

## THE EFFECT ON SURFACE PASSIVATION OF THE DEPOSITION POWER IN PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITED SILICON NITRIDE

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**ABSTRACT:** In this paper we present an investigation on the influence of RF power ( $P_{RF}$ ) on the passivating properties of silicon nitride ( $SiN_x:H$ ) in a direct plasma enhanced chemical vapour deposition (PECVD) system and found that  $P_{RF}$  greatly affected the passivation quality. Minority carrier lifetime measurements revealed a monotonous decrease in effective lifetime from 470 $\mu$ s at 5.4 mW/cm<sup>2</sup> to 103 $\mu$ s at 13.5 mW/cm<sup>2</sup> above which the decrease was less pronounced. Capacitance-voltage measurements were performed using a bias from -15 V to 15 V at frequencies from 1kHz to 1MHz and showed strong dependence on frequency, suggesting a high concentration of electronically active traps near the  $SiN_x:H/Si$  interface for all values of  $P_{RF}$ . Admittance spectroscopy measurements suggested an increasing number of shallow traps in the band gap with increasing  $P_{RF}$ . We argue that increase in the number of traps with  $P_{RF}$  that cause the decrease in minority carrier lifetime is due to ion bombardment of the Si surface during PECVD in combination with a reduced concentration of passivating Si-H bonds.

Keywords: PECVD, Passivation, Silicon-Nitride

### 1. INTRODUCTION

Silicon nitride ( $SiN_x:H$ ) deposited by plasma enhanced chemical vapour deposition (PECVD) utilising silane ( $SiH_4$ ) and ammonia ( $NH_3$ ) as process gases has become the industry standard for the anti-reflective coating on multicrystalline silicon (Si) solar cells. This is mainly due to its controllable refractive index ( $n$ ) and excellent surface and bulk passivation of Si. Many studies have been carried out on the influence of different PECVD parameters on the optical and passivating properties of  $SiN_x:H$  films, of which the most studied parameters are the gas flow ratio [1-3], plasma frequency [4,5] and temperature [5,6]. The effect of these parameters on the optical properties of the deposited films have been fairly well understood. The understanding of the fundamental processes in surface and bulk passivation of Si wafers is also improving. However, there are disagreements as to whether the refractive index [3], the Si-N bond density [7] or other properties of  $SiN_x:H$  film determine the optimal passivation properties.

Previous studies fail to agree conclusively on several aspects of increasing the RF power ( $P_{RF}$ ) during  $SiN_x:H$  deposition by direct PECVD. Using a plasma excitation frequency of 13.56MHz, Cotler et al. [8] found an increasing incorporation of hydrogen (H) into the  $SiN_x:H$  film with increasing  $P_{RF}$ , whilst Morello [9] did not observe this relationship. Using a lower excitation frequency of 50kHz, Jaeger et al. [10] found an increasing interface surface state density with increasing  $P_{RF}$ . Leguijt et al. [11], who found no influence of  $P_{RF}$  on surface recombination velocity, attributes Jaeger's result to ion bombardment a 10nm passivating oxide present on their samples. However, there exists agreement on the fact that higher  $P_{RF}$  results in increased activation of  $NH_3$  in the plasma, resulting in more incorporation of nitrogen (N) in the film and thus lower  $n$ .

In this paper we have investigated the influence of  $P_{RF}$  on the passivating properties of  $SiN_x:H$  in a direct PECVD system utilising 13.56MHz excitation frequency and found that  $P_{RF}$  affected the passivation quality.

### 2. EXPERIMENTAL

Two sets of samples were prepared, one set for lifetime measurements and another for optical characterisation, capacitance-voltage (CV) measurements and admittance spectroscopy (AS). The former were as-cut single crystal <100> oriented Czochralski silicon (Cz-Si) with a resistivity of 3-6  $\Omega$ cm which were etched in a  $HNO_3:CH_3COOH:HF$  mixture for chemical polishing. The latter samples were single side polished, 525 $\mu$ m thick <100> oriented Cz-Si. All samples received treatments in RCA-1 and dilute HF to clean the surfaces. Prior to PECVD a 1 minute immersion in 3% HF was followed by a rinse in DI- $H_2O$  and drying in  $N_2$ .  $SiN_x:H$  was deposited on both sides of the samples for lifetime measurements. In between the two depositions the samples again received an HF dip. The parameters chosen for the PECVD process are listed in Table I.

**Table I:** Deposition parameters used in this work

Temperature	400 °C
Pressure	0.5 Torr
$NH_3$ flow	100 sccm
$SiH_4$ flow	20 sccm
Electrode spacing	30 mm
Minimum $P_{RF}$	25 W = 5.4 mW/cm <sup>2</sup>
Maximum $P_{RF}$	87.5 W = 18.9 mW/cm <sup>2</sup>
$P_{RF}$ increment	12.5 W = 2.7 mW/cm <sup>2</sup>

Effective minority carrier lifetime,  $\tau_{eff}$ , was measured on a WCT-100 from Sinton Consulting, where both quasi-steady state photoconductance decay and generalised analysis tools were available in the software. The lifetimes were measured over a wide range of injection levels, but single quotes refer to an injection level of  $10^{15}$  cm<sup>-3</sup>. By using high quality Cz-Si for these studies one can attribute the difference in measured  $\tau_{eff}$  to the surface passivation quality only [12].

Film thickness and  $n$  were measured with an ellipsometer (Rudolph Research) at wavelength a of 633 nm. For CV and AS measurements the samples were

divided into 5mm x 5mm and Al contacts were deposited by thermal evaporation in order to form a metal-insulator-semiconductor (MIS) structure. CV measurements were carried out using a bias from -15V to 15V at frequencies from 1 kHz to 1 MHz. AS measurements were carried out from 50K to 300K on the same samples at gate voltage,  $V_g = 0$ .

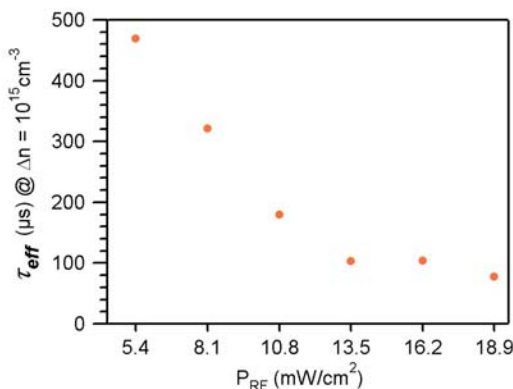
### 3. RESULTS AND DISCUSSION

#### 3.1 $\tau_{\text{eff}}$ versus $P_{\text{RF}}$

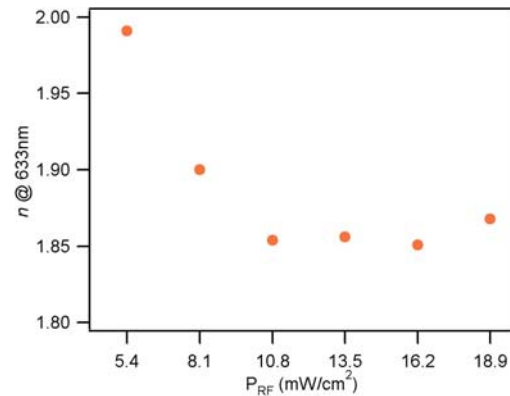
Figure 1 shows the measured  $\tau_{\text{eff}}$  versus  $P_{\text{RF}}$ . Increasing  $P_{\text{RF}}$  from 5.4 mW/cm<sup>2</sup> to 18.9 mW/cm<sup>2</sup> lead to a decrease in  $\tau_{\text{eff}}$  from 470 $\mu$ s to 76 $\mu$ s, clearly illustrating the detrimental effect of an increased  $P_{\text{RF}}$  on the passivating quality of the deposited SiN<sub>x</sub>:H films.

However, as seen in Figure 2,  $n$  also varied with  $P_{\text{RF}}$ , from 1.98 for  $P_{\text{RF}} = 5.4$  mW/cm<sup>2</sup> to 1.85 for  $P_{\text{RF}} = 10.8$  mW/cm<sup>2</sup>. Above  $P_{\text{RF}} = 10.8$  mW/cm<sup>2</sup>  $n$  remained fairly constant. The decrease is caused by a higher rate of oxidant activation (in our case NH<sub>3</sub> to \*NH<sub>n</sub>) with  $P_{\text{RF}}$ . The activated oxidant species react with the already abundant activated reactant (in our case SiH<sub>4</sub> to \*SiH<sub>n</sub>) [13]. This results in an increased N/Si ratio in the films and a lower  $n$ . When  $P_{\text{RF}}$  reaches a level where enough oxidant is activated to consume all the reactant, the N/Si ratio and  $n$  stays constant.

Hence, from  $P_{\text{RF}} = 5.4$  mW/cm<sup>2</sup> to  $P_{\text{RF}} = 10.8$  mW/cm<sup>2</sup> there was a decrease in both  $\tau_{\text{eff}}$  and  $n$ , from 470 $\mu$ s to 180 $\mu$ s and from 1.98 to 1.85, respectively. This correlation between  $n$  and  $\tau_{\text{eff}}$  has been observed in the literature [3]. However, such studies usually use the NH<sub>3</sub>/SiH<sub>4</sub> gas flow ratio to adjust  $n$  while keeping  $P_{\text{RF}}$  constant. In both cases though, an increase in  $n$  is accompanied by an increase in Si-H bond concentration and a fall in N-H bond concentration. As H is known to passivate surface recombination sites by bonding to Si dangling bonds, it seems reasonable that the passivation quality of a SiN<sub>x</sub>:H film is more dependent on the Si-H bond concentration than the total H content. The probable decrease in Si-H bond concentration expected to accompany a falling  $n$  with increasing  $P_{\text{RF}}$  can therefore, in part at least, explain the decrease in  $\tau_{\text{eff}}$  for higher values of  $P_{\text{RF}}$ .



**Figure 1:** Minority carrier lifetime vs.  $P_{\text{RF}}$  illustrates the detrimental effect an increased  $P_{\text{RF}}$  can have on the passivating quality of the deposited SiN<sub>x</sub>:H films.



**Figure 2:**  $n$  at 633nm versus  $P_{\text{RF}}$  show a fall in  $n$  up to  $P_{\text{RF}} = 10.8$  mW/cm<sup>2</sup>, above which it is fairly constant.

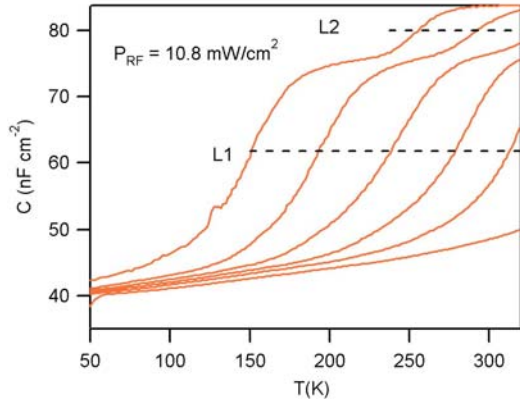
However,  $\tau_{\text{eff}}$  decreases further from 180 $\mu$ s to 76 $\mu$ s from  $P_{\text{RF}} = 10.8$  mW/cm<sup>2</sup> to  $P_{\text{RF}} = 18.9$  mW/cm<sup>2</sup> while  $n$  stays relatively constant, indicating that the origin of the decreasing lifetime with increasing  $P_{\text{RF}}$  lies not solely in the decrease in Si-H bond concentration, as seen by changing  $n$ , but increased ion bombardment of the Si surface during deposition. This seems plausible as during the deposition process, both measured electrode current and voltage increased with  $P_{\text{RF}}$ , implying both that the plasma contained a higher density of ionic species and that the bombarding energy of these species was increased. Ion bombardment of the surface can lead to creation of surface recombination sites, such as Si dangling bonds [14], and thus lower the measured effective lifetime.

#### 3.2 CV and AS analysis

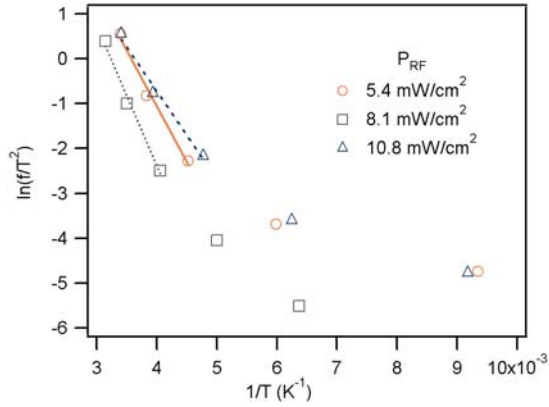
To broaden our understanding of the decrease in  $\tau_{\text{eff}}$  with higher  $P_{\text{RF}}$ , AS and CV measurements were carried out on the three samples with  $P_{\text{RF}}$  of 5.4 mW/cm<sup>2</sup>, 10.8 mW/cm<sup>2</sup> and 18.9 mW/cm<sup>2</sup> at different frequencies.

Figure 3 shows AS spectra of the sample with  $P_{\text{RF}} = 10.8$  mW/cm<sup>2</sup> measured at a zero DC bias and different frequencies (1kHz-1MHz). The step-like increases in the capacitance represent electronic states in the band gap. The spectra reveal at least 2 trap levels (L1 and L2) near the SiN<sub>x</sub>:H/Si interface.

Figure 4 shows an Arrhenius plot of  $\ln(f/T^2)$  versus  $1/T$ , where  $T$  is the temperature of the step-like increase in capacitance and  $f$  is the measurement frequency. Ideally, for a single level, this plot would reveal a linear relationship which slope can be used to estimate the level's position in the band gap. As can be seen, however, a purely linear relationship does not exist. This suggests that (i) emission from the trap has not a pure activation mechanism or (ii) the trap is a continuum of energy levels rather than a single one. Using the data points from frequencies of 5kHz, 30kHz and 150kHz gives trap level energies ( $E_T$ ) of 0.21 eV, 0.27 eV and 0.17 eV ( $\pm 10\%$ ) above the valence band for  $P_{\text{RF}} = 5.4$  mW/cm<sup>2</sup>, 10.8 mW/cm<sup>2</sup> and 18.9 mW/cm<sup>2</sup>, respectively. From the curvature of the Arrhenius plot one can see that these energies would represent the maximum estimates for  $E_T$ , as using points at higher values of  $1/T$  would yield a smaller slope.



**Figure 3:** AS spectra of  $P_{RF} = 10.8 \text{ mW/cm}^2$ . The line L1 shows the capacitance value which was used for the Arrhenius plot in Figure 4.



**Figure 4:** Arrhenius plot for estimation of the trapping level energy,  $E_T$ .

The CV measurements revealed considerable frequency dependence of the capacitance, similarly to AS measurements. In the accumulation mode, however, significant leakage current was observed. The increased leakage prohibited quantitative analysis of the density of surface states,  $D_{it}$ , from the CV curves. It was instead chosen to use the parallel conductance versus voltage ( $G_p/V$ ) curves [15] and plot  $G_p/\omega$  at  $V_g = 0V$  against  $\omega = 2\pi f$ . Shallow traps appear as an increase in  $G_p/\omega$  at lower  $\omega$  [16], whilst deep levels appear as peaks, from which one can deduce  $D_{it}$  by

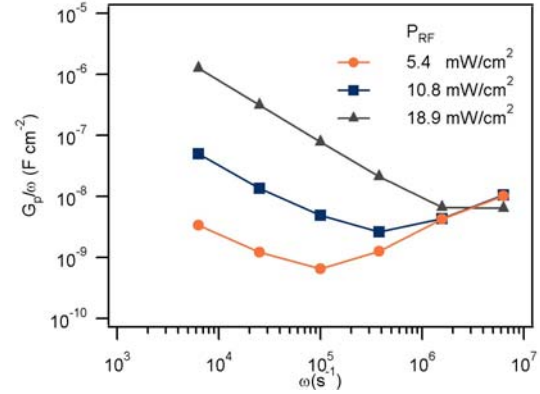
$$D_{it} = \frac{2}{q} \left( \frac{G_p}{\omega} \right)_{Peak} \quad (1)$$

and the interface trap constant by

$$\tau_{it} = \frac{1}{\omega_{Peak}} \quad (2)$$

The plot of  $G_p/\omega$  versus  $\omega$  in Figure 5 show the characteristic shape for shallow traps for all values of  $P_{RF}$ . Using the highest values of  $G_p/\omega$  to calculate  $D_{it}$  from equation 1 gives  $4 \times 10^{10}$ ,  $6 \times 10^{11}$  and  $2 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$  for  $P_{RF}$  of  $5.4 \text{ mW/cm}^2$ ,  $10.8 \text{ mW/cm}^2$  and  $18.9 \text{ mW/cm}^2$ , respectively.

This relatively rough estimation of  $D_{it}$  is in line with the observation of the shorter carrier life-time in the samples prepared with higher  $P_{RF}$ . Thus, for good surface



**Figure 5:**  $G_p/\omega$  vs.  $\omega$  at  $V_g=0$ .

passivation, the  $P_{RF}$  should be kept as low as possible in order to avoid excessive formation of surface recombination sites.

#### 4. CONCLUSION

In this paper we have investigated the influence of the RF power on the passivating properties of a PECVD  $\text{SiN}_x\text{:H}$  film on Si. Increasing  $P_{RF}$  from  $5.4 \text{ mW/cm}^2$  to  $18.9 \text{ mW/cm}^2$  had a pronounced effect on the effective minority carrier lifetime. In the lower half of the power range this decrease could be attributed to the decreasing refractive index and thus the lowering of the Si-H bond concentration which is the determining factor for hydrogen passivation of Si dangling bonds at the Si/SiN<sub>x</sub>:H interface. In the upper half of the power range, where  $n$  stayed relatively constant, the fall in  $\tau_{eff}$  is most probably due to increased ion bombardment of the Si surface. This implies that the decrease in  $\tau_{eff}$  at  $P_{RF} < 10.8 \text{ mW/cm}^2$  is caused by a combination of ion bombardment and falling Si-H bond concentration.

Admittance spectroscopy suggested that there was a continuum of electronically active traps close to the surface in samples deposited at all power ranges. In addition, analysis of conductance-voltage measurements suggested that these traps were shallow and that their concentration increased with higher  $P_{RF}$ .

#### 5. ACKNOWLEDGEMENTS

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