ANOMALOUS THERMAL BEHAVIOUR OF SURFACE PASSIVATION BY PECVD SILICON NITRIDE ON P-TYPE CRYSTALLINE SILICON

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ABSTRACT: An anomalous behaviour, which we term 'second lifetime recovery effect', was observed when studying the thermal behaviour of the surface passivation of silicon nitride (SiN) deposited by Plasma Enhanced Chemical Deposition (PECVD) on p-type silicon wafers. The behaviour can be characterized by two local maxima in the effective lifetime vs. anneal duration curve. The existence of a second local maximum suggests a previously unexplained behaviour in PECVD SiN films. Several possible mechanisms that could explain the effect are explored in this work. Initial characterization of the thermal behaviour suggests that the mechanism is thermally activated, with an initial time delay in the activation, and is a transient process once activated.
Keywords: PECVD, Silicon-Nitride, Passivation

1 INTRODUCTION

After more than 20 years of research, plasma enhanced chemical vapour deposition (PECVD) silicon nitride (SiN) has firmly established itself as an excellent material to passivate the surface of crystalline silicon wafers. Previous studies conducted by various research groups indicate that the passivation quality provided by PECVD SiN is comparable to that of thermally grown oxide. Good-quality surface passivation provided by SiN can be satisfactorily achieved at the relatively low deposition temperature, typically in the vicinity of 400°C.

A brief post-deposition anneal is frequently found to improve the quality of surface passivation. On the other hand, prolonged, high temperature cycles are known to degrade the passivation quality. The main focus of this work is the thermal behaviour of the surface passivation of PECVD SiN deposited on p-type silicon wafers when annealed at higher temperatures (>650°C). We have observed an anomalous behaviour characterized by two local maxima in the effective lifetime vs. anneal duration curve (see Figure 1). To date, the thermal behaviour observed by various groups only exhibits one local maximum in the carrier lifetime vs. anneal time curve. The existence of a second local maximum suggests a previously unexplained behaviour in PECVD SiN films. A better understanding in the thermal behaviour of SiN films may lead to improved SiN films, and higher efficiencies in commercial silicon solar cells. Theoretical modeling may allow prediction of the effect, and hence the prediction of the range of optimum annealing times at different anneal temperature or firing process for different refractive indices.

2 EXPERIMENTAL DETAILS

A baseline set of nine 1.4 Ω.cm, <100>, 300-µm thick, p-type, single crystalline silicon, 5-inch diameter wafers was prepared, and neither RCA cleaning nor HF dip was performed prior to the deposition. An in-line, industrial-type Roth and Rau PECVD system was used to deposit the SiN using a NH_3 and SiH_4 gas mixture that was varied in order to achieve different film refractive index, and the deposition temperature was fixed at 400°C. The deposition pressure varied from 0.13 – 0.27 mbar, and the wafer carrier transport speed varied from 80 cm/sec to 120 cm/sec to acquire optimum optical film thickness for each different refractive index.

Four more sets of 1 ohm-cm, <100>, 250 micron thick, p-type, single crystalline silicon, 4-inch diameter quarter wafers were prepared to further investigate the anomalous thermal behaviour. These wafers were RCA cleaned and HF dip prior to the SiN deposition. The SiN deposition was carried out in a static, laboratory-type Roth and Rau PECVD system, also with NH_3 and SiH_4 mixture. The deposition pressure was fixed at 0.2 mbar, the pre-heating duration of the stage was set to 10 min once the temperature reached desired temperature. Two different deposition temperatures, 350°C and 400°C, were compared. The duration of SiN deposition ranged from 90 sec to 120 sec to obtain optimal optical film thickness of about 80nm for the different refractive indices.

The thermal behaviour of two different post-deposition anneal temperatures was studied, and annealing was conducted in rapid thermal processor in forming gas (5-10% H_2) ambient. The effective carrier lifetime was measured using the QSSPC technique after annealing the wafers for increasing periods of time. As we are using high-lifetime float zone silicon wafers, we assume that observed changes in the effective lifetime, as measured by QSSPC, are the result of the changes in the surface passivation quality. Ellipsometry was used to determine the refractive index and thickness of the films at 630 nm wavelength. Fourier Transformation Infra-Red (FTIR) was used to measure various bonds densities at as-deposited condition, after the first maximum in the effective lifetime vs. anneal duration curve, and at the end of the RTA. X-Ray Diffraction (XRD) was used to detect Si precipitates and crystallized SiN.

3 ANOMALOUS THERMAL BEHAVIOUR OF THE SURFACE PASSIVATION

The evolution of the effective lifetime of PECVD SiN passivated silicon at lower anneal temperatures was

well documented in a previous study [1], where the effective lifetime was found to reach a peak and then slowly decay and saturate. The lifetime recovery effect is usually attributed to enhanced surface passivation from the release of hydrogen from the film, which binds to surface trap states. The thermal behaviour of the lifetime after RTA treatment at 650°C in this study, however, is strikingly different to that observed at lower anneal temperatures.

As illustrated in Figure 1, during RTA the effective minority carrier lifetime of the set of samples deposited by the in-line system first increases rapidly, reaching a peak value within the first three seconds and then falls sharply to a local minimum that is higher than the as-deposited value. The effective lifetime recovers again and reaches a second peak, which in some cases (not shown in Figure 1), is as high as the first local maximum. After a plateau of a few minutes, the effective lifetime decreases again and eventually stabilizes. The effect is only evident at anneal temperatures higher than about 600°C. The rapid annealing treatment of the sister set of samples at 700°C also shows a similar thermal behaviour.

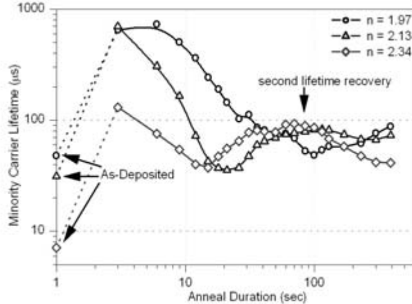

Figure 1: Thermal behaviour of surface passivation of three representative SiN films having refractive indices of 2.34, 2.13, and 1.97 deposited by in-line industrial type PECVD system. The annealing was performed by RTA at 650°C in forming gas ambient. The 1 second data points correspond to the as-deposited condition. The lines are to guide the eyes.

The characteristic 'valley' can be seen to shift to longer cumulative anneal times as the refractive index of the SiN layer decreases, which suggests that SiN layers with lower refractive index tend to have a better thermal stability electrical-wise. The fact that this anomalous behaviour is not observed at lower annealing temperatures but only during the RTA experiments at higher temperature, hints at a mechanism that is thermally activated, with a likely threshold temperature in the proximity of 600°C.

Initial characterisation of the thermal behaviour indicates that the process(es) responsible for the second lifetime recovery effect has the following characteristics: 1) it is a thermally activated process, with an initial time delay in the activation; 2) it is a transient process once activated; and 3) the process eventually saturates.

Several hypotheses were explored to explain the second lifetime recovery effect, including: 1) wafer preparation and cleaning prior to deposition; 2) type of PECVD system (in-line vs. static); 3) non-optimum deposition temperature; 4) different bond dissociation rates and densification of SiN film; 5) phase separation of SiN film (nucleation and precipitation of excess silicon in silicon nitride); and 6) phase transformation of SiN film (crystallisation of amorphous silicon nitride to crystalline silicon nitride).

4 WAFER PREPARATION, SYSTEM TYPE, AND DEPOSITION TEMPERATURE

Several sets of samples with different surface preparation were SiN-coated using the static laboratory type Roth and Rau PECVD system, as described in section 2. The second lifetime recovery effect was also observed in films deposited by the static laboratory-type PECVD system (see Figure 2). This indicates that the effect is not a spurious result, and wafer preparation and cleaning, system type, or deposition temperature are not likely to explain the effect. However these factors seem to have an influence on how strong the second lifetime recovery is. They also affect the as-deposited passivation, clearly superior in the static deposition experiment.

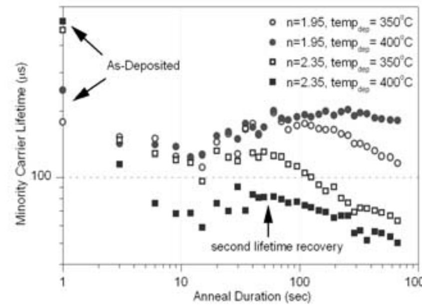

Figure 2: A comparison of the thermal behaviour of surface passivation when RTA at temperature of 650°C of two different deposition temperatures (T = 350°C and T = 400°C) for two different refractive index SiN films (n = 1.97 and n = 2.34). 1 second of anneal duration indicates as-deposited condition. The deposition was carried out in the static laboratory type PECVD system.

5 DIFFERENT BOND DISSOCIATION RATES AND DENSIFICATION OF SILICON NITRIDE FILM

It is well known that free atomic hydrogen released from the SiN film plays an important role in passivating the surface of crystalline silicon. Therefore it is important to understand the evolution and diffusion of atomic hydrogen in the film. One possible explanation for the second lifetime recovery effect is the different free hydrogen release rate from the dissociation of Si-H and N-H bonds, and the concurrent densification of the SiN film, thereby reducing the diffusivity of free hydrogen in the SiN film during RTA treatment.

Various groups previously studied bond dissociations within silicon-rich SiN films. Most came to the conclusion that upon annealing, the N-H bond is less stable than the Si-H bond, and therefore N-H bond has a higher dissociation rate than the Si-H bond [2-4]. It has also been reported that the Si-H bond density increases slightly at the initial stage of RTA, and only starts to decrease after a period of time [2].

The bond interaction can be represented in mathematical terms by several sets of linear differential equations:

$$\frac{\partial[H_N]}{\partial t} = -k_1[H_N]$$

$$\frac{\partial[H_{Si}]}{\partial t} = k_2[H_{free}] - k_3[H_{Si}]$$

$$\frac{\partial[H_{free}]}{\partial t} = k_3[H_{Si}] - k_2[H_{free}] + k_1[H_N] - k_4[H_{free}]$$

where H_N, and H_{Si}, are the concentration of free atomic hydrogen released from the N-H bond and Si-H bond respectively, H_{free} is the total concentration of free atomic hydrogen in the film, and $k_{1...4}$ is the rate constant of the flow of hydrogen in that particular direction.

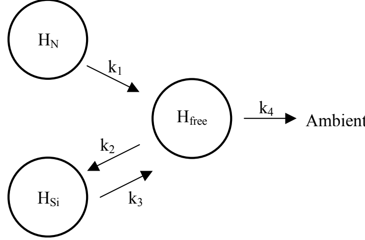

Figure 3: Diagrammatic representation of the interactions between atomic hydrogen released from different bonds. The arrows indicate the direction of the flow of atomic hydrogen within the SiN film.

By varying the rate constants in the differential equations, the concentration of free atomic hydrogen in the film can be modelled. The following assumptions were made in the model: 1) the initial $[H_{Si}]$ is one order of magnitude greater than the initial $[H_N]$, as measured by FTIR in our experiments; 2) the flow of hydrogen in the direction towards $[H_N]$ (not shown in diagram) is negligible [2]; and 3) the dissociation of N-H (k_1) is one to two orders of magnitude faster than that of Si-H (k_3) [2]. However, the modelling results indicated that unequal bond dissociation rates *alone* are not likely to be sufficient to describe the 'second lifetime recovery effect'.

It is fairly well established that during annealing, the void concentration in the SiN film decreases, resulting in densification of the film [5-6]. Weeber et al showed that the Si-N bond density is related to the mass density of the film; and the hydrogen diffusivity decreases as the density of the film increases [15]. We believe the decrease in hydrogen diffusivity would affect the rate constant of free atomic hydrogen escaping to the ambient (k_4), and lead to an accumulation of free atomic hydrogen in the film available for surface passivation.

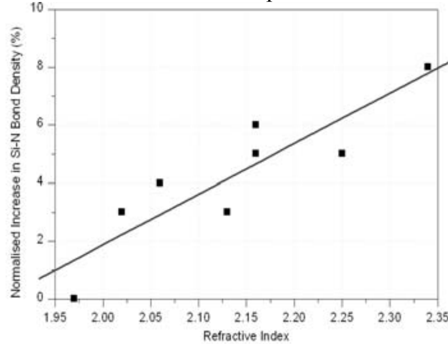

Figure 4: The increase in Si-N bond density (normalised) of various refractive index samples between the 6th second and the end of RTA at 650°C.

Our FTIR data of Si-N bond density indicates that most of the densification of the low refractive index films occurred during the initial stage of RTA. As the RTA continued, a significant increase in the Si-N bond density was observed in the high refractive index samples, whereas there was little increase in low refractive index samples. This observation corresponds to the fact that high refractive index samples have a more apparent second lifetime recovery effect than the low refractive index samples, as most of the densification happens in the initial stage of the RTA for the low refractive index samples.

We therefore extended our model to include the change of diffusivity of hydrogen in the film as it densifies. The escape of hydrogen to the ambient, k_4, would thus be controlled by the changing diffusivity of hydrogen in the film, which changes as the film densifies. While the exact form of this dependence is not yet well determined, we assume that k_4 has the following form

$$k_4 = k_f + \frac{k_i - k_f}{1 + \exp((t_0 - t)/b)}$$

where k_i and k_f are the initial and final rate constant respectively, and b is the porportional constant that describes the sharpness of the transient curve. This form incorporates the features of a time delay, transient behaviour, and eventual saturation that we have observed in the effective lifetime measurements.

Figure 5 shows the predicted evolution of free atomic hydrogen against time together with the experimentally measured effective lifetime. The good agreement in the dominant characteristics of the behaviour of the hydrogen in the film and the resulting surface passivation lends credibility to this model, but further investigation is needed to corroborate it.

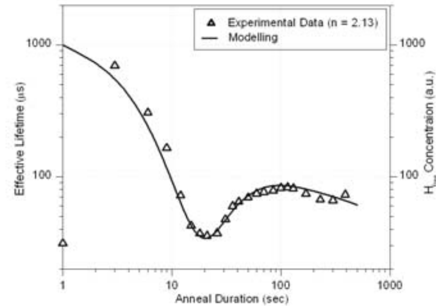

Figure 5: Theoretical modelling of free hydrogen concentration in the film (solid line, right y-axis), and experimental data of effective lifetime (open square, left y-axis). SiN film with n=2.13.

6 PHASE SEPARATION AND TRANSOFMRATION

Another possible mechanism responsible for the second recovery effect is the nucleation of excess dissolved silicon into a separate crystalline silicon phase, whereby the crystallizing silicon would free atomic hydrogen as a result of a reduced amount of available excess silicon bonds. Figure 6 shows the binary phase diagram of the Si-N system [7]. X_N on the x-axis of the phase diagram represents the ratio of N atoms with respect to the total amount of N and Si atoms (X_N = [N] / ([N] + [Si])), which in the case of this work, ranges from 0.41 to 0.55, as roughly indicated by the line in the phase diagram. As shown in the phase diagram, the Si-N system prefers to be in a combination of diamond

(crystalline) silicon and stoichiometric SiN (Si_3N_4) phase at thermal equilibrium when X_N is below 0.57 at temperature less than around 1400ºC.

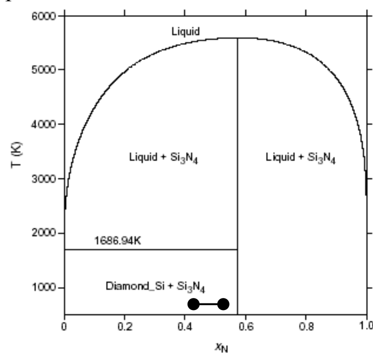

Figure 6: Binary phase diagram of the Si-N system [7]. The line indicates the rough position in the phase diagram for the SiN films studied in this work.

The SiN in this work is silicon rich, and is not in its preferred state at as-deposited condition due to the fact that the silicon is in excess. As a result, the film re-adjusts itself to be in its preferred form at thermal equilibrium if given sufficient time and temperature treatment. In the case of the SiN studied in this work, the excess silicon will nucleate and form silicon precipitates, leaving the host silicon nitride with a stoichiometric composition. This phase separation phenomenon has been observed and reported by various studies on Si-O systems as well as Si-N systems [8-10], where nano-crystalline silicon precipitates were detected by Transmission Electronic Microscopy (TEM) or X-Ray Diffraction (XRD) techniques in SiO_2 and SiN films after giving adequate thermal treatment to the films.

The possibility of the precipitation and nucleation process affecting the release of free H atoms within the film, and hence the concentration of hydrogen at the SiN-Si interface and the passivation quality at the interface has been evaluated using the Fokker-Planck equations. This set of differential equations is frequently used to simulate excess oxygen precipitation in silicon [11-14], and has been adapted here to model the precipitation of excess silicon in silicon nitride. However, the results of this modelling indicate that Si precipitation is less likely to explain the anomalous effect, as there is no initial time delay in the precipitation process [12], and therefore in the release of free atomic hydrogen.

XRD technique was performed on some of the SiN samples in an attempt to detect 1) crystallized silicon resulting from possible phase separation and 2) crystallized silicon nitride resulting from possible phase transformation. These limited measurements failed to detect significant amounts of either crystallized silicon or crystallised silicon nitride. It cannot be excluded, however, that some precipitation may occur, possibly accompanied by changes to the bonding species at the Si/SiN interface. The second lifetime peak may be produced when the interface conditions resemble those of stoichiometric SiN, while further annealing would result in net hydrogen loss from the film and from the interface.

7 CONCLUSIONS

Our experiments with two different PECVD reactors indicate that the surface passivation of p-type silicon wafers by SiN generally degrades after annealing for prolonged times or high temperatures, as may be expected based on considerations of hydrogen evolution from the interface. Unexpectedly, we have also detected that, within an intermediate range of annealing times, the surface passivation recovers and reaches a second peak. The effect is only evident at temperatures higher than about 600°C. Characterization of the thermal behaviour suggests that the mechanism is thermally activated, with an initial time delay in the activation, and is a transient process once activated. Several possible mechanisms that could explain the second lifetime recovery effect were investigated. While different bond dissociation rates and phase separation/transformation is less likely to explain this anomalous effect, film densification may play an important role in causing this anomalous effect. Further work is needed to verify the validities of these hypotheses.

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