# Lowest surface recombination velocity on *n*-type crystalline silicon using PECVD a-Si:H/SiN$_x$ bi-layer passivation

Dmitri S. Stepanov[1], Zahidur R. Chowdhury[2], Nazir P. Kherani[1,2,*]
[1]Department of Materials Science and Engineering
[2]Department of Electrical and Computer Engineering
University of Toronto, Toronto, ON M5S 3E4
[*]kherani@ecf.utoronto.ca

## ABSTRACT

Energy conversion efficiency of crystalline silicon (c-Si) solar cells manufactured on thin substrates is strongly influenced by the recombination losses of photo-generated charge carriers at the surface and in its proximity. Intrinsic hydrogenated amorphous silicon (*i*-a-Si:H) deposited using DC saddle-field plasma enhanced chemical vapour deposition (PECVD) at a low temperature of ~200°C reduces recombination losses of photo-generated carriers through passivation of defects at the surface. This study reports on high quality surface passivation achieved using a dual layer approach wherein a 70nm amorphous silicon nitride (SiN$_x$) capping layer is deposited on a less than 10nm thin *i*-a-Si:H layer. While the a-Si:H layer is effective in passivating the interface recombination sites, SiN$_x$ is deemed to incorporate field-effect passivation, thus providing a minority carrier mirror. Additionally, SiN$_x$ layer acts as an anti-reflection coating with a low absorption coefficient in the optical frequency range of interest. The SiN$_x$ deposition conditions, known to strongly influence the passivating quality of the dual layer structure, were systematically investigated using the response surface methodology (RSM). The optimal deposition parameters obtained from the RSM study were experimentally verified to yield the lowest surface recombination velocity of 3.5 cm/s on 1-2 Ω-cm *n*-type FZ c-Si using a PECVD a-Si:H/SiN$_x$ bi-layer passivation stack.

**Keywords**: Passivation, amorphous silicon, silicon nitride, silicon solar cells

## 1 INTRODUCTION

High quality passivation is a prerequisite for high energy conversion efficiency in crystalline silicon (c-Si) solar cells [1]. The importance of surface passivation is magnified in back-contact solar cell designs, which rely on long diffusion length of photogenerated carriers [2]. This becomes even more important in thin crystalline silicon solar cells, where the drive is to attain the highest conversion efficiency while dramatically reducing the absorber thickness [3]. State of the art passivation attained using thermally grown silicon dioxide (SiO$_2$) films on both *n*- and *p-type* c-Si has yielded surface recombination velocities (SRVs) of 2.4 cm/s and 2.5 cm/s, respectively, as reported by Kerr and Cuevas [4]. While the high temperature synthesis process yields excellent SRV, it is not deemed to be an ideal process option considering the diffusion of impurities and defects in bulk of c-Si absorber, and thus adversely affecting carrier collection, as well as the accompanying thermal stresses. Accordingly, the pursuit of low-temperature synthesis options that mitigate the drawbacks associated with thermal oxidation are desirable while concurrently providing the highest quality of passivation. One option that has the potential of meeting these requirements is hydrogenated amorphous silicon nitride (SiN$_x$) films deposited by plasma enhanced chemical vapor deposition (PECVD) at temperatures of around 400°C. The built in fixed charges in SiN$_x$ provide for field effect passivation while the hydrogen provides for interfacial defect passivation. Lauinger et al.[5] report an SRV of 4cm/s on low resistivity 1.5 Ω-cm float zone (FZ) wafer. Additionally, a tunable refractive index of SiN$_x$ in the range of 2.0-2.4 improves optical coupling between air and c-Si and hence reduces light reflection losses.

A dual layer structure consisting of hydrogenated amorphous silicon (a-Si:H) and SiN$_x$, which is a cornerstone of this work, was introduced by Bentzen et al.[6] in a study on passivation and distribution of hydrogen within the PECVD dual layer stack and at the c-Si interface. An improvement of passivation quality with the dual layer stack on *p*-type 2 Ω-cm wafer compared to single layer a-Si:H was attributed to the release and diffusion of hydrogen toward the amorphous silicon – crystalline silicon interface thus relaxing the amorphous silicon network and passivating the dangling bonds at the interface. The dual layer structure was synthesized by PECVD technique on *n-type* wafers by Tucci and Serenelli[7],

Photonics North 2011, edited by Raman Kashyap, Michel Têtu, Rafael N. Kleiman, Proc. of SPIE Vol. 8007,
800720 · © 2011 SPIE · CCC code: 0277-786X/11/$18 · doi: 10.1117/12.905624

showing an initial lifetime of 720µs and a corresponding SRV of 36 cm/s on 1 Ω-cm c-Si; the lifetime improved to approximately 1300µs upon annealing at 400°C for 60 min. Focsa et al. [8] have reported an SRV of 10.7 cm/s on *n-type* 1-10 Ω-cm FZ c-Si wafers using a remote PECVD deposition technique. Catalytic chemical vapor deposition (Cat-CVD) has also been used for the synthesis of high quality amorphous films. Using Cat-CVD Koyama et al. [9] have recently produced a a-Si:H/ $SiN_x$ passivating stack yielding the lowest reported SRV of 1.5 cm/s on *n-type* 2.5 Ω-cm c-Si. While Cat-CVD is a promising technique and has garnered significant research interest, industrial processes continue to rely on PECVD techniques.

## 2 EXPERIMENTAL

This work reports on significant improvement in the passivation of the c-Si surface using the a-Si:H/$SiN_x$ bi-layer stack deposited by PECVD techniques. The bi-layer stack is deposited on 280 µm thick *n-type* FZ wafers with a resistivity of 1-2 Ω-cm. The motivation for *n-type* wafers is its stability under solar irradiation in contrast to the light induced degradation in *p*-type material owing to the formation of boron-oxygen complexes. The thin (< 10 nm) a-Si:H layer is grown in the Direct Current Saddle Field (DCSF) PECVD system using the tetrode electrode configuration. The saddle-field PECVD chamber consists of four parallel electrodes; the two central electrodes are semi-transparent while the two outer electrodes are solid. All the electrodes are held at ground potential with the exception of one of the semitransparent electrodes, the anode, which is powered by a dc power supply. The parallel electrodes are oriented vertically, the substrate placed on the uppermost solid and grounded electrode, and the semitransparent electrode closest to the substrate is held at ground potential. The substrate is directly heated with a calibrated conduction heater. In this context, it is worth noting that the saddle-field system has been demonstrated to produce state-of-the-art amorphous-crystalline silicon interface comparable to RF diode PECVD [10]. The $SiN_x$ layers are grown in Oxford PlasmaLab 100 system, featuring a loadlock and a main chamber, which consists of a showerhead electrode, grounded heater, and a 13.56 MHz power supply setup in a RF diode configuration.

As-received double-side polished wafers are dipped in 5% hydrofluoric (HF) acid solution for 30 s to etch the native oxide and hydrogen terminate the surface. This process was carried out in an oxygen-free dry-nitrogen glovebox with a load-lock interface to the saddle-field deposition chamber. Identical deposition conditions were used to deposit the amorphous silicon films on both sides of the wafer in order to build a symmetric structure; between depositions, the wafer was also similarly dipped in HF in the nitrogen glovebox. Amorphous silicon depositions were carried out using a silane ($SiH_4$) flow rate of 30 sccm, chamber pressure of 160 mTorr, fixed anode current of 34.5 mA, anode voltage of 600-700 V and substrate temperature of 170 °C. The deposition time was set to attain a nominal thickness of 10 nm a-Si:H. The a-Si:H passivated wafers were cleaved into 1 $cm^2$ samples and subsequently transferred into the RF PECVD system for $SiN_x$ deposition. The typically $SiN_x$ layer thickness was > 70 nm, prepared using ammonia ($NH_3$) and 95% nitrogen diluted $SiH_4$. The deposition time for all the $SiN_x$ films was constant, recognizing that the passivation effect is virtually independent of the $SiN_x$ film thickness above 20 nm [11].

Effective minority carrier lifetime ($\tau_{eff}$), refractive index (*n*) and growth rate were used as response variables in the optimization experiments. $\tau_{eff}$ was measured on symmetrical $SiN_x$/a-Si:H/*n*-type c-Si/a-Si:H/$SiN_x$ structures using microwave-detected photoconducatance decay (MW-PCD) by Semilab WT-2000, operating with a 904 nm, 200 ns laser pulse, and estimated incident photon density of $5x10^{13}$ $cm^{-3}$. The sample size was 1 $cm^2$. Optimized films were also prepared on full 100 mm diameter wafer and $\tau_{eff}$ was measured using the Sinton WCT-120 solar lifetime tester, with the measurements taken in transient mode at excess carrier density of $1x10^{15}$ $cm^{-3}$. Spectroscopic ellipsometry (SE) measurements were carried out with SopraLab 5E on all samples. An optical model, confirmed by transmission electron microscopy (TEM) (Figure 1), based on the Tauc-Lorentz dielectric function models for a-Si:H and $SiN_x$ films was developed in order to extract film thickness, growth rate, and optical constants from the SE measurements [12].

The optimal development of a dual layer passivation stack using PECVD techniques involves a large number of parameters making it impractical to pursue an experimental approach of sequential varying of single variables. This challenge provides an opportunity for application of the response surface methodology (RSM) for the development of bi-layer passivation materials. In particular, RSM was used in this study to explore effects of SiNx deposition parameters on the passivation quality of the bi-layer stack while maintaining the hydrogenated amorphous silicon parameter space fixed. Some of the deposition parameters known to influence the passivation quality are: substrate temperature, deposition pressure, plasma power, gas mixture ($NH_3$/$SiH_4$ flow ratio). These parameters and associated ranges of interest were chosen as the RSM input factors; they are summarized in Table 1.

Table 1: Parameter space studied with RSM

| NAME | UNITS | -1 LEVEL | +1 LEVEL |
|---|---|---|---|
| **$P_o$ - Plasma Power** | W | 20 | 80 |
| **$R_g$ - Gas Ratio** | $[NH_3]/[5\%SiH_4]$ | 1 | 5 |
| **P - Chamber Pressure** | mTorr | 500 | 1500 |
| **T - Substrate Temperature** | °C | 180 | 300 |

A second-order model was chosen to represent the response behavior based on its inherent flexibility[13]. Subsequently, D-Optimal RSM design established a minimum set of experimental runs. Parameters of the second-order model for each response ($\tau_{eff}$ , n, $r_g$) were estimated with least squares method and checked for their significance with analysis of variance (ANOVA). Resulting response models were then optimized under constraints by means of standard numerical methods.

## 3 RESULTS AND DISCUSSION

The $\tau_{eff}$ response model is shown as a function of T and P for $R_g$ equal to 1 and 5 with power $P_o$ fixed at 20 W in Figure 2a; the same model is shown at a fixed plasma power of 80 W in Figure 2b. $SiN_x$ deposition temperature features a consistent influence over the bi-layer passivation performance in the RSM parameter space, whereby the highest passivation quality materials were synthesized at 220-260 °C. This behavior could be associated with annealing of underlying a-Si:H and the corresponding improvement of the interface quality. Pressure and power appear to be interacting factors, mutually affecting $\tau_{eff}$; regional low pressure (< 500 mTorr) and high power (> 70 W), and regional high pressure (> 1000 mTorr) and low power (< 30 W) are observed to increase $\tau_{eff}$ at temperatures above 220 °C. Low temperature deposition favours high pressure and low power region for best passivation properties. Two sets of deposition conditions of the $SiN_x$ capping layer (Table 2) enabling maximum $\tau_{eff}$ were confirmed experimentally on a full size c-Si wafer, showing scalability of results to larger areas.

According to a simple relationship between SRV and $\tau_{eff,}$

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S}{W},$$

where $\tau_{bulk}$ is the bulk carrier lifetime, W is the wafer thickness and S represents the SRV, the optimal measured QSSPC $\tau_{eff}$ corresponds to maximum SRV of 3.5 cm/s, assuming $\tau_{bulk} = \infty$ . To our knowledge, this is the lowest SRV reported with a-Si:H/$SiN_x$ bi-layer passivation synthesized by PECVD.

Table 2: Optimized deposition conditions, corresponding $\tau_{eff}$, SRV

| $SiN_x$ deposition conditions | Predicted $\tau_{eff}$ (MW-PCD) | Measured $\tau_{eff}$ (MW-PCD) | SRV, (calculated from QSSPC $\tau_{eff}$ measurement) |
|---|---|---|---|
| **$R_g$=8, Po=80 W, T=250 °C, P=500 mTorr** | 1950±350 μs | 1940 μs | 3.5 cm/s |
| **$R_g$=7, Po=30 W, T=230 °C, P=1000 mTorr** | 1590±320 μs | 1710 μs | 3.6 cm/s |

Elemental analysis using energy-dispersive X-ray spectroscopy (EDS) on a sample of c-Si passivated by a-Si:H/$SiN_x$ bi-layer reveals the presence of oxygen at the a-Si:H/$SiN_x$ interface (Figure 3). Oxygen accumulation extends about 5 nm into the $SiN_x$ layer; it is likely present in a form of silicon oxynitride (SiON), which is associated with charge accumulation and thus potentially further enhancing the field-effect passivation.

## 4 CONCLUSIONS

In summary, we have demonstrated the lowest SRV attained with PECVD a-Si:H/$SiN_x$ bi-layer passivation for 1-2 Ω cm *n*-type c-Si substrate. The low temperature synthesis process enables the use of these passivating materials for very thin (< 50 μm) c-Si solar cells. Furthermore, PECVD-based synthesis is readily transferable to industrial use.

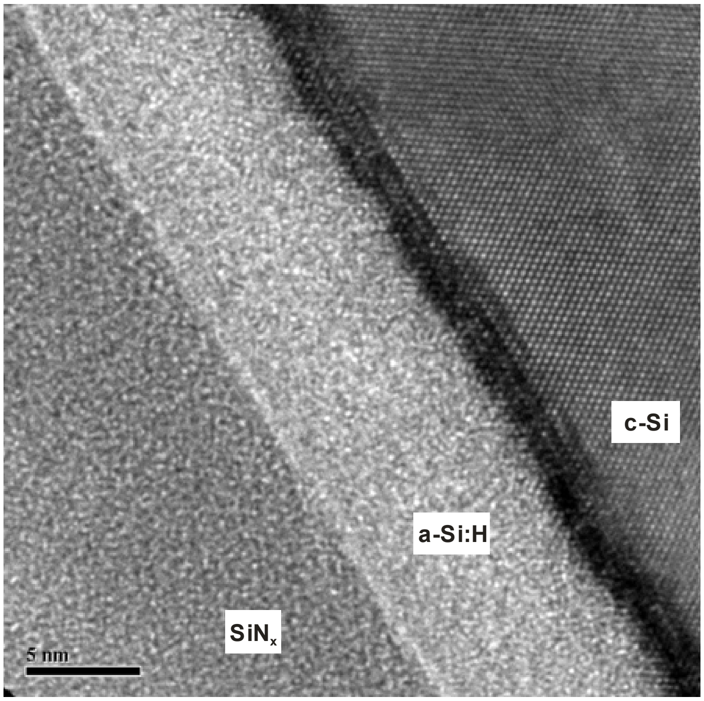

Figure 1: TEM image of bi-layer passivation structure

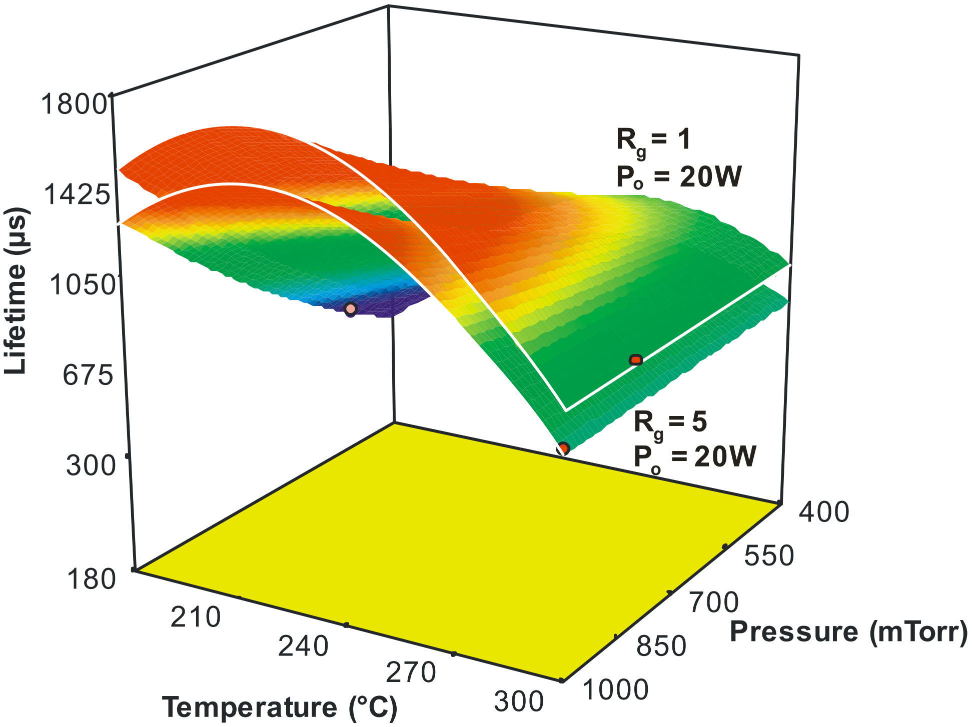

Figure 2(a): Surface plot of $\tau_{eff}$ of *n-type* c-Si wafer with a-Si:H/SiN$_x$ bi-layer passivation as a function of SiN$_x$ deposition conditions at plasma power of 20W

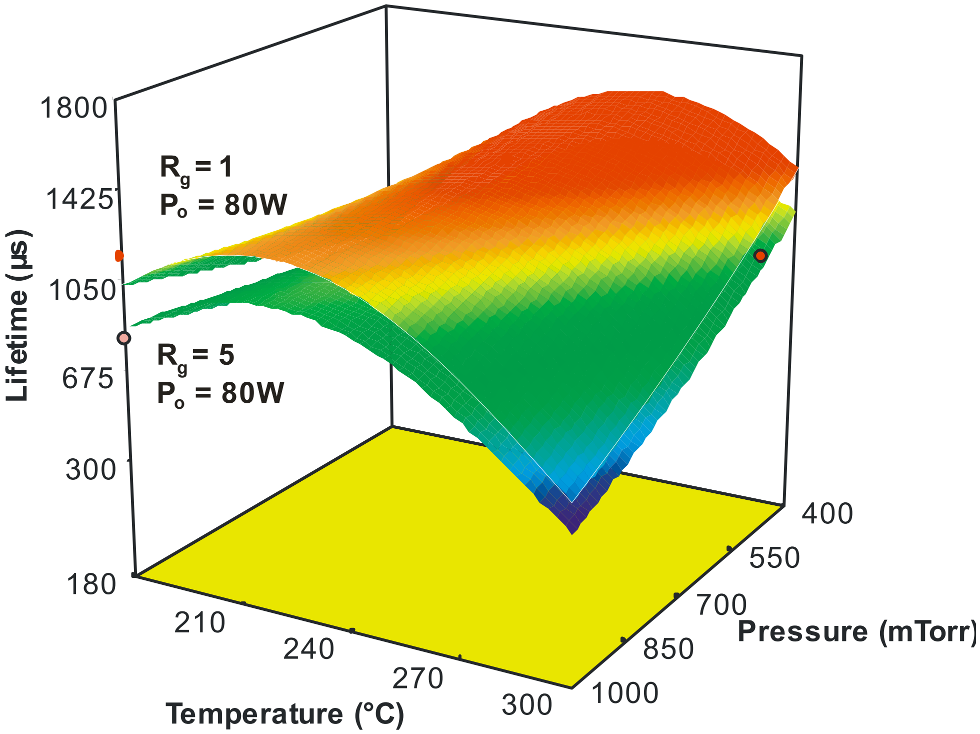

Figure 2(b): Surface plot of $\tau_{eff}$ of *n-type* c-Si wafer with a-Si:H/SiN$_x$ bi-layer passivation as a function of SiN$_x$ deposition conditions at plasma power of 80W

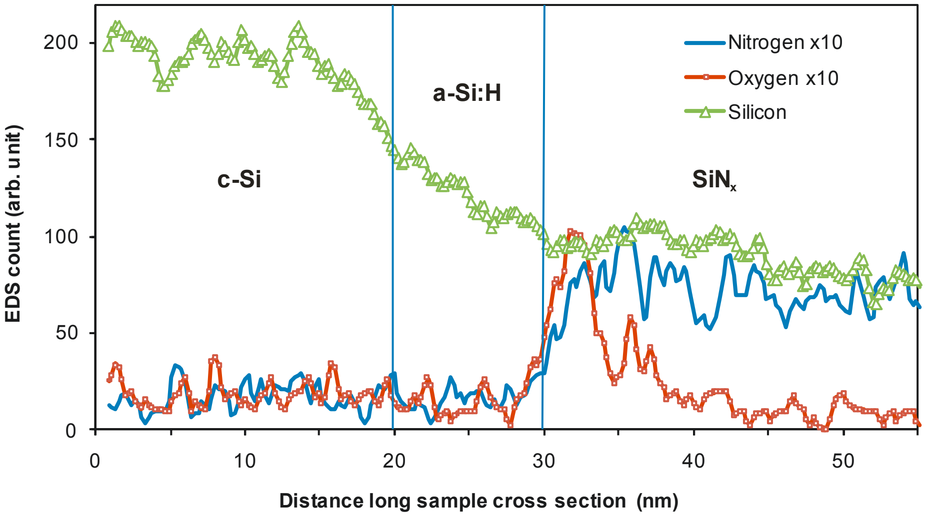

Figure 3: Elemental analysis of bi-layer passivation and interfaces with EDS

## References:

[1] Wenham, S.R., et al., "Surface passivation in high efficiency silicon solar cells", Solar Energy Materials and Solar Cells, 65, 377-384 (2001).

[2] Chowdhury, Z.R., et al. "Two-dimensional modeling of the back amorphous-crystalline silicon heterojunction (BACH) photovoltaic device", Proc. SPIE 7750, (2010).

[3] Kray, D., et al. "Analysis of very thin high-efficiency solar cells", Proceedings of 3rd World Conference on Photovoltaic Energy Conversion, 1021-1024 (2003).

[4] Kerr, M. and A. Cuevas, "Very low bulk and surface recombination in oxidized silicon wafers", Semiconductor Science and Technology, 17, 35-38 (2002).

[5] Lauinger, T., et al., "Optimization and characterization of remote plasma-enhanced chemical vapor deposition silicon nitride for the passivation of p-type crystalline silicon surfaces", Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films, 16(2), 530-543 (1997).

[6] Bentzen, A., et al., "Surface Passivation of Silicon Solar Cells by Amorphous Silicon/Silicon Nitride Dual Layers", 15th International Photovoltaic Science & Engineering Conference, (2005).

[7] Tucci, M. and L. Serenelli, "Metastability of SiNx/a-Si:H crystalline silicon surface passivation for PV application", Thin Solid Films, 516(20), 6939-6942 (2008).

[8] Focsa, A., "Surface passivation at low temperature of p- and n-type silicon wafers using a double layer a-Si:H/SiNx:H", Materials Science and Engineering B, 159, 242-247 (2009).

[9] Koyama, K., K. Ohdaira, and H. Matsumura, "Extremely low surface recombination velocities on crystalline silicon wafers by catalytic chemical vapour deposited SiNx/a-Si stacked passivation layers", Applied Physics Letters, 97, (2010).

[10] Bahardoust, B., et al., "Passivation study of the amorphous–crystalline silicon interface formed using DC saddle-field glow discharge", Physica status Solidi A, 207(3), 539-543 (2010).

[11] Aberle, A.G., [Crystalline silicon solar cells - Advanced surface passivation and analysis], University of New South Wales, Sydney (1999).

[12] Jellison Jr, G.E. and F.A. Modine, "Parametrization of the optical functions of amorphous materials in the interband region", Applied Physics Letters, 69(3), (1996).

[13] Myers, R.H., D.C. Montgomery, and C.M. Anderson-Cook, [Response surface methodology : process and product optimization using designed experiments], John Wiley & Sons (2009).