Journal of The Electrochemical Society, **154** (1) H5-H8 (2007)
0013-4651/2006/154(1)/H5/4/$20.00 © The Electrochemical Society

The Effect of LPCVD Silicon Nitride Deposition on the Si-SiO_2 Interface of Oxidized Silicon Wafers

H. Jin and K. J. Weber

Centre for Sustainable Energy Systems, Faculty of Engineering and Information Technology, The Australian National University, Canberra ACT 0200, Australia

Low-pressure chemical vapor deposition (LPCVD) of silicon nitride on thermally oxidized silicon wafers changes the fundamental properties of the Si-SiO_2 interface as a result of nitridation of the interface. This change results in an increase in the recombination rate of minority carriers at the silicon surface. The ammonia to dichlorosilane flow ratio during nitride deposition is a key parameter which affects the extent of this change. In addition, the recombination properties of the Si-SiO_2 interface following nitride deposition are also influenced by charge in the nitride layer and by a change in the degree of hydrogen passivation of interface defects.
© 2006 The Electrochemical Society. [DOI: 10.1149/1.2382455] All rights reserved.

Manuscript submitted June 27, 2006; revised manuscript received August 23, 2006. Available electronically November 8, 2006.

Low-pressure chemical vapor deposition (LPCVD) is a reliable, mature technology widely used in the microelectronics field to produce nearly stoichiometric silicon nitride (Si_3N_4). LPCVD Si_3N_4 is an excellent oxidation and diffusion mask and resistant to chemical attack by alkaline or acidic silicon etchants. Because of the unique combination of physical and optical properties, LPCVD Si_3N_4 is potentially useful for solar cell structures.

However, direct deposition of LPCVD Si_3N_4 does not provide good Si surface passivation.[1] LPCVD nitride deposition usually occurs at 750–800°C, resulting in a relatively low hydrogen concentration[2,3] (~2 to 10%) in the nitride film compared to PECVD SiN_x films[4] (~20 to 25%). Previous work[1] has shown that a thin SiO_2 layer should be grown before Si_3N_4 deposition to prevent irreversible bulk damage caused by stress[5] from the nitride layer. Such LPCVD Si_3N_4/SiO_2/Si stacks can act as effective antireflection coatings and simultaneously allow good surface passivation to be achieved. In this paper, the effect of LPCVD Si_3N_4 deposition on the interface properties of oxidized silicon wafers is studied in some detail. Of particular interest for potential photovoltaic applications is the recombination rate of minority carriers at the interface. The effect of varying the ammonia to dichlorosilane (DCS) ratio during nitride deposition is discussed. The thermal stability of LPCVD Si_3N_4/SiO_2/Si stacks is studied and compared with that of oxidized silicon wafers.

Experimental

Minority carrier lifetime measurements.— Float-zoned, p-type, ~100 Ω-cm Si (100) wafers were used for minority carrier lifetime measurements. The wafers were given a light phosphorus diffusion ($R \sim 300$ to 400 Ω/□ after thermal drive in), and passivated with a thermally grown 50 nm oxide, followed by a N_2 in situ anneal at 1000°C for 30 min. Hydrogenation of the Si-SiO_2 interfaces was achieved using a forming gas anneal (FGA, 95% Ar, 5% H_2) at 400°C for 30 min. Dehydrogenation (i.e., the removal of hydrogen from these interfaces without significantly affecting the interface defect density) was achieved using rapid thermal anneals[6] (RTAs) at 800°C for 3 min in dry nitrogen.

LPCVD Si_3N_4 depositions were carried out at 775°C and 0.5 Torr with an ammonia flow rate of 120 standard cubic centimeters per minute (sccm) and a DCS flow rate of 30 sccm. For some samples, the ammonia flow rate was varied between 120 and 210 sccm while the DCS flow rate was kept constant at 30 sccm to investigate the effect of the gas flow ratio on the interface properties.

To compare the thermal stability of LPCVD Si_3N_4/SiO_2/Si stacks and oxidized silicon wafers, isothermal (550C up to 360 s) and isochronal (500 to 800°C for 180 s) RTAs were carried out on samples of each type.

The effective lifetime was determined using quasi steady-state photoconductivity decay (QSSPCD) measurements[7] and from this, the emitter saturation current (J_{oe}) was deduced.[7,8] Diffusion control samples showed that the sheet resistance of all samples changed little during the process steps following oxidation and in situ annealing in N_2. Thus, measurement of J_{oe} allows direct comparison of the degree of surface passivation of the samples following the various process steps.

Capacitance-voltage measurements.— CZ, p-type, 10–23 Ω-cm, Si (100) samples were used for high-frequency (1 MHz) capacitance-voltage (C-V) measurements to quantify the density of charges in the insulator layers. To ensure a clear comparison, ~100 nm thick LPCVD Si_3N_4 and ~100 nm thermally grown layers of SiO_2 stacks were prepared. About 80 nm aluminum was deposited with an area of around 4.7×10^{-3} cm^2 through a shadow mask to form metal-insulator-semiconductor (MIS) structures. Ohmic contacts were realized by spreading a thin GaIn layer on the back side of the substrate.

Results and Discussion

Effect of nitride layer deposition on emitter saturation current density.— Table I shows the emitter saturation current (J_{oe}) values for two Si/SiO_2 samples, A and B, after different processes. Sample A had initially been hydrogenated with an FGA, while sample B had been dehydrogenated with an 800°C RTA (step 1). Subsequently, silicon nitride was deposited on both samples in three separate steps, resulting in a nitride layer of increasing thickness. The total nitride thickness at steps 2, 3, and 4 was around 3, 31, and 53 nm, respectively. The nitride layers were not removed between the three depositions. In step 5, the nitride layers were removed in hot phosphoric acid at 170°C. The oxide layer was not significantly etched by this procedure. Finally, both samples received an FGA to rehydrogenate the interface at step 6.

As shown in Table I, a 1 min deposition of ~3 nm Si_3N_4 increases J_{oe} from 9 to 35 fA/cm^2 per side for sample A. For comparison, a simulated deposition was carried out in the LPCVD nitride deposition reactor for 1 min on another sample (sample C). The simulated deposition involved admitting pure N_2 instead of ammonia and DCS, so that no deposition took place. For this sample,

Table I. J_{oe} values for samples A and B after different thermal steps. Step 1: Oxidization and FGA at 400°C for 30 min on sample A, RTA at 800°C for 3 min on sample B. Steps 2 to 4: Nitride deposition for 1, 6, and 5 min, respectively. Step 5: Nitride removal using phosphoric acid. Step 6: FGA.

Step	1	2	3	4	5	6
J_{oe} for sample A (fA/cm^2/side)	9	35	24	22	31	14
J_{oe} for sample D (fA/cm^2/side)	190	39	30	24	34	16

J_{oe} increased from 9 to 20 fA/cm^2 per side. The increase of J_{oe} for sample C is due to a loss of hydrogen from the Si-SiO_2 interface, as a fraction of the interface defects which are initially terminated with hydrogen lose their hydrogen atom, changing the defects from electrically inactive to electrically active. However, this type of treatment does not affect the density or the fundamental properties of interface defects, except for their bonding state.[9] The larger increase in J_{oe} of sample A compared to sample C indicates that the nitride deposition has additionally resulted in a change in the density and/or the physical or electronic properties of the defects at the Si-SiO_2 interface.

At the beginning of the LPCVD Si_3N_4 deposition, atomic nitrogen or other nitrogen containing species are able to react with SiO_2 layer and may diffuse to the Si-SiO_2 interface,[10] resulting in the formation of an oxynitride. Such an oxynitride interface is believed to act as a barrier to hot electron radiation[11] and dopant diffusion.[12,13] However, the introduction of nitrogen atoms to the interface also increases the interface rigidity and therefore degrades the device's long term stability.[9] The increase of J_{oe} for sample A is speculated to be the result of nitridation of the oxide and the Si-SiO_2 interface.

A comparison of the J_{oe} values of samples A and B following a 1 min nitride deposition indicates that hydrogen also plays an important role during this initial stage of the deposition. Sample B had nearly the same as-oxidized J_{oe} value and sheet resistance as samples A and C. After an RTA at 800°C for 3 min in N_2, its J_{oe} increased to 190 fA/cm^2 per side, which represents a dehydrogenated Si-SiO_2 interface for this sample. After a 1 min LPCVD nitride deposition, J_{oe} decreased to 39 fA/cm^2 per side, similar to sample A. The passivation of this initially depassivated sample is due to hydrogen made available by the nitride deposition process. The change in the fundamental properties of the Si-SiO_2 interface as a result of nitridation of both samples A and B is also evidenced by the results at step 6, after the complete removal of the nitride layer and repassivation of the interfaces with another FGA. The higher J_{oe} values compared with those at step 1 indicate either an increase in the number of residual, unpassivated defects, or an increase in the recombination activity of the residual defects, or both. In separate work on silicon (111) wafers, we have shown that nitride deposition on oxidized silicon leads to a substantial increase in the density of the dominant P_b center defect.[14] Hence it is likely that nitride deposition on the samples discussed here also leads to an increase in interface defect density.

Effect of ammonia to DCS flow ratio during deposition on emitter saturation current density.— The degree of change in the properties of the Si-SiO_2 interface as a result of nitride deposition may be influenced by the choice of LPCVD Si_3N_4 deposition parameters. Among the deposition parameters, the ammonia to DCS flow ratio is the most important. Figure 1 shows the influence of ammonia to DCS ratio on the J_{oe} values of samples immediately after nitride deposition, and following a subsequent removal of the nitride in phosphoric acid.

It can be seen that an increase in the ammonia to DCS ratio leads to a monotonic increase in J_{oe} values. Because the nitridation of the Si-SiO_2 interface is believed to be due to the reaction of ammonia at the oxide interface, a higher ammonia content could be expected to result in an increase in the degree of nitridation of the interface due to a greater availability of N containing species. Following removal of the nitride film, the trend in the J_{oe} values remains unchanged, although all J_{oe} values have increased.

To further investigate the influence of interface nitridation on Si surface properties, two extreme surface conditions were investigated. The first is the hydrogenated interface, which is realized by an FGA at 400°C for 30 min. The second is the completely or nearly completely dehydrogenated interface, which is realized by an RTA in N_2 flow at 800°C for 3 min. The ammonia to DCS flow ratio dependence of J_{oe} under hydrogenated and dehydrogenated conditions is shown in Fig. 2 and 3. Under both conditions, a high ammonia to DCS ratio results in greater degradation of the electronic properties of the Si surface.

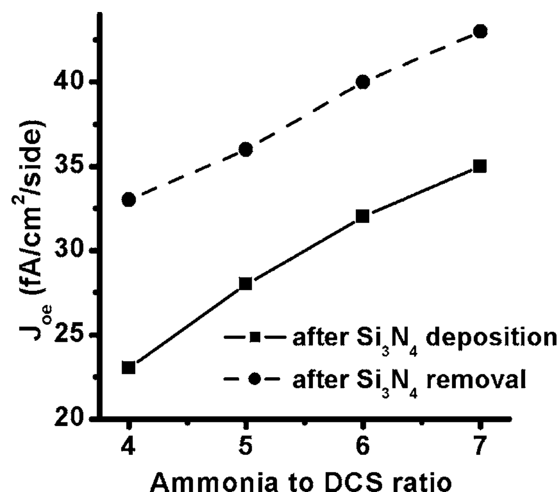

Figure 1. Dependence of emitter saturation current density J_{oe} on the ammonia to DCS flow ratio (a) immediately after LPCVD deposition of ~50 nm of Si_3N_4 on oxidized Si (solid line) and (b) following subsequent removal of the nitride layer (dashed line).

Effect of charge on the emitter saturation current density.— As shown in Table I, deposition of a thicker Si_3N_4 layer (steps 3 and 4) results in a further improvement of the passivation of the Si-SiO_2 interface. These improvements may be due both to the passivation of the interface by hydrogen from the LPCVD nitride film, and the effect of positive charges in the nitride film.[15]

Figure 4 shows the high-frequency C-V curves for metal-LPCVD Si_3N_4-Si and metal-SiO_2-Si structures. The flatband shifts (relative to an ideal MIS structure with Al gate and no insulator charge) for the nitride and oxide samples are −8.1 and −1.25 V, respectively. The calculated values for the effective net interface charge densities are 3.1×10^{12} and 2.5×10^{11} cm^{-2}, respectively.[16]

The large amount of charge in nitride films is believed to result from the type of defect known as a K center.[17] The effect of charge in LPCVD nitride films has also been discussed by other authors,[15] who presented evidence that the charge is distributed at least

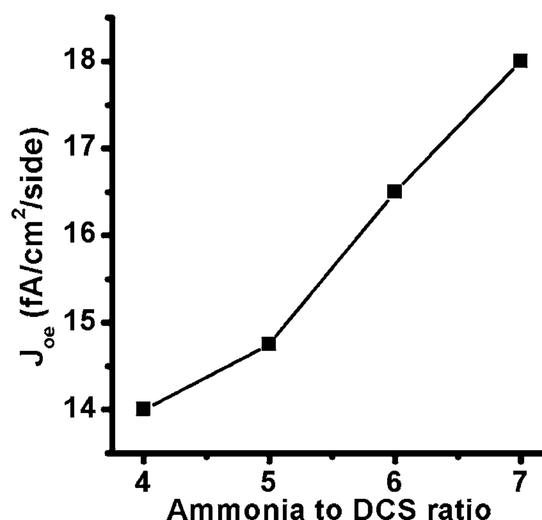

Figure 2. Dependence of emitter saturation current density J_{oe} on the ammonia to DCS flow ratio for the hydrogenated oxynitride interface.

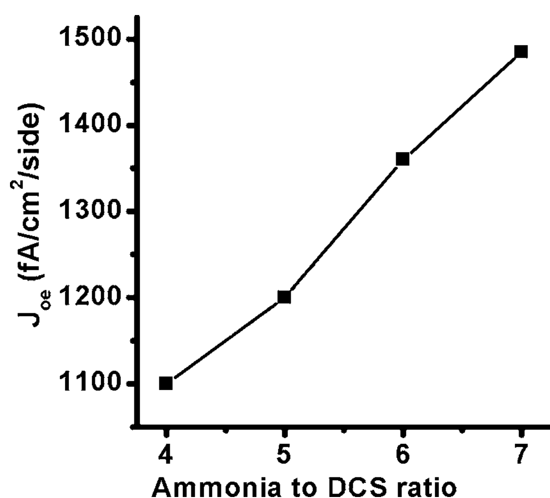

Figure 3. Dependence of emitter saturation current density J_{oe} on the ammonia to DCS flow ratio for the dehydrogenated oxynitride interface.

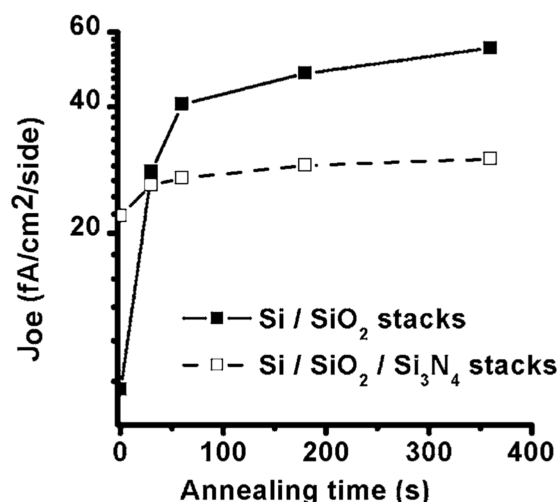

Figure 5. Emitter saturation current density (J_{oe}) isothermal RTA curves for (a) hydrogenated Si/SiO_2 stacks (solid line) and (b) $Si/SiO_2/Si_3N_4$ stacks (dashed line).

through the first 15 nm of their nitride films, which can be observed by comparing the J_{oe} values at steps 4 and 5 in Table I. The increase of J_{oe} at step 5 is due to the removal of the nitride layer and the charge it carries. Note that another sample D, which underwent the same processing steps as sample A (including hot phosphoric acid etch) except for the nitride deposition, showed little change in J_{oe}, confirming that the nitride removal process has little effect on the defect properties at the $Si\text{-}SiO_2$ interface. In Fig. 1, the J_{oe} for all samples increases by ~ 10 fA/cm^2/side after nitride removal, regardless of the reaction gas ratio. Once again, this change can be attributed to charges in the nitride film. However, it should be kept in mind that the effect of nitride charge would be less for most diffusions used in solar cells, because such diffusions are typically significantly heavier.

Thermal stability of the surface passivation for surfaces with thermal oxides and oxide/nitride stacks.— Figures 5 and 6 compare the thermal stability of $Si_3N_4/SiO_2/Si$ stacks and oxidized, initially hydrogenated Si samples. The nitride/oxide stacks display better thermal stability during both isothermal annealing and isochronal annealing than samples with an oxide only. The improved thermal stability of the nitride/oxide stack is likely to be due to hydrogen in the nitride layer, in the form of N-H and Si-H bonds. During thermal annealing, some of these hydrogen bonds (particularly the less stable Si-H bonds) in the nitride layer may dissociate and the liberated hydrogen diffuse toward the $Si\text{-}SiO_2$ interface, where it passivates interface defects. The amount of hydrogen released in this way is small compared with the total bonded hydrogen concentration, as little change in hydrogen content is observed by Fourier transform infrared spectroscopy at annealing temperatures below the deposition temperature and annealing times up to several hours. The gradual release of hydrogen from the nitride film means that it is possible to carry out some thermal processing steps following nitride layer deposition with only a small degradation of surface passivation.

Conclusions

LPCVD Si_3N_4 deposition on oxidized silicon wafers changes the electronic (recombination) properties of the $Si\text{-}SiO_2$ interface. We have shown that at least three factors are responsible for this change: (*i*) nitridation of the $Si\text{-}SiO_2$ interface, (*ii*) a change in the degree of hydrogen passivation of interface defects, and (*iii*) charge in the nitride layer. The nitridation of the interface leads to a degradation in its recombination properties, as evidenced by higher values of J_{oe}. A higher ammonia content in the deposition gas causes greater deg-

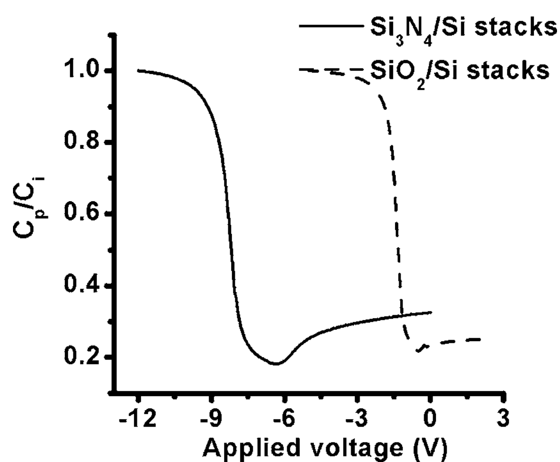

Figure 4. High-frequency C-V curve for ~ 100 nm LPCVD nitride and thermally grown oxide layers on silicon.

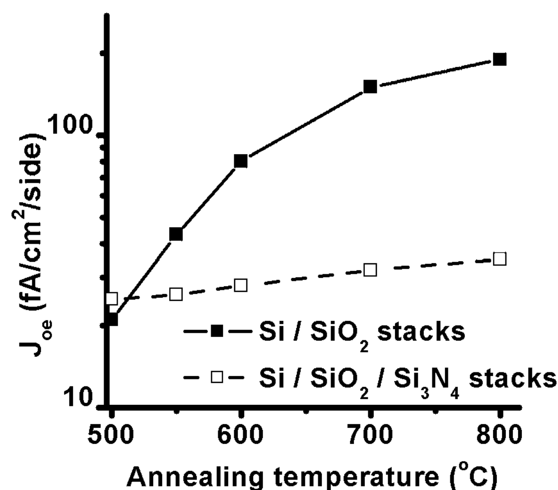

Figure 6. Emitter saturation current density (J_{oe}) isochronal RTA curves for (a) hydrogenated Si/SiO_2 stacks (solid line) and (b) $Si/SiO_2/Si_3N_4$ stacks (dashed line).

radation of the Si interface. The deposition process can result in an increase or a decrease in the degree of hydrogen passivation of interface defects, depending on the initial state of the Si-SiO_2 interface prior to nitride layer deposition. Positive charges in the nitride layer help to somewhat improve the passivation of the Si surface. Finally, $Si_3N_4/SiO_2/Si$ stacks display improved thermal stability compared to oxidized silicon wafers. This is attributed to the gradual release of bonded hydrogen from the nitride layer, resulting in a continuous supply of atomic hydrogen for interface passivation.

Acknowledgments

Financial support for this project by the Australian Research Council is gratefully acknowledged.

The Australian National University assisted in meeting the publication costs of this article.

References

1. M. J. McCann, K. J. Weber, and A. W. Blakers, *Prog. Photovoltaics*, **13**, 195 (2005).
2. F. H. P. M. Habraken, R. H. G. Tijhaar, W. F. van der Weg, A. E. T. Kuiper, and M. F. C. Willemsen, *J. Appl. Phys.*, **59**, 447 (1986).
3. H. J. Stein, P. S. Peercy, and R. J. Sokel, *Thin Solid Films*, **101**, 291 (1983).
4. R. Chow, W. A. Lanford, W. K. Ming, and R. S. Rosler, *J. Appl. Phys.*, **53**, 5630 (1982).
5. J. G. E. Gardeniers, H. A. C. Tilmans, and C. C. G. Visser, *J. Vac. Sci. Technol. A*, **14**, 2879 (1996).
6. P. K. Hurley, B. J. O'Sullivan, F. N. Cubaynes, P. A. Stolk, F. P. Widdershoven, and J. H. Das, *J. Electrochem. Soc.*, **149**, 194 (2002).
7. R. A. Sinton and A. Cusvas, *Appl. Phys. Lett.*, **69**, 2510 (1996).
8. H. Nagel, C. Berge, and A. G. Aberle, *J. Appl. Phys.*, **86**, 6218 (1999).
9. A. Stesmans and G. Van Gorp, *Phys. Rev. B*, **52**, 8904 (1995).
10. O. Jintsugawa, M. Sakuraba, T. Matsuura, and J. Murota, *Surf. Interface Anal.*, **34**, 456 (2002).
11. E. Cartier and D. A. Buchanan, *Appl. Phys. Lett.*, **64**, 901 (1994).
12. D. Mathiot, A. Straboni, E. Andre, and P. Debenest, *J. Appl. Phys.*, **73**, 8215 (1993).
13. D. Wristers, L. K. Han, T. Chen, H. H. Wang, D. L. Kwong, M. Allen, and J. Fulford, *Appl. Phys. Lett.*, **68**, 2094 (1996).
14. H. Jin, P. J. Smith, and K. J. Weber, In preparation.
15. L. Zhong and F. Shimura, *Appl. Phys. Lett.*, **62**, 615 (1993).
16. S. M. Sze, *Physics of Semiconductor Devices*, p. 395, Wiley, New York (1981).
17. D. Jousse, J. Kanicki, and J. H. Stathis, *Appl. Phys. Lett.*, **54**, 1043 (1989).