# Investigation of surface passivation thin film materials for improved predictable quantum efficiency detectors

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We report the preliminary results from our study of different surface passivation thin film materials and deposition processes for development of PQEDs with excellent performance and stability at room temperature and cryogenic temperatures. Our work aims at maximizing the fixed charge density in the dielectric and the effective minority charge carrier lifetime as well as reducing the optical absorption of the dielectric in the visible range to a negligible level. We have so far demonstrated a fixed charge density of >  $5x10^{12}$  cm<sup>-2</sup> and effective lifetime of > 4 ms for ptype FZ wafers passivated with PECVD SiN<sub>x</sub> or a stack of thermal SiO<sub>2</sub> and PECVD SiN<sub>x</sub>. For ntype FZ wafers passivated with ALD Al<sub>2</sub>O<sub>3</sub>, we have obtained an effective lifetime of ~20 ms.

#### INTRODUCTION

The predictable quantum efficiency detector (PQED) has shown a strong promise to replace the cryogenic radiometer (CR)- which is bulky, expensive and complex - as a primary standard for ultra-high accuracy measurements of optical power<sup>1-3</sup>. To keep up with the increasing measurement accuracy needs of National Metrology Institutes (NMIs), the internal quantum deficiency (IQD) of PQEDs -which is around 0.01% - needs to be reduced by one order of magnitude, which may require operation at cryogenic temperatures. The aim of our work is therefore to develop PQEDs with superior performance and stability at both room and cryogenic temperatures.

The PQED is made of an induced-junction photodiode in which the p-n junction is formed by the inversion of the silicon surface due to the fixed charges in the passivation dielectric unlike the conventional p-n junction formed by doping. Increasing the fixed charge density  $-Q_{f^{-}}$  in the dielectric has been theoretically predicted to improve the quantum efficiency of the diode by decreasing the surface recombination velocity (*SRV*) at the dielectric-silicon interface, as well as improving the linearity and dynamic range of the detector.

## **METHODS**

We investigate different passivation materials and methods to achieve high fixed charges  $(Q_f)$  and low interface traps  $(D_{it})$  that can potentially lead to very low SRVs and consequently to extremely low IQDs. Since it would be too costly to make photodiodes with all possible types of passivation and experimentally difficult to compare their performance at both room temperature and cryogenic temperatures, we follow a different approach. Improved 3D simulation models enable us to limit the study to specific properties of the surface passivation materials. Through this approach, the challenge of improving PQEDs is transformed into high resolution material analysis at various temperatures, which saves cost and makes it possible to predict the response of photodiodes made from the various passivation techniques without having to complete the photodiodes production process. The best passivation material/process for cryogenic temperatures will then be used to manufacture a set of improved POEDs.

Our research focuses on three different surface passivation dielectrics. For p-type Si wafers, we investigate i) thermally grown SiO<sub>2</sub>, *ii*) SiN<sub>x</sub> deposited by plasma enhanced chemical vapor deposition (PECVD)<sup>4</sup>, and *iii*) stacks of these two dielectrics, due to their positive fixed charge. Simulations have shown that the IQD of PQEDs made with n-type silicon substrate is a factor of 2-3 times better than that of those made with p-type substrate, if all other parameters are kept the same<sup>5</sup>. For n-type wafers, we study Al<sub>2</sub>O<sub>3</sub> deposited by atomic layer deposition (ALD), due to its negative fixed charge, as passivation dielectric for PQEDs.

In our work, we optimize the growth or deposition processes for these dielectrics to minimize the *SRV* by maximizing  $Q_f$  and keeping  $D_{it}$  as low as possible. The effective minority charge carrier lifetime ( $\tau_{eff}$ ) is measured by photoluminescence (PL) imaging.  $Q_f$  is extracted from C-V measurements on MOS capacitors. The optical characterization of the dielectric thin films is performed with spectroscopic ellipsometry. The results we have obtained so far were measured at room temperature, but we are currently also working on development of variable temperature setup for lifetime measurements at cryogenic temperatures.

### **RESULTS AND DISCUSSION**

Figure 1 shows the carrier lifetime map of a 6-inch ptype FZ Si wafer with PECVD SiN<sub>x</sub> passivation. The PECVD reactor used for deposition is APM from SPTS. The deposition was carried out at temperature of 350 °C and total pressure of 2000 mTorr. The gas flow of both SiH<sub>4</sub> and NH<sub>3</sub> was 60 sccm. The film thickness was measured with ellipsometer to be ~140 nm. As can be seen in Figure 1, a uniform carrier lifetime of 4.1 ms is obtained. The fixed charge density extracted from MOS C-V measurements is about  $3x10^{12}$  cm<sup>-2</sup>.



**Figure 1.** Carrier lifetime map at carrier density of  $7.1 \times 10^{14}$  cm<sup>-3</sup> of 6-inch p-type FZ wafer passivated with PECVD SiN<sub>x</sub>. The gas flow used for deposition was 60 sccm of SiH<sub>4</sub> and 60 sccm of NH<sub>3</sub>. The color bar shows  $\tau_{eff}$  in  $\mu$ s.

In order to examine the effect of stoichiometric ratio of SiN<sub>x</sub> on the lifetime, fixed charge and optical properties of the dielectric, the gas flow ratio of SiH<sub>4</sub> to NH<sub>3</sub> was varied from 1/3 to 3, keeping the NH<sub>3</sub> flow fixed at 60 sccm. Figure 2 shows the C-V characteristics of a MOS capacitor measured at a frequency of 10kHz for each deposition. The C-V shift to more negative values for lower SiH<sub>4</sub> indicate that the  $Q_f$  increases with decreasing SiH<sub>4</sub>:NH<sub>3</sub> ratio, reaching a value of  $6 \times 10^{12}$  cm<sup>-2</sup> for a flow ratio of 1:3. This is ~2 orders of magnitude higher than the  $Q_f$  we have obtained in thermally grown SiO<sub>2</sub>.

Table I summarizes the key characteristics of  $SiN_x$  depositions with different gas flow ratios. The charge and optical characteristics improve significantly with decreasing  $SiH_4$ :NH<sub>3</sub> ratio while the carrier lifetime

does not show a strong dependence on the gas flow ratio.



Figure 2. MOS C-V characteristics of PECVD  $SiN_x$  films with varied  $SiH_4/NH_3$  gas flow ratio.

**Table I:** Key characteristics of PECVD  $SiN_x$  passivation with different stoichiometric ratios. The NH<sub>3</sub> flow was kept constant at 60 sccm and SiH<sub>4</sub> flow was varied to obtain the given ratios.

SiH <sub>4</sub> /NH <sub>3</sub>	$ au_{e\!f\!f}$	$Q_f$ (cm <sup>-2</sup> )	n @	k @
flow ratio	(ms @ cm <sup>-3</sup> )		632 nm	632 nm
1/3	4.4 @7.1x10 <sup>14</sup>	6.0x10 <sup>12</sup>	1.84	0
2/3	4.2 @6.8x10 <sup>14</sup>	5.2x10 <sup>12</sup>	1.98	1.9x10 <sup>-5</sup>
1	4.1@ 6.5x10 <sup>14</sup>	3.1x10 <sup>12</sup>	2.12	1.9x10 <sup>-3</sup>
2	4.1@6.5x10 <sup>14</sup>	2.2x10 <sup>12</sup>	2.44	1.7x10 <sup>-2</sup>
3	4.1@6.6x10 <sup>14</sup>	2.1x10 <sup>12</sup>	2.67	4.8x10 <sup>-2</sup>

We also investigated the passivation of p-type FZ wafers with a stack of ~5 nm thermal oxide and ~140 nm thick PECVD SiN<sub>x</sub>, which leverages the low interface trap density and good stability of thermal SiO<sub>2</sub> as well as high fixed charge density of PECVD SiN<sub>x</sub>. This stack has exhibited a few times higher lifetime than bare SiN<sub>x</sub> deposited directly on Si.

The preliminary measurement of 60 nm ALD Al<sub>2</sub>O<sub>3</sub> films deposited at 300°C shows a  $\tau_{eff}$  of ~20 ms on n-type FZ Si, *n*-index of 1.6 and *k*-index of  $3.0 \times 10^{-6}$  (at wavelength of 632 nm), which is very promising. Further characterization of these films (including  $Q_f$ ) and optimization of the deposition process is ongoing.

With the results we have obtained so far, there is a good chance of achieving the desired IQD of <1ppm at room temperature, eliminating the need for cryogenic operation, which is to be verified.

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