

Research

SHORT COMMUNICATION

Surface Passivation by Rehydrogenation of Silicon-nitride-coated Silicon Wafers

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A silicon wafer with a silicon nitride layer deposited by low pressure chemical vapour deposition may be subjected to high-temperature treatments without adversely affecting the electronic properties of the silicon on the condition that a thin oxide is present under the nitride. After high-temperature treatments there is an apparent degradation in effective lifetime, probably due to a loss of hydrogen from the silicon/oxide interface. Effective lifetimes can be completely recovered by thermal treatment in a hydrogen-containing ambient. This work has useful applications for solar cells as many of the properties of these nitrides can be used to advantage. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS: silicon nitride; surface passivation; LPCVD; silicon oxide

INTRODUCTION

Silicon nitride (SiN_x) is becoming an important material in silicon photovoltaics and plasma enhanced chemical vapor deposition (PECVD) of SiN_x is now an established industrial process. PECVD SiN_x has several properties that make it useful for photovoltaic applications, including excellent surface passivation of the as deposited layer¹ and a refractive index that can be adjusted to produce a good anti-reflection coating. PECVD silicon nitride also contains a high concentration of atomic hydrogen, which can be used during a subsequent drive-in step to provide bulk passivation of heavily defective substrates.² To provide the most effective surface passivation, the SiN_x layer must be deposited as one of the final stages in a cell fabrication process because once the nitride has been subjected to high-temperature treatments the surface passivation is severely degraded due to a loss of hydrogen.

SiN_x can also be deposited by low-pressure chemical vapor deposition (LPCVD), which is a standard process in the integrated circuit industry. In batch mode it is a very economical and reliable deposition process. Deposition is usually done with ammonia and dichlorosilane (DCS) as the precursor gases. Near-stoichiometric films

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(Si₃N₄) can result when an excess of ammonia is used. The hydrogen content in these films is typically 2–10 atomic%.^{3–5} For comparison, in the case of PECVD SiN_x films, a comprehensive study by Chow *et al.*⁶ using different deposition systems operating under standard operating conditions showed the deposited hydrogen content to be 15–30 atomic%. LPCVD SiN_x films have a number of potentially useful properties; for example they are very hard and scratch resistant; are highly resistant to chemical attack by alkaline or acidic silicon etchants; are an excellent barrier to the diffusion of many harmful impurities and can be used to mask against diffusion or oxidation. If an LPCVD SiN_x layer is deposited in the early stages of a cell fabrication process, then advantage can be taken of these properties to allow the development of novel cell processes.

In order to be able to achieve high cell efficiencies, it is necessary to ensure that the LPCVD silicon nitride layer does not lead to degradation in bulk lifetime, and that good surface passivation is maintained. The thermal stability of a silicon oxide/PECVD silicon nitride stack was investigated by Schmidt *et al.*⁷ They found an 8-nm-thick oxide under a 60-nm-thick SiN layer to be relatively stable after a 12 min anneal at 600°C. The thermal stability of their stacks is possibly explained by the out-diffusion of hydrogen; we found, for our oxide/nitride stacks that thinner nitrides resulted in a faster degradation in surface passivation,⁸ which we attribute to the nitride acting as a limited source of hydrogen. The thermal stability seen by Schmidt *et al.* may be useful in the case of screen printed cells, which are typically subjected to only a short fire-through step after deposition of the nitride. For cells that require further high-temperature processing steps such as diffusion and/or thermal oxidation, the thermal stability of the oxide/PECVD SiN would need to be further tested. To date, the degree of surface passivation achievable from such a structure following high-temperature treatments has not been extensively studied.

EXPERIMENTAL DETAILS

The wafers used for our experiments were 100–400 Ω cm, *p*-type, boron-doped (100) orientated FZ wafers. All wafers were acid etched, cleaned in Radio Corporation America (RCA) 1, RCA 2 and dilute hydrofluoric acid solutions. Both sides of the wafers were then given a light (approximately 800 Ω/square) phosphorus diffusion. For some wafers, a 25-nm-thick thermal oxide was grown, on both sides of the wafers, at 900°C and followed by a 30 min anneal in 5% hydrogen in argon at 400°C. Nitride depositions were done on both sides of the wafers at 750°C with an ammonia flow rate of 120 scc/min and a dichlorosilane flow rate of 30 scc/min. The wafers were characterised by effective lifetime measurements, made with the quasi-steady state photo conductance (QSS-PCD) system (Sinton Consulting WCT100),⁹ and values for the emitter saturation current J_{oe} and maximum bulk minority carrier lifetime τ_{bulk} were extracted using the equations of Sinton and Cuevas⁹ and Nagel *et al.*¹⁰

RESULTS AND DISCUSSION

Figure 1 shows the QSS-PCD data for three measurements. The first (top) curve shows effective lifetime for a wafer with a 25-nm-thick SiO₂ layer. The emitter saturation current density J_{oe} for this wafer was 12 fA/cm² per side. The second (middle) curve shows the effective lifetimes for the same wafer immediately after deposition of a 54-nm-thick layer of Si₃N₄. It can be seen that there was negligible change in effective lifetime as a result of the nitride deposition. The third (bottom) curve shows effective lifetime measurements of a plain silicon wafer onto which a 37-nm-thick layer of Si₃N₄ was deposited. There was no oxide present on the surfaces of this wafer. It is clear that the surface passivation of this sample was poor, and J_{oe} was 615 fA/cm² per side.

Wafers with a 25 nm SiO₂/54 nm Si₃N₄ stack were annealed in nitrogen at 900 or 1000°C for 1 h to simulate the effect of high-temperature treatments. Table I shows the J_{oe} values following these treatments. There was a dramatic degradation of the surface passivation of the wafers. Importantly, however, the bulk lifetime of the wafers was not irretrievably affected. This was ascertained by removing the nitride and oxide layer and growing a second thermal oxide. The effective lifetime curve and J_{oe} value following this treatment closely matched the value measured prior to the high-temperature treatment.

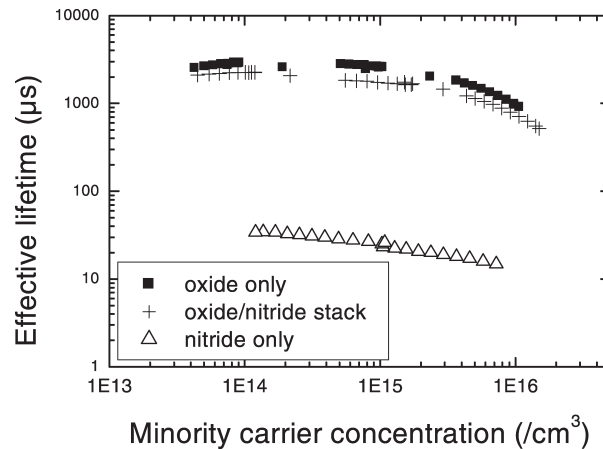


Figure 1. Effective lifetime curves for (a) a wafer with a passivating thermal oxide (squares); (b) the same wafer with a silicon nitride deposited over the oxide (+), (c) a wafer with a silicon nitride layer deposited directly on silicon

Table I. J_{oe} values for wafers with a 25 nm SiO_2 /54 nm Si_3N_4 stack that were annealed at 900 or 1000°C after the nitride deposition. Values are given after initial oxide growth, after nitride deposition and after the high-temperature anneal

Anneal temperature (°C)	J_{oe} oxide only (fA/cm ² per side)	J_{oe} oxide/nitride stack (fA/cm ² per side)	J_{oe} annealed (fA/cm ² per side)
900	15	19	83
1000	12	17	545

Conversely, for a wafer without an oxide layer between the silicon and the silicon nitride, permanent degradation in bulk lifetime was observed following high-temperature treatments. Four wafers were processed together as described above. The effective lifetime at an excess carrier density of $1.5 \times 10^{14}/\text{cm}^3$ after nitride and oxide removal and growth of a second oxide was 2.0–4.5 ms for the wafers that originally had an oxide between the silicon and the nitride, but only 260 μs for the wafer that had no protective oxide under the silicon nitride. This degradation in bulk minority-carrier lifetime is likely to be the result of defect generation in the silicon, caused by the mismatch in coefficients of thermal expansion between silicon and silicon nitride, together with the high level of intrinsic stress in the as-deposited nitride film,¹¹ typically of the order of 1 GPa. In order to prevent bulk degradation, a layer of silicon dioxide (SiO_2) can be grown on the wafer prior to nitride deposition.⁸

The loss of surface passivation following high-temperature treatments can be attributed primarily to a loss of hydrogen from the silicon/oxide interface. This is illustrated in Figure 2. There are four curves in this figure. The first shows the expected high lifetimes after oxide passivation and deposition of the LPCVD silicon nitride layer. The second curve shows lifetimes apparently degraded after a high-temperature (1000°C for 1 h) anneal. The third curve shows the same wafer after removal of the silicon nitride (in hot orthophosphoric acid, which does not etch the silicon oxide layer). There is no significant change in lifetime following removal of the silicon nitride layer, therefore ruling out the possibility that the low lifetimes are due only to the presence of the nitride. The fourth curve shows the wafer following an anneal in a forming gas ambient at 400°C for 30 min. In the absence of the silicon nitride layer, which acts as an effective diffusion barrier to hydrogen at 400°C, hydrogen diffuses readily through the oxide to the silicon/oxide interface. Following this forming gas anneal the wafer lifetime is not significantly different from that of the starting wafer.

Hydrogen diffusion in LPCVD deposited Si_3N_4 is much slower than in SiO_2 films. Passivation of the silicon/oxide interface in the presence of an overlying nitride film requires the diffusion of hydrogen to the interface,

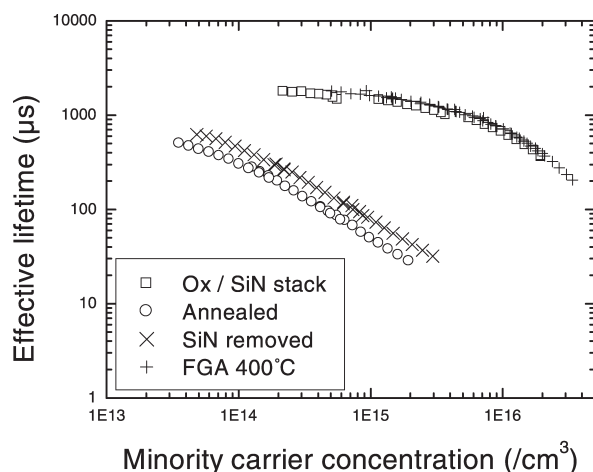


Figure 2. Effective lifetime curves for a single wafer (a) after surface passivation with an oxide and deposition of an LPCVD SiN layer (Ox/SiN stack); (b) after annealing the wafer at 1000°C (Annealed); (c) after removal of the SiN layer (SiN removed); (d) after an anneal in forming gas at 400°C for 30 min (FGA 400°C)

Table II. J_{oe} values for wafers with a 100 nm SiO₂/25 nm Si₃N₄ stack that were first annealed in nitrogen at 900 or 1000°C and then recovered with a forming gas anneal (FGA). FGA 1 was done for 30 min at 800°C and FGA 2 for 4 h at 840°C

Anneal temperature (°C)	J_{oe} SiO ₂ (fA/cm ² per side)	J_{oe} SiO ₂ /SiN (fA/cm ² per side)	J_{oe} annealed (fA/cm ² per side)	J_{oe} FGA 1 (fA/cm ² per side)	J_{oe} FGA 2 (fA/cm ² per side)
900	8	10	2400	25	20
1000	9	8	2600	1500	14

followed by the capture of hydrogen by defect states. In general the efficiency of passivation of a particular defect state depends on the nature of the defect, the nature of the hydrogen species, the hydrogen flux and the temperature. The temperature for passivation must be chosen to minimise hydrogen re-emission from traps while at the same time ensuring a sufficient hydrogen flux to the interface. In an attempt to reintroduce hydrogen to the silicon oxide interface, and thereby restore surface passivation without removing the nitride, higher temperature forming gas anneals were used.

Table II shows J_{oe} values for wafers with an oxide/nitride stack that were subjected to a high-temperature nitrogen anneal and then to subsequent forming gas anneals at 840°C. The J_{oe} values after the high-temperature anneal are much higher than for the wafers shown in Table I because the silicon nitride layer, which acts as a limited hydrogen source,⁸ was thinner. The difference may also be partly due to a lighter phosphorus diffusion, which makes the surface more sensitive to changes in hydrogen levels. These results show that it was possible to recover a significant degree of surface passivation and to maintain the original high bulk lifetimes without removing the silicon nitride layer through the use of a forming gas anneal. Recovery of surface passivation was slower in the case of the nitride that had been annealed at 1000°C. This is probably due to densification of the nitride film at higher temperatures,^{12,13} which would likely result in slower diffusion of molecular hydrogen through the wafer.

In order to determine the optimum forming gas temperature for hydrogen reintroduction, wafers with a 25 nm SiO₂/51 nm Si₃N₄ stack were subjected to forming gas anneals in the temperature range 840–1000°C. These results are shown in Figure 3. It should be noted that these wafers had not been given a high-temperature nitrogen anneal. Separate experiments showed that after a 1 h anneal in nitrogen at 800°C, surface passivation was degraded. It is clear that J_{oe} increased as the temperature of the forming gas anneal was increased, indicating a decrease in the hydrogen concentration at the silicon/silicon dioxide interface. The optimal temperature for

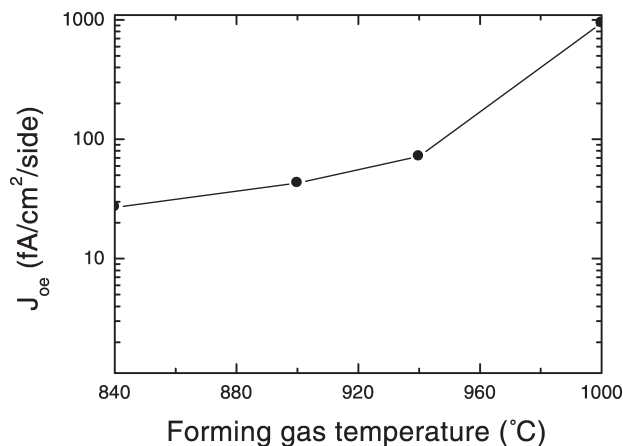


Figure 3. Effect of forming gas anneal temperature on J_{oe} for wafers with an oxide/nitride stack that did not have a high-temperature nitrogen anneal. The oxide thickness was 25 nm and the nitride thickness 51 nm. FGA were done for 1 h. J_{oe} values after oxide nitride stack formation were 14–16 fA/cm² for all wafers

hydrogen reintroduction will be a compromise between a temperature that is high enough to allow hydrogen diffusion through the silicon nitride and yet not so high that hydrogen bonds at the silicon/oxide interface are broken at a faster rate than they are formed. From the results shown in Figure 3, it appears that a temperature of around 840°C is a good compromise that allows effective repassivation of the silicon oxide interface within a reasonable time period.

The presence of a 25-nm-thick oxide under the nitride layer results in a slight reduction in the anti-reflection properties of the silicon surface. This results in an increase in the solar weighted reflectance of a polished surface¹⁴ from 7.2% to 9.0%. The incorporation of texturing would reduce this difference significantly.

CONCLUSIONS

In conclusion, we have shown that LPCVD SiN_x deposition onto a bare silicon wafer results in very poor surface passivation and can also lead to a degradation of the bulk minority-carrier lifetime if the wafer is subsequently heated. Excellent bulk lifetimes and surface passivation can be maintained with an LPCVD silicon nitride layer deposited on a silicon wafer, even following high-temperature treatments, provided a thin layer of silicon oxide is present under the nitride. The apparent drop in effective lifetimes following a high-temperature treatment is probably due to a loss of hydrogen from the silicon/oxide interface. Effective lifetimes can be recovered with a high-temperature treatment in a hydrogen-containing ambient. This allows the nitride layer to be deposited early in the cell fabrication process, and thereby used as a processing aid, without compromising the potential for high cell efficiencies. The LPCVD silicon nitride layer may also serve as an anti-reflection coating in the finished cell.

REFERENCES

1. Aberle AG. Surface passivation of crystalline silicon solar cells: a review. *Progress in Photovoltaics: Research and Applications* 2000; **8**: 473.
2. Rohatgi A, Jeong J-W. High-efficiency screen-printed silicon ribbon solar cells by effective defect passivation and rapid thermal processing. *Applied Physics Letters* 2003; **82**(2): 224.
3. Habraken FHPM, Tijhaar RHG, van der Weg WF, Kuiper AET, Willemsen MFC. Hydrogen in low-pressure chemical-vapor-deposited silicon (oxy)nitride films. *Journal of Applied Physics* 1986; **59**(2): 447.

4. Stein HJ, Peercy PS, Sokel RJ. Post-deposition high temperature processing of silicon nitride. *Thin Solid Films* 1983; **101**: 291.
5. Stein HJ, HAR Wegener. *Solid State Science and Technology* 1977; **124**(6): 908.
6. Chow R, Lanford WA, Ke-Ming W, Rosler RS. Hydrogen content of a variety of plasma-deposited silicon nitrides. *Journal of Applied Physics* 1982; **53**(8): 5630.
7. Schmidt J, Kerr M, Cuevas A. Surface passivation of silicon solar cells using plasma-enhanced chemical-vapour-deposited SiN films and thin thermal SiO₂/plasma SiN stacks. *Semiconductor Science and Technology* 2001, **16**: 164–170.
8. McCann M, Weber K, Blakers A. An early deposited LPCVD silicon nitride: allowing the possibility of novel cell designs. *Proceedings of the 3rd World Conference and Exhibition of Photovoltaic Energy Conversion, Osaka*, 2003; 1135.
9. Sinton RA, Cuevas A. Contactless determination of current-voltage characteristics and minority-carrier lifetimes in semiconductors from quasi-steady-state photoconductance data. *Applied Physics Letters* 1996; **69**(17): 2510.
10. Nagel H, Berge C, Aberle AG. Generalized analysis of quasi-steady-state and quasi-transient measurements of carrier lifetimes in semiconductors. *Journal of Applied Physics* 1999; **86**(11): 6218.
11. Gardeniers JGE, Tilmans HAC. LPCVD silicon-rich silicon nitride films for applications in micromechanics, studied with statistical experimental design. *Journal of Vacuum Science and Technology A* 1996; **14**(5): 2879.
12. Arnoldbik WM, Marée CHM, Maas AJH, van Boogaard MJ, Habraken FHPM, Kuiper AET. Dynamic behaviour of hydrogen in silicon nitride and oxynitride films made by low-pressure chemical vapor deposition. *Physical Review B* 1993; **48**(8): 5444.
13. Denisse CMM, Troost KZ, Habraken FHPM, van der Weg WF, Hendriks M. Annealing of plasma silicon oxynitride films. *Journal of Applied Physics* 1986; **60**(7): 2543.
14. Buie D, McCann MJ, Weber KJ, Dey CJ. Full day simulations of anti-reflection coatings for flat plate silicon photovoltaics. *Solar Energy Materials and Solar Cells* 2003; **81**: 13–24.