

PASSIVATION OF LPCVD NITRIDE SILICON STACKS BY ATOMIC H

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ABSTRACT

In this paper, H introduction into low pressure chemical vapor deposited silicon nitride (LPCVD SiN) films using molecular and atomic hydrogen is discussed and compared. Infra-red Multiple Internal Reflection (MIR) measurements were taken to analyse the hydrogen bond content in the nitride films. Quasi-steady state photoconductivity decay (QSSPCD) measurements on phosphorus diffused samples were used to determine the effective lifetime and the emitter saturation current J_{oe} . Long process times and high temperatures are required for molecular hydrogen introduction whereas shorter times and low temperatures are sufficient for atomic hydrogen introduction. Hydrogen introduced into the nitride layer in this way can passivate the Si-SiO₂ interface of oxide/nitride stacks on silicon. An anneal following atomic H re-introduction at elevated temperatures in N₂ further improves the properties of the Si-SiO₂ interface.

INTRODUCTION

LPCVD is a reliable, mature technology widely used in microelectronics to produce nearly stoichiometric Si₃N₄ films. LPCVD SiN is an excellent oxidation and diffusion mask and is resistant to chemical attack by alkaline or acidic silicon etchants. LPCVD SiN / SiO₂ stacks on silicon have potentially useful properties for novel solar cell designs. Previous work [1-3] has shown that SiN will cause serious bulk damage to the silicon wafer if no intermediate oxide layer is present due to stress from the SiN film and the mismatch in thermal expansion coefficient between Si and SiN. SiN/SiO₂ stacks can act as good antireflection coatings if the SiO₂ layer is kept thin enough (~20-25nm).

However, high temperature anneals on SiN/SiO₂ stacks on silicon cause hydrogen loss from the Si-SiO₂ interface and Si-H and N-H bond breaking in the nitride layer. As a result, surface passivation immediately following such treatments is poor and requires improvement.

In this paper, molecular hydrogen and atomic hydrogen are used in order to introduce H to SiN films and passivate the Si-SiO₂ interface under the SiN film. Forming gas (5% H₂ in 95% Ar) is used as the molecular hydrogen source while atomic hydrogen is created by operating a Plasma Enhanced Chemical Vapor Deposition (PECVD) system with only ammonia at 400°C and an RF power of 200W. A high frequency (12.56MHz), direct PECVD reactor was used. The differences

in the results from the two methods were analyzed and possible reasons for these differences are discussed.

EXPERIMENTAL DETAILS

Double sided polished, 1cm long, 500µm thick wafers were used for the infra-red Multiple Internal Reflection (MIR) measurements. 200nm thick nitride layer were deposited on both sides to achieve a good signal to noise ratio.

Float zoned, (100) high resistivity ($\geq 100\Omega\text{-cm}$), 500µm and float zoned, (111) high resistivity ($\geq 100\Omega\text{-cm}$), 550µm thick wafers were used for the quasi-steady state photoconductivity decay (QSS-PCD) measurements. These wafers were etched in HF:HNO₃ solution. After an RCA clean, both sides were passivated by a light phosphorus diffusion (with a sheet resistance R_{sh} of $\sim 400\Omega/\square$ after thermal drive in) and a thermally grown 50nm oxide (grown in oxygen at 1000°C followed by a 30 minute in-situ anneal in N₂ at the same temperature). Samples were annealed in forming gas at 400°C. 50 nm thick LPCVD SiN layers were then deposited. All nitride depositions were carried out at 775°C, a pressure of 0.5 torr and an ammonia to dichlorosilane (DCS) gas flow ratio of 5 to 1.

Some samples were annealed in N₂ at 900°C or 1000°C for 30minutes to dissociate Si-H and N-H bonds in the nitride layer and de-passivate the Si-SiO₂ interface. Selected post N₂ annealing nitride stacks were then annealed in forming gas from 30minutes to 4 hrs. Other annealed or pre-annealed nitride stacks were annealed on both sides in an atomic H atmosphere at 400°C for 10 minutes, followed by an anneal in N₂ at 500°C for 10 minutes.

The effective lifetime was determined using quasi-steady state photoconductivity decay (QSSPCD) measurements and from this, the emitter saturation current (J_{oe}) and a minimum value for the bulk lifetime were deduced.

The hydrogen bond content of the nitride films was determined from MIR measurements, shown in figure 1. 500µm thick, double-side polished wafers were used. A 200nm thick layer of LPCVD silicon nitride was deposited on both sides of the wafers. Such a relatively thick layer was necessary in order to achieve a good signal to noise ratio, and ensure good accuracy of the results. MIR Samples had the same thermal process as the QSSPCD samples before measurements.



Figure 1: MIR measurement. Light enters the edges of the sample, which have been cut at 45°, and is trapped, interacting with the surfaces ~20 times before escaping.

RESULTS AND DISCUSSION

H reintroduction to nitride film

Figure 2 shows the N-H and Si-H bond concentrations in the nitride layers measured after high temperature forming gas anneals (HTFGA) at 840°C from 0 to 4 hours. Figure 3 shows the H bond concentrations in the nitride film measured after atomic H anneals.

Both figure 2 and figure 3 show an increase of N-H and Si-H bond concentration with time. Table I lists the bonded H atomic concentration. After annealing in N₂ at 900°C or 1000°C for 30min, the [H] is 1.09% and 0.62%, respectively. Atomic H anneals increase the H concentration much faster than the HTFGA. A 20 minute atomic H anneal results in a total H bond concentration [H] of ~3.2%, approximately equal to the [H] from a 2.5 hr HTFGA. A 35 minute anneal in atomic H result in saturation of [H] in SiN film, whereas 4 hours of HTFGA are needed to reach the saturation level. The saturation [H] in both Si-H bonds and N-H bonds are almost the same despite the difference in methods of introduction of the hydrogen, indicating that the saturation [H] is a parameter that only depends on the nitride properties after annealing.

It is hypothesized that the saturation density of hydrogen bonds is determined by the density of unterminated bonds ('defects') in the nitride film. As the nitride film is annealed it densifies, leading to a reduction in the number of defects and consequently in the bonded hydrogen concentration. A higher anneal temperature leads to a greater reduction in the defect density. Following a 900°C 30 minute N₂ anneal, the saturated nitride [H] was about 3.7%, whereas following a 1000°C 30 minute N₂ anneal [H] was only about 1.9%, as shown in table I.

In figure 2, the rate of [H] increase decreases with reaction time whereas in figure 3, the rate of [H] increase increases with reaction time within the first 20 minutes. The difference in rate of [H] increase may indicate a difference in the mechanism of the reaction between HTFGA and atomic hydrogen anneals. Atomic H is believed to have a much larger diffusion coefficient than molecular hydrogen. It is hypothesized that during HTFGA, molecular hydrogen reacts with top nitride layer at high temperatures to form N-H and Si-H bonds. Parts of these formed bonds dissociate to release atomic H. The atomic H then diffuses rapidly into the nitride layer and bonds with dangling N or Si.

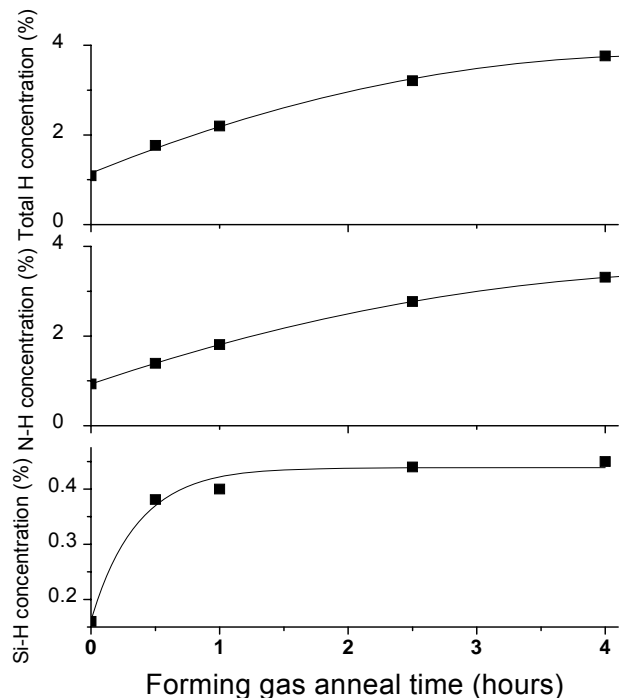


Figure 2. H content after HTFGA

			[Si-H] (%)	[N-H] (%)	Total [H] (%)
post 900°C anneal	Post Anneal		0.16	0.93	1.09
	HTFGA		0.47	3.25	3.73
	Atomic H		0.45	3.31	3.76
post 1000°C anneal	Post Anneal		0.02	0.6	0.62
	HTFGA		0.21	1.68	1.89
	Atomic H		0.21	1.74	1.95

Table I. H atomic saturation concentration in Si-H and N-H bonds post HTFGA or Atomic H treatments

Virtually all the hydrogen is present in bonded form due to the rapid diffusion of atomic hydrogen at these temperatures. Thus, the effective diffusion rate is limited by the rate of Si-H and N-H bond breaking in the surface region. However, during atomic H anneals, atomic H may diffuse into the nitride layer more rapidly. The dissociation of N-H and Si-H bonds at the processing temperature of 400°C is negligibly small so that H bonds are only formed but not broken. Some of the hydrogen present in the nitride at any time during the annealing process will be un-bonded (interstitial) hydrogen. As the un-bonded hydrogen diffuses into the film, the amount of hydrogen available for Si-H and N-H bond formation increases, accounting for the increase in the rate of H bond formation during the first 20 minutes of the atomic H anneal.

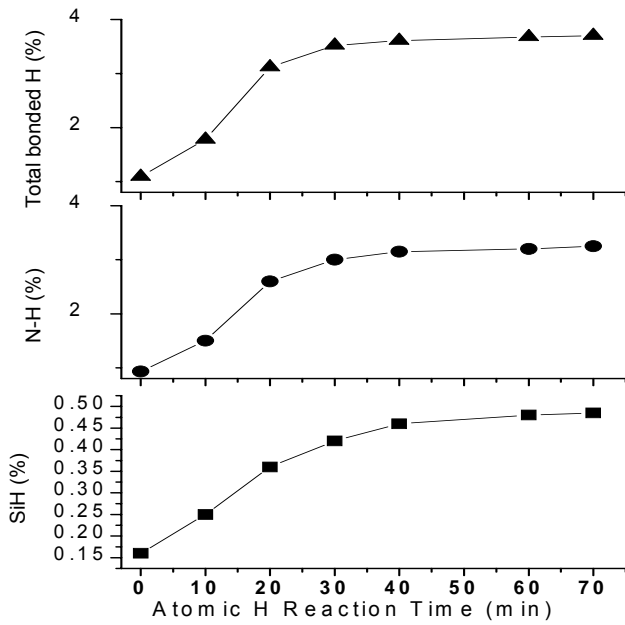


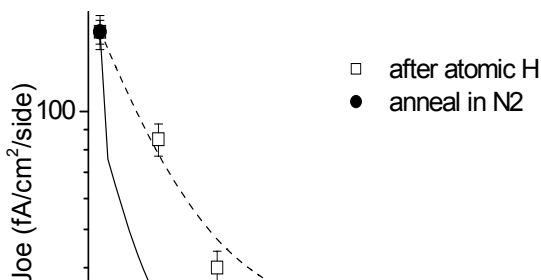
Figure 3. H content after Atomic H

The influence of hydrogen reintroduction on the Si-SiO₂ interface

The phosphorus diffused Si-SiO₂ interface recombination rate is indicated by the emitter saturation current (J_{oe}). After LPCVD SiN deposition, the value of J_{oe} for the Si / SiO₂ / SiN stacks is 19fA/cm²/side. A HTA at 900°C in N₂ increases the J_{oe} value to about 160fA/cm²/side. The great increase in J_{oe} after HTA is due to the loss of H from the Si-SiO₂ interface. Figure 4 shows the change in J_{oe} following atomic H exposure and subsequent annealing in N₂. Each value has an error about 5-10% due to the measurement accuracy. Table II shows the effective lifetime for the same sample during the thermal processes. The J_{oe} values were measured at an injection level of 5×10^{15} /cm². The effective lifetime values were measured at an injection level of 2×10^{14} /cm².

In figure 4, the open circles represent the J_{oe} values just after atomic H exposure. The solid circles represent the J_{oe} values after a subsequent N₂ anneal for the same sample. It can be concluded from figures 3 and 4 that atomic H diffuses into the nitride film during atomic H exposure and reacts to passivate the dehydrogenated Si-SiO₂ interface. Since the nitride film in the samples used for J_{oe} measurements is only 50nm, which is much thinner than the samples used in the MIR measurement, only a 10 minute treatment is sufficient to reach the minimum value of J_{oe} .

The subsequent anneal in N₂ at 500°C for 10 minutes results in a further reduction in J_{oe} . The reason is still unclear. One hypothesis is that defects in the nitride film, and particularly near the nitride/oxide interface, act as hydrogen 'traps' which are filled during the hydrogen plasma treatment. During the subsequent 500°C N₂ anneal, some of this hydrogen is released, providing a much larger flux of atomic hydrogen, and enabling the passivation of more interface defects.



While we have observed that an ammonia plasma treatment (such as the one used here as a source of atomic hydrogen) leads to the generation of more interface defects on oxidised wafers, there is no evidence that the plasma treatment or the subsequent N₂ anneal generates further interface defects on oxide/nitride stacks. Shown in table II, after atomic H and annealing treatments the effective lifetime is about 5.1ms, similar to the value just taken after LPCVD SiN deposition (5.2ms). The values of J_{oe} after the annealing treatment and post LPCVD SiN deposition are both about 19fA/cm²/side.

lifetime after LPCVD (ms)	lifetime after HTA (ms)	lifetime after 20min H (ms)	lifetime after annealing (ms)
5.2	2.5	3.5	5.1

Table II. Effective lifetime vs thermal processes

Further evidence is given in table III. This shows J_{oe} values for both (100) and (111) samples just after nitride deposition, and after a subsequent atomic H treatment. The values of J_{oe} are unchanged within measurement error. This indicates that no additional interface defects were introduced by the plasma treatment. We believe that N containing species which are able to diffuse through an oxide layer and cause nitridation of the interface (and an increase in interface defect density) are not able to diffuse through the nitride film, thus preventing similar damage.

Orientation	RF power (W)	LPCVD J_{oe} (fA/cm ² /side)	Atomic H J_{oe} (fA/cm ² /side)
(100)	5	26.5	25.5
(100)	25	28.5	29
(100)	50	27.5	27
(100)	100	29	29
(100)	150	27	28
(100)	200	26	27.5
(111)	5	64	69
(111)	25	67	66
(111)	50	66	70
(111)	100	70	63

Table III. Comparison of J_{oe} after LPCVD SiN deposition and after subsequent atomic H annealing for (100) and (111) orientation Si at various RF powers.

CONCLUSION

For SiN/SiO₂/Si stacks, post LPCVD nitride deposition anneals in N₂ at high temperatures decrease the H bond concentration in the nitride layer and de-passivate the Si-SiO₂ interface. An atomic H anneal allows rapid re-introduction of hydrogen to the nitride layer and the Si-SiO₂ interface. A subsequent anneal in N₂ at 500°C is shown to help passivate the Si-SiO₂ interface as indicated by a decrease of J_{oe} .

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