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 > $5x10^{12}cm^{-2}$ and effective lifetime of > 4 ms for p-type FZ wafers passivated with PECVD SiN_x or a stack of thermal SiO_2 and PECVD SiN_x. For n-type FZ wafers passivated with ALD Al_2O_3, 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[1-3]. 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 *SRV*s 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 PQEDs.

Our research focuses on three different surface passivation dielectrics. For p-type Si wafers, we investigate i) thermally grown SiO_2, *ii)* SiN_x deposited by plasma enhanced chemical vapor deposition (PECVD)[4], 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[5]. For n-type wafers, we study Al_2O_3 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 (τ_{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 p-type FZ Si wafer with PECVD SiN_x 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_4 and NH_3 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^{-2}.

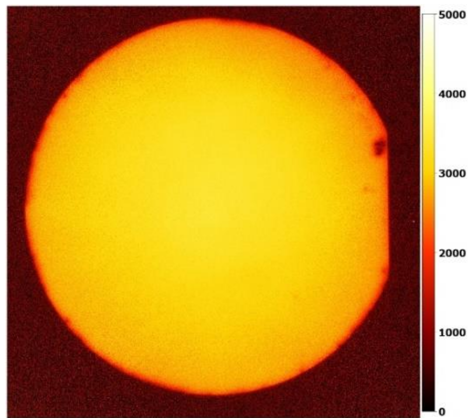

Figure 1. Carrier lifetime map at carrier density of $7.1x10^{14}$ cm^{-3} of 6-inch p-type FZ wafer passivated with PECVD SiN_x. The gas flow used for deposition was 60 sccm of SiH_4 and 60 sccm of NH_3. The color bar shows τ_{eff} in µs.

In order to examine the effect of stoichiometric ratio of SiN_x on the lifetime, fixed charge and optical properties of the dielectric, the gas flow ratio of SiH_4 to NH_3 was varied from 1/3 to 3, keeping the NH_3 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_4 indicate that the Q_f increases with decreasing SiH_4:NH_3 ratio, reaching a value of $6x10^{12}$ cm^{-2} 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_2.

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_3 ratio while the carrier lifetime does not show a strong dependence on the gas flow ratio.

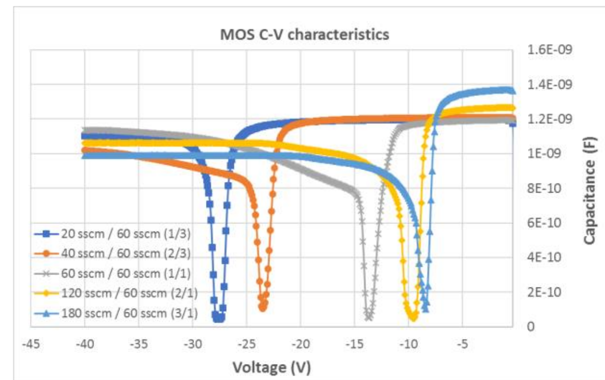

Figure 2. MOS C-V characteristics of PECVD SiN_x films with varied SiH_4/NH_3 gas flow ratio.

Table I: Key characteristics of PECVD SiN_x passivation with different stoichiometric ratios. The NH_3 flow was kept constant at 60 sccm and SiH_4 flow was varied to obtain the given ratios.

SiH_4/NH_3 flow ratio	**τ_{eff} (ms @ cm^{-3})**	**Q_f (cm^{-2})**	***n* @ 632 nm**	***k* @ 632 nm**
1/3	4.4 @$7.1x10^{14}$	$6.0x10^{12}$	1.84	0
2/3	4.2 @$6.8x10^{14}$	$5.2x10^{12}$	1.98	$1.9x10^{-5}$
1	4.1@ $6.5x10^{14}$	$3.1x10^{12}$	2.12	$1.9x10^{-3}$
2	4.1@$6.5x10^{14}$	$2.2x10^{12}$	2.44	$1.7x10^{-2}$
3	4.1@$6.6x10^{14}$	$2.1x10^{12}$	2.67	$4.8x10^{-2}$

We also investigated the passivation of p-type FZ wafers with a stack of ~5 nm thermal oxide and ~140 nm thick PECVD SiN_x, which leverages the low interface trap density and good stability of thermal SiO_2 as well as high fixed charge density of PECVD SiN_x. This stack has exhibited a few times higher lifetime than bare SiN_x deposited directly on Si.

The preliminary measurement of 60 nm ALD Al_2O_3 films deposited at 300°C shows a τ_{eff} of ~20 ms on n-type FZ Si, *n*-index of 1.6 and *k*-index of $3.0x10^{-6}$ (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 <1 ppm at room temperature, eliminating the need for cryogenic operation, which is to be verified.

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