flexibility and hence the realisation of novel cell designs. We have shown previously that excellent surface passivation can be achieved provided at least a thin oxide is present under the nitride. Surface passivation is lost once the wafer is heated, due to a loss of hydrogen from the silicon/oxide interface, but can be recovered entirely by re-introducing hydrogen to this interface. The work presented in this paper is concerned with hydrogen re-introduction using a high temperature forming gas anneal. We show that the thermal history of the wafer and the thickness of the silicon nitride layer both affect the time necessary to recover surface passivation.

1. INTRODUCTION

Silicon nitride, deposited using plasma enhanced chemical vapour deposition (PECVD), is often used in high efficiency silicon photovoltaic devices. PECVD silicon nitride provides both excellent surface passivation and a good anti-reflection coating. It is typically deposited as one of the final stages in a cell fabrication process, since the surface passivation is degraded if the wafer is heated. Silicon nitride may also be deposited using low pressure chemical vapour deposition (LPCVD). This is a standard process in the integrated circuit industry and is both reliable and economical for batch mode deposition. LPCVD silicon nitride layers are very hard and therefore scratch resistant, they are resistant to many alkaline and acidic silicon etchants, are an excellent diffusion barrier for many impurities and can be used to mask against both diffusions and oxidations. LPCVD silicon nitride has a much lower hydrogen content, typically 2-10 atomic% [1,2], compared with 20-25 atomic% for PECVD silicon nitride. If deposited in the early stages of cell fabrication, then advantage may be taken of these properties, thereby allowing the possibility of increased processing flexibility and the realisation of novel cell designs.

LPCVD silicon nitride provides very little surface passivation if deposited directly onto silicon. Excellent surface passivation can be achieved provided a thin oxide is present under the nitride. The presence of the oxide does not significantly increase reflection. Assuming normally incident light and no oxide, a minimum reflection of 6.5% occurs with a 78nm thick nitride. With a 25nm thick oxide, the minimum reflection is 8.6%, which occurs with a 50nm thick nitride. This difference is still smaller for textured wafers. As with PECVD silicon nitride, the surface passivation properties

are lost once a wafer with an LPCVD silicon nitride is heated, even when an oxide is present under the nitride. We have shown previously that this is due to a loss of hydrogen from the silicon/oxide interface and that the hydrogen can be re-introduced using a high temperature forming gas (5% hydrogen in argon) anneal [3].

Figure 1 shows the effect of high temperature anneals on the effective lifetime of wafers with a 100nm thick oxide and a 33nm thick nitride. Values are shown firstly after oxide growth and nitride deposition, at which point the effective lifetime is high. Although it is not shown in this graph, the effective lifetime after nitride deposition was essentially the same as that after oxide growth. Figure 1 also shows that after an anneal in nitrogen, in this case for 30 minutes at 900°C, the effective lifetime was clearly degraded. This degradation was thought to be due to either 1) permanent damage to the wafer bulk caused by a mismatch in the thermal expansion coefficients between silicon and the overlying silicon nitride or 2) to a loss of hydrogen from the silicon/oxide interface, thereby causing a drop in surface passivation and hence an apparent drop in the effective lifetime. Previous work has shown the first possibility not to be true since the effective lifetime can be completely recovered by removing the oxide/nitride stack and re-passivating the surface with a second oxide [1]. An easier way to recover surface passivation is to use a high temperature forming gas anneal, the affect of which is shown by the third curve in figure 1. This forming gas anneal was done for 60 minutes at 840°C after which the effective lifetimes were completely recovered. This result lends strong support to the theory that the apparent drop in effective lifetimes after the high temperature nitrogen anneal was due only to a loss of hydrogen from the silicon/oxide interface.

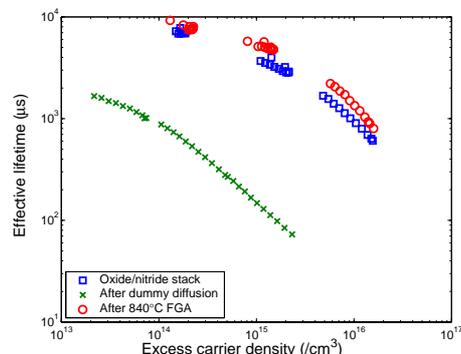


Figure 1: Effective lifetime curves a) after oxide/nitride stack formation (squares), b) after high temperature nitrogen anneal or “dummy diffusion” (crosses) and c) after a high temperature anneal in forming gas (circles). For this wafer the oxide was 100nm thick and

the nitride 33nm thick. The nitrogen anneal was done for 60 minutes at 900°C and the forming gas anneal for 30 minutes at 840°C.

2. EXPERIMENTAL DETAILS

For the work presented in this paper, surface passivation was measured using J_{oe} values, which were obtained from effective lifetime measurements made using the quasi-steady-state photo-conductance technique and the equations of Sinton and Cuevas [4] and Nagel *et al.* [5]. Hydrogen levels at the silicon/oxide interface were not measured directly, but inferred qualitatively from the measurements of J_{oe} . In order to obtain a highly sensitive surface, high resistivity (100-400Ωcm) wafers were used. All wafers -used for this work were p-type and (100) orientated FZ wafers.

The wafers all had first a saw damage etch in a 1:10 HF:HNO₃ solution, which removes approximately 20μm of silicon from each side. They were then RCA cleaned and given a short HF dip before a light phosphorous diffusion. The sheet resistance after phosphorous diffusion was approximately 800Ω/□. Oxidations were done at 900°C for the 25nm thick oxides and 1100°C for the thicker oxides. In both cases a 30 minute nitrogen anneal was done at 1000°C before unloading the wafers. LPCVD silicon nitride was deposited at a pressure of 0.6torr and a temperature of 750°C, with a DCS:NH₃ flow rate of 1:4. Various nitride thicknesses were achieved by varying the deposition time. Forming gas (5% H₂ in Ar) anneals were used for hydrogen re-introduction to the silicon/oxide interface. These were typically done at 840°C.

3. RESULTS

If hydrogen re-introduction is done using a high temperature process, then re-introduction of hydrogen to the silicon/oxide interface must compete with a loss of hydrogen due to the higher temperatures.

In order to determine the optimal temperature for hydrogen re-introduction, wafers were prepared with an oxide/nitride stack and subjected to a high temperature forming gas anneal at temperatures between 840-1000°C. Figure 2 shows J_{oe} values after forming gas anneals. From these results we concluded that the optimum temperature for hydrogen re-introduction was approximately 840°C. At temperatures higher than this, the rate of hydrogen loss from the silicon/oxide interface was greater than the rate of hydrogen re-introduction. This finding is in agreement with other authors who have measured the rate of hydrogen loss and uptake at different temperatures in an LPCVD silicon nitride from a 4% deuterium in nitrogen ambient [6].

3.1 Effect of Nitride Thickness

In order to determine the effect of the nitride thickness on hydrogen re-introduction, wafers were prepared with varying nitride thicknesses.

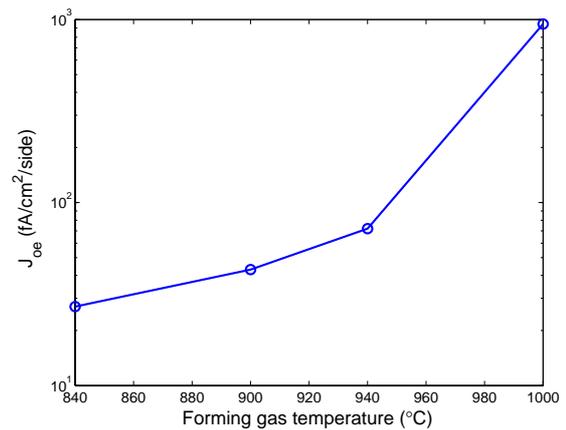


Figure 2: Effect of a high temperature forming gas anneal on J_{oe} for wafers with a 25nm thick oxide and a 51nm thick nitride. The forming gas anneals were done for 1 hour and J_{oe} values before the anneal were in the range 14-16fA/cm²/side for all wafers.

Figure 3 shows J_{oe} values for wafers that had a 25nm thick oxide and nitride thicknesses of 21 and 65nm. Values are shown after oxide growth and after nitride deposition, at which point they were low, indicating good surface passivation. After a 1 hour anneal in nitrogen at 900°C, the J_{oe} of the wafer with the 65nm thick nitride was significantly lower than the wafer with the 21nm thick nitride. This can be explained by assuming the nitride to be a limited source of hydrogen. Although most of the hydrogen in the nitride is most probably lost to the ambient gas, as suggested by Arnoldbik *et al.* [6] and Habraken *et al.* [1], a small percentage may diffuse towards the silicon/oxide interface and is evidently in sufficient quantities to affect the surface passivation in this region.

Three recovery forming gas anneals were done, the first for 30 minutes. After this time, the J_{oe} of the wafer with the 21nm thick nitride had dropped, but J_{oe} of the wafer with the 65nm thick nitride remained unchanged. Further anneals in forming gas resulted in a decrease in both J_{oe} values to close to original values. These results suggest that, perhaps not surprisingly, a thicker nitride means that hydrogen re-introduction to the silicon/oxide interface requires a longer time. They also show that, even with a thick nitride, recovery of J_{oe} values is possible.

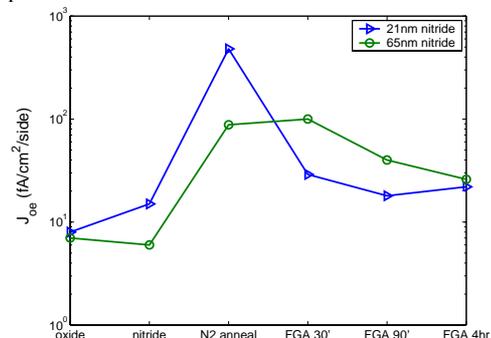


Figure 3: J_{oe} values at various stages for wafers with 21 and 65nm of silicon nitride. The oxide thickness was 25nm for both wafers and the nitrogen anneal was done for 1 hour at 900°C. Anneals in forming gas were done at 840°C for the indicated times. Note that the final recovery point is approximately equal for both wafers.

3.2 Effect of Wafer Thermal History

In order to determine the effect of the thermal history of the wafer on hydrogen re-introduction, wafers were prepared with an identical oxide/nitride stack and subjected to various nitrogen anneals. Anneals were done at 900 and at 1000°C for 15 and 60 minutes. The effect of temperature was assumed to be important since at higher temperatures, hydrogen is lost from an LPCVD silicon nitride and the number of Si-N and N-N bonds increases, thereby resulting in a denser nitride [6].

Figure 4 shows J_{oe} values throughout this experiment. After oxide growth and silicon nitride deposition, the surface passivation was excellent, due to the oxide layer. After the nitrogen anneal, J_{oe} values for all wafers increased, due to a loss of hydrogen from the silicon/oxide interface. The wafer annealed for only 15 minutes at 900°C had a lower J_{oe} than all other wafers, indicating that hydrogen was not fully removed from the silicon/oxide interface with this shorter time and lower temperature.

The wafers each had two anneals in forming gas in an attempt to recover surface passivation. After the first anneal, J_{oe} values were completely recovered for the two wafers annealed at 900°C and partially recovered for the wafer annealed for 15 minutes at 1000°C. This is probably indicative of the “densification” of the nitride film that occurs at higher temperatures. From these results it can be inferred that hydrogen diffusion through the denser silicon nitride film was noticeably slowed. Nevertheless, these results show that even after a 1 hour anneal at 1000°C, J_{oe} values can be completely recovered with a high temperature anneal in forming gas, providing the time is optimised.

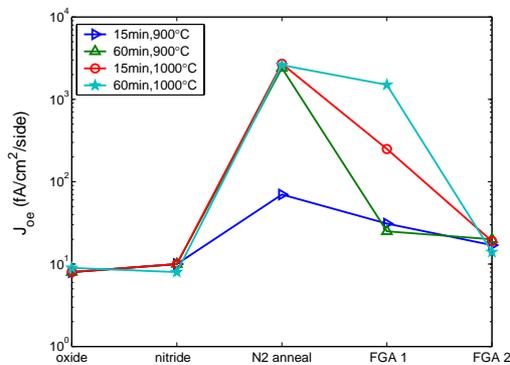


Figure 4: J_{oe} values at various stages for wafers with a 100nm thick oxide under a 25nm thick nitride that were subjected to various high temperature anneals in nitrogen. The times and temperatures of these anneals are indicated in the legend.

4. DISCUSSION

The behaviour of these wafers under high temperatures may be at least qualitatively explained by a hydrogen loss model. Figure 5 shows possible hydrogen profiles through an oxide/nitride stack on silicon after deposition and after subsequent anneals in nitrogen. It is based on measurements made by Habraken *et al.* [1] and Xie *et al.* [7]. Part a) of figure 5 shows the situation immediately

after deposition of the nitride. The concentration of hydrogen in the nitride is uniform and high (approximately 2-10 atomic% [1,2,8]). The concentration at the silicon/oxide interface is high and surface passivation is unaffected by nitride deposition. Part b) shows the situation after an anneal in a high temperature nitrogen ambient. The hydrogen concentration in the nitride remains uniform, but is decreased. The hydrogen concentration at the silicon/oxide interface is also decreased. Part c) shows the situation after a nitrogen anneal at a higher temperature than used for part b). Hydrogen is almost completely removed from the silicon/oxide interface and levels are low, but uniform, in the nitride. (For a 1.5 hour anneal in a vacuum at 1000°C, Habraken *et al.* [1] observed that the hydrogen concentration dropped from approximately 3 atomic % after deposition to approximately 0.3 atomic %). As mentioned earlier, the relative rates of increase and decrease in hydrogen concentration levels at the silicon/oxide interface will also be influenced by the nitride thickness, since the nitride acts as a limited hydrogen source.

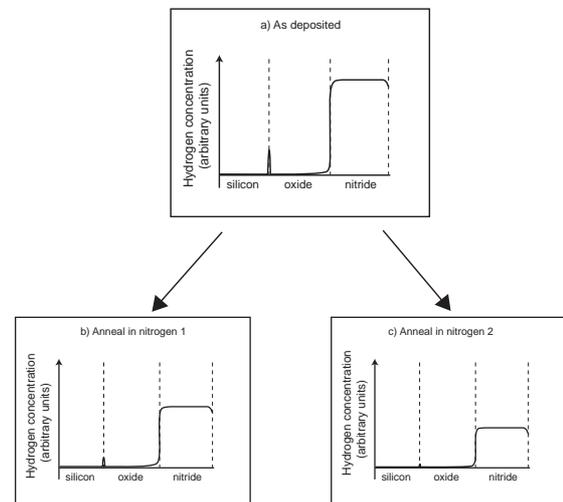


Figure 5: Possible hydrogen profiles for the removal of hydrogen from an oxide/nitride stack on silicon. Part a) shows the situation immediately after nitride deposition, part b) after a high temperature anneal in nitrogen and part c) after a second (higher temperature) anneal in nitrogen. The profiles in the nitride are inferred, based on the results of Habraken *et al.* [1] and Xie *et al.* [7].

Hydrogen movement through the nitride is important for a solar cell as it influences the amount that reaches the silicon/oxide interface. Diffusion of hydrogen through the silicon nitride is complicated by the reaction of hydrogen with the nitride. It is, however, illuminating to first consider the simple case where hydrogen does not react with the nitride. Assuming also that the hydrogen comes from an unlimited supply, then the surface concentration is constant, which will result in error function concentration profiles in the nitride.

Assuming firstly a constant nitride thickness, constant temperature and only one diffusing species, then figure 6 shows possible hydrogen profiles at successively later times. With L equal to the diffusion length for a given time and W equal to the nitride thickness, the profiles are shown for the cases where $L/W < 1$ (curve a), $L/W \sim 1$ (curve b) and $L/W > 1$ (curve c).

As stated, the three curves shown in figure 6 could represent diffusion of the same species in the same material at different times. It is also possible to move from a situation where $L/W < 1$ (curve a) to a situation where $L/W > 1$ (curve c) either by decreasing the nitride thickness or by increasing the diffusion coefficient. A different diffusion coefficient could be realised with:

- a different diffusing hydrogen species, for example atomic versus molecular hydrogen;
- a different temperature or
- a change in the properties of the nitride layer (for example, silicon nitride is more dense after anneals at higher temperatures due to an increased density of Si-N and N-N bonds).

In reality, diffusion of hydrogen through the nitride is complicated because the hydrogen reacts with the nitride. Hydrogen from both atomic and molecular sources will be incorporated into the nitride (as evidenced by the fact that a molecular hydrogen source can be used to increase bonded hydrogen levels in the nitride after they have been reduced during a high temperature anneal [2]). At elevated temperatures, N-H and Si-H bonds in the nitride will be broken and formed simultaneously. Starting from a nitride that has been depleted of hydrogen, levels will increase to a steady-state value, which will depend on the temperature. The solubility of hydrogen in silicon nitride therefore directly affects the diffusion of hydrogen through the nitride to the silicon/oxide interface.

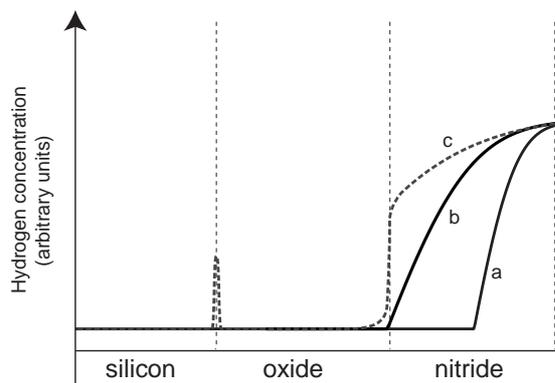


Figure 6: Possible hydrogen profiles for the re-introduction of hydrogen to the silicon/oxide interface through a nitride layer. The three curves indicate three different times, of increasing length. For this scenario, only time c) results in an appreciable increase in hydrogen levels at the silicon/oxide interface. Curve a) illustrates the situation where $L/W < 1$, curve b) where $L/W \sim 1$ and curve c) where $L/W > 1$.

5. CONCLUSION

In conclusion, a wafer with an oxide/LPCVD silicon nitride stack may be subjected to high temperature treatments without irreversible damage to the wafer and therefore the nitride may be deposited in the early stages of cell fabrication. Two conditions must be met for this to be successful. Firstly, there must be a thin oxide underneath the nitride. Secondly, a hydrogen re-introduction step must be done after any high temperature treatments. If a high temperature forming

gas anneal is used for hydrogen re-introduction, then our results suggest it should be done at a maximum temperature of 840°C. The length of time necessary for hydrogen re-introduction is dependant on the thermal history of the wafer and on the thickness of the nitride. We have shown that surface passivation can be recovered even when the wafer is subjected to high temperatures and has a silicon nitride that is sufficiently thick to act as a good anti-reflection coating.

REFERENCES

- [1] F.H.P.M. Habraken, R.H.G. Tijhaar, W.F. van der Weg, A.E.T. Kuiper and M.F.C. Willemsen "Hydrogen in low-pressure chemical-vapor-deposited silicon (oxy)nitride films", *Journal of Applied Physics* **59** (2):447, (1986).
- [2] H.J. Stein, P.S. Peercy and R.J. Sokel "Post-deposition high temperature processing of silicon nitride", *Thin Solid Films* **101:291**, (1983)
- [3] M.J. McCann, K.J. Weber, M.J. Stocks and A.W. Blakers Oxide / LPCVD Nitride Stacks on Silicon: The Effects of High Temperature Treatments on Bulk Lifetime and on Surface Passivation. *17th EC PV Conference, Munich*, 1708-1711(2001).
- [4] R.A. Sinton and A. Cuevas "Contactless determination of current-voltage characteristics and minority-carrier lifetimes in semiconductors from quasi-steady-state photo-conductance data" *Applied Physics Letters*, **69** (17):2510, (1996).
- [5] H. Nagel, C. Berge and A.G. Aberle "Generalised analysis of quasi-steady-state and quasi-transient measurements of carrier lifetimes in semiconductors", *Journal of Applied Physics* **86(11):6218**, (1999).
- [6] W.M. Arnoldbik, C.H.M. Maree, A.J.H. Maas, M.J. van Boogaard, R.H.P.M. Habraken and A.E.T. Kuiper "Dynamic behaviour of hydrogen in silicon nitride and oxy-nitride films made by low-pressure chemical vapour deposition", *Physical. Review. B*, **48** (8):5444, (1993).
- [7] Joseph Z. Xie, Shyam P. Murarka, Xin S. Guo and William A. Landord "Stability of hydrogen in silicon nitride films deposited by low-pressure and plasma enhanced chemical vapour deposition techniques" *Journal of Vacuum Science and Technology B* **7(2)** (1989)
- [8] H.J. Stein and H.A.R. Wegener "Chemically bound hydrogen in CVD Si₃N₄: Dependence on NH₃/SiH₄ ration and on annealing", *Solid State Science and Technology*, **124(6)** (1977)