

Silicon Nitride Surface Passivation in Silicon Solar Cells

Abstract

One of the most important factors for achieving high efficiency solar cells is good quality surface passivation. Good quality surface passivation leads to reduced recombination rates and better cell performance. The use of silicon nitride (SiNx) as a material for surface passivation is investigated in this study. SiNx is deposited via PECVD and then put through a rapid thermal anneal to densify the SiNx layer and relieve stress acquired during the PECVD process. The film characteristics are investigated using spectroscopic ellipsometry and photoconductive decay (PCD). Ellipsometric characterization reveals SiNx film thickness between 50-60 nm and uniform film quality. PCD characterization reveals effective carrier lifetimes of around 800 μ s, which is significantly larger than the original carrier lifetimes without surface passivation, around 70 μ s. Open circuit voltage V_{oc} was measured to be 670 mV. Inverse lifetime (Auger corrected) and carrier density show a linear relationship until carrier density of 1.5×10^{16} carriers per cm^3 , indicating good surface passivation.

Key words: *silicon nitride, PECVD, surface passivation, carrier lifetime*

1 Introduction

Over the last few decades, there has been a tremendous effort to increase the conversion efficiency of incident light into electrical current in silicon solar cells. One crucial aspect of optimizing silicon solar cells lies in the development of effective surface passivation techniques,

which play a pivotal role in reducing recombination losses and enhancing the overall device performance. This is because surface passivation is one of the most important factors affecting cell efficiency. It has a direct effect on how many photo-generated charge carriers are collected by the metal contacts to be used for external applications. The recombination rate of holes and electrons U_s is the rate at which the generated electron-hole pair will recombine without the electrons going through the external circuit. This means that the energy from incident light is essentially wasted when carriers recombine immediately. The expression for the recombination rate derived from the Shockley-Read-Hall formalism is[2,21,22]

$$U_s = (n_s p_s - n_i^2) \int_{E_v}^{E_c} \frac{v_{th} D_{it}(E) dE}{\sigma_p^{-1}(E) (n_s + n_1(E)) + \sigma_n^{-1}(E) (p_s + p_1(E))} \quad (1)$$

As we can see in the equation above, the recombination rate is directly correlated to n_s , which is the electron density at the interface and p_s , which is the hole density at the interface. The D_{it} (density of states at the interface per energy interval) is directly related to the number of defects at the interface. These are the variables that we will be discussing primarily. This recombination rate can also be expressed as surface recombination velocity S_{eff} within the following expression:

$$S \equiv \frac{U_s}{\Delta n} \quad (2)$$

In equation 2, Δn is the excess carrier density [20-22]. We can now clearly see which variables S is dependent on and discuss ways to reduce it. One option would be to reduce the density of defect states at the surface, which is often known as chemical passivation. In chemical passivation the defect states at the surface are reduced via saturation of "dangling bonds". See Figure 2 for a visualization of chemical passivation.

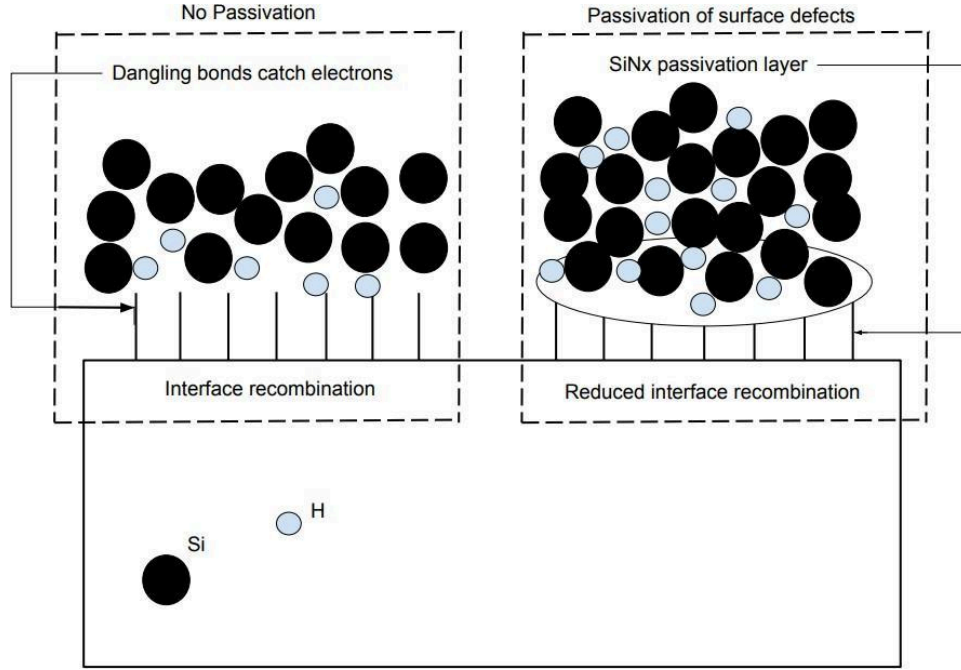


Figure 1: Chemical Passivation Visualization

However, as expected, there is another set of variables that can be controlled to reduce the recombination rate at the interface which is known as “field effect passivation”. This field effect passivation can be realized by adding a charge Q_f at the interface, which reduces n_s and p_s , the electron and hole densities at the interface. The relationship between surface recombination velocity and the surface carrier lifetime, τ_{surf} , is as follows[2]:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surf}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S_{\text{eff}}}{W} \quad (3)$$

Now we can begin to see why both chemical and field-effect passivation are necessary components of a solar cell. As carrier lifetimes increase, this means that the metal contacts at the top and bottom of the cell will have more time to collect the electrons and generate electrical current. These are essentially probabilistic functions and by increasing carrier lifetimes, we increase the probability that the electron will be used to generate electrical current.

The goal of this research is to deposit SiNx films via PECVD to achieve high-quality surface

passivation. This research builds upon a foundation of prior studies that have explored silicon nitride passivation and PECVD techniques. Notable works by Wan et al. (2013) [1], Bonilla et al. (2017) [3], Aberle et al. (2000) [4], and Al-Ezzi et al.[5] have provided fundamental insights into the advantages and challenges associated with silicon nitride passivation, serving as guiding references for this research. By combining advanced characterization techniques with state-of-the-art deposition methods, this research aims to contribute to the ongoing efforts to optimize silicon solar cell performance, ultimately advancing the feasibility and competitiveness of solar energy as a cost-effective power source.

Next, we will discuss the fabrication steps involved in depositing the passivating SiN_x layer via Plasma Enhanced Chemical Vapor Deposition (PECVD) followed by sample characterization methods and tools. This section will then be followed by a section discussing the results and the conclusion.

2 Methodology

2.1 Silicon Surface Cleaning and Oxide Growth

After procuring an n-type silicon wafer, the first step is to clean and prepare the surface for further processing. Initially, the wafer sample is rinsed in clean deionized water (referred to as DIW from here on). Due to the lack of charge carriers in DIW, it is extremely useful in silicon processing and is often used as a solvent for other substances or liquids. Next, the sample is placed in DIW with UV-ozone dissolved in it (referred to as DI-O₃ water) at roughly 14.7 parts per million concentration of ozone. This submersion is five minutes long and creates a layer of native oxide on the silicon sample's surface. Once the native oxide layer is formed, the sample is placed in hydrofluoric acid (HF) to etch away the native oxide, cleaning all organic and inorganic contaminants from the surface of the silicon sample [7]. Now, that all the contaminants

on the surface have been removed, the sample is submerged in DI-O₃ water for 5 minutes to grow a native silicon oxide layer roughly

2 nm thick. The thin native silicon oxide layer helps reduce the “dangling bond” defect density at the interface[25]. Now the sample is ready for PECVD deposition. The process flow for surface cleaning of the sample is shown in Figure 2.

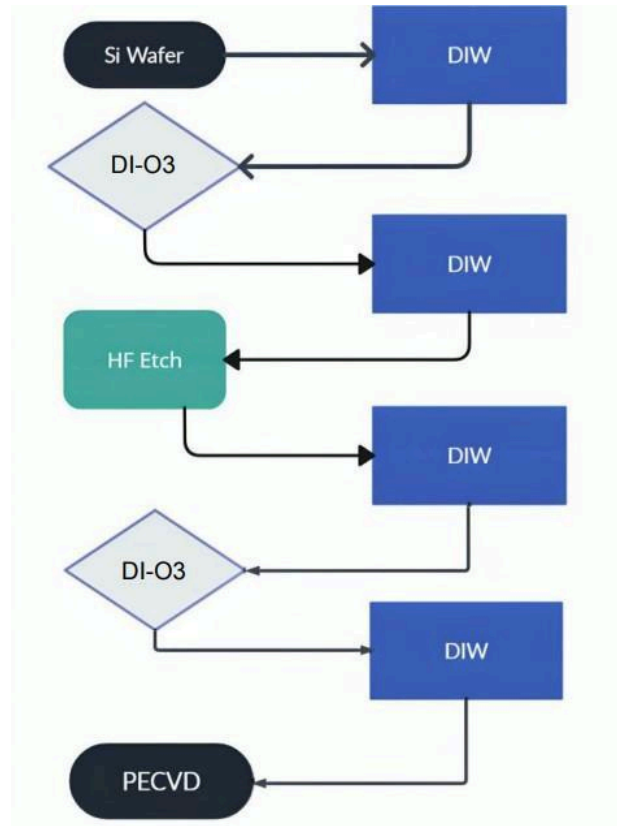


Figure 2: Fabrication Procedures Flowchart

2.2 PECVD Deposition of SiNx

PECVD (Plasma-Enhanced Chemical Vapor Deposition) was used to deposit the SiNx films. The chemicals are deposited with the help of plasma, reducing the overall temperature of the deposition process. An overview of the PECVD chamber is shown in Figure 3.

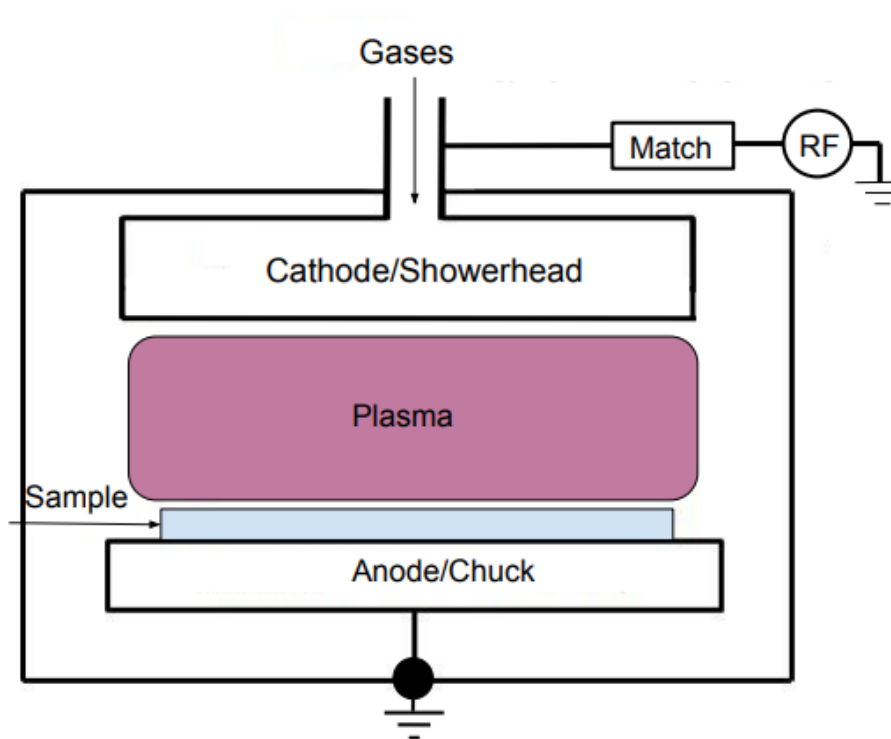


Figure 3: PECVD Reactor Overview

Our PECVD process was done with the substrate being heated at 350°C and the chamber at 60°C. The chamber pressure was 11 mTorr and the flow rates were set for relatively low throughput depositions. In 7 minutes and 30 seconds, we were able to deposit SiN_x films with thicknesses ranging from 50-60 nm.

2.3 Rapid Thermal Annealing

During the PECVD process, stress can be introduced into the SiN_x layer due to differences in thermal expansion coefficients between silicon and SiN_x. The deposited SiN_x layer may also contain defects or have non-ideal properties that could degrade device performance. The annealing process can help densify the SiN_x layer, and also reduce the stress on the film by atomic rearrangements, which in turn improves barrier properties, quality of electrical insulation, and reliability [19]. The process involves loading the silicon sample with SiN_x layers into a box furnace and subjecting them to high temperatures for a short duration. Inside the furnace, the

temperature is raised rapidly to the desired annealing temperature and held there for a specific duration, in our case at 435°C for 2 minutes [19,20]. After the annealing process is complete, the furnace is cooled down, and the wafers are unloaded for further processing or characterization. The Solaris 150 furnace was used for our research, as shown in Figure 4.



Figure 4: Solaris 150 RTA Furnace

3 Results and Discussion

3.1 Spectroscopic Ellipsometry

Spectroscopic Ellipsometry can be used to determine the deposition layer thickness of SiN_x thin films. Precisely polarized light (parallel component p and perpendicular component s) with known intensity falls on the sample at a predetermined incident angle. As the light reflects off of the wafer surface and the sample, the polarization, and intensity of this light are altered. This rotational change in p and s components, along with a change in intensity, is then captured and analyzed [2]. A basic configuration of our ellipsometer, FilmSense FS-1 is shown in Figure 5.

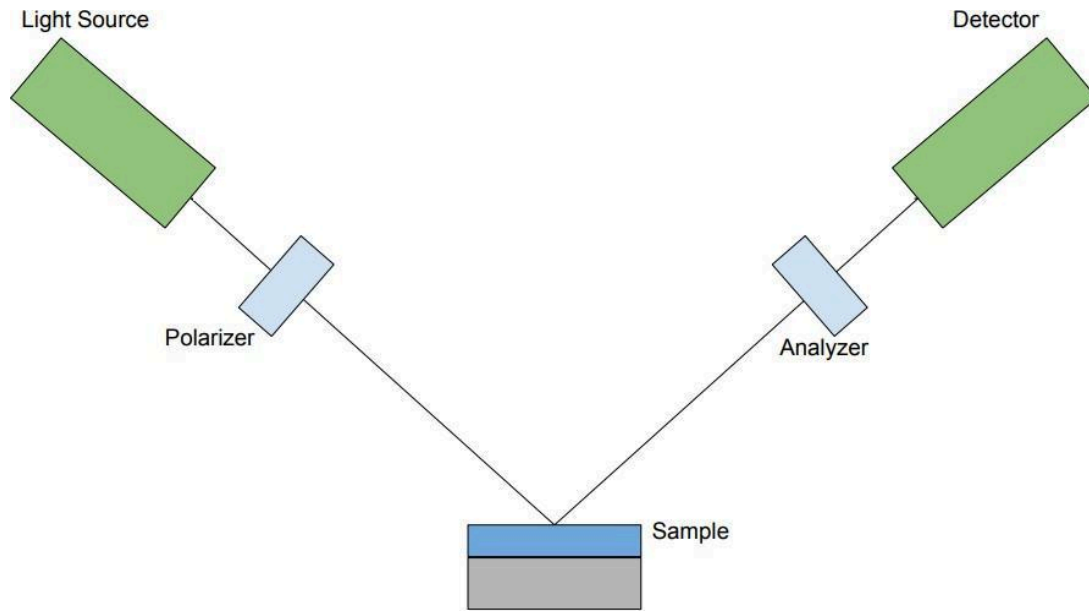


Figure 5: Ellipsometer Configuration

Using ellipsometry measurements, we measured SiNx film thickness using a 5 point pattern. Thickness was measured at 5 separate points and the average film thickness was found to be 58 nm on the front side, and 51 nm on the back side of the sample. The fit difference, difference between the measurement model and actual measured data, was less than 4%, meaning that the measurements fit well within the computer model for SiNx thin film measurements. The refractive index n , a measure of bending of a light ray when passing from a medium, was around $n = 2.21$ for ellipsometry light wavelength of 633 nm. A schematic diagram of the final sample, with the thickness of each film is shown in Figure 6. A 300 μm thick n-type silicon wafer, 2-4 nm silicon oxide layer on both sides, and 50-60 nm SiNx layers on top of the silicon oxide layers.

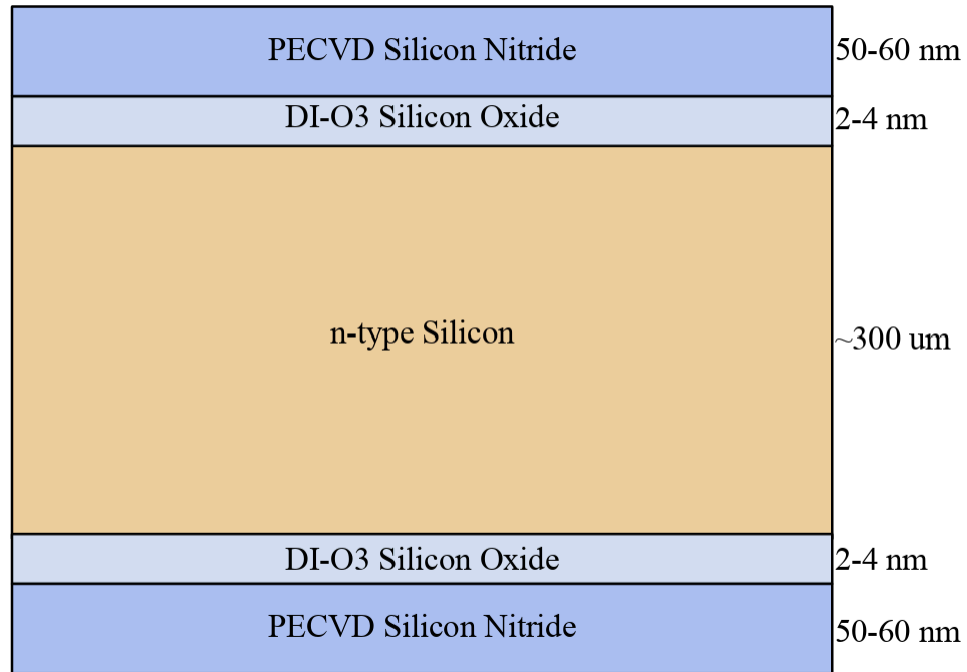


Figure 6: Schematic diagram of the Si/SiO₂/SiN_x stack fabricated for this research

3.2 Carrier Lifetime Measurements

Measuring surface carrier lifetime for silicon nitride (SiN_x) films deposited via PECVD is done via photoconductive decay (PCD) techniques. In PCD, a short pulse of light is used to generate excess carriers within the material. The carriers then recombine, leading to a decay in the photo-generated current. By analyzing the decay of the photocurrent over time, we can extract information about the carrier lifetime in the material [1,23]. A common setup for PCD measurements is shown in Figure 7.

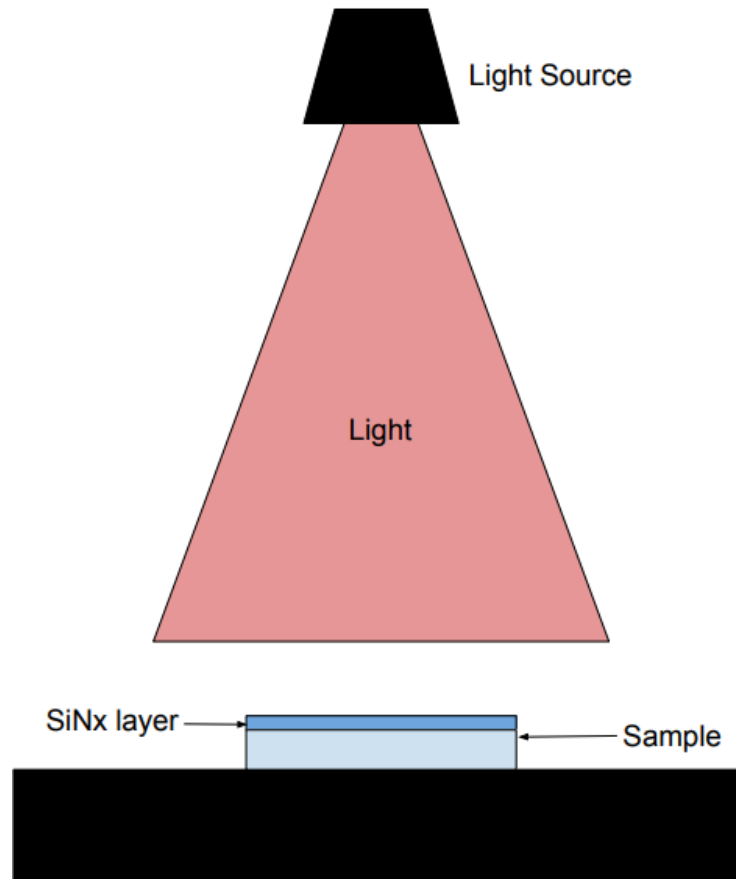


Figure 7: PCD Measurement Layout

In our experiments, we used a Sinton WCT-120PL to conduct PCD characterization on the sample. The results of the PCD measurements as shown in Figure 8.

Lifetime @ Spec. MCD (μs)	801.1
Total Sheet Resistance (Ω/sq)	67.52
Measured Resistivity ($\Omega\text{-cm}$)	1.96
J_0 at 25°C (A/cm^2)	4.65E-14
Est. Bulk Lifetime (μs)	1016.18
Doping Lifetime Product ($\mu\text{s}\cdot\text{cm}^{-3}$)	7.39E+17
Doping (cm^{-3})	9.23E+14
1-sun Implied Voc (V)	0.675
Implied FF (%)	80.4551

Figure 8: PCD Measurements

Resistivity and doping levels are predetermined for us, as the wafers come slightly doped straight from the manufacturer. Voc refers to open circuit voltage across the terminals of a solar cell when there is no external load and 0 current. This variable represents the maximum amount of power a solar cell can create for a given intensity and wavelength of light. The maximum value of Voc depends on the material properties of the substrate used for solar cells and a higher value implies better power conversion ability of the solar cell.

Without the passivation layer, the average effective carrier lifetime was around 70 μs . The passivation layer is highly effective as it has raised the carrier lifetime to around 800 μs , which is more than 10 times the original lifetime. The increased carrier lifetime means that when energy from a certain wavelength of incident light is absorbed by the material, electrons will be excited into higher energy states, allowing them to generate electrical current. Before passivation, these electrons would almost immediately drop back down to their original energy states, making it very challenging for the external circuit to receive any current. This passivation layer allows the electrons to be collected by the metal contacts more efficiently, and in turn, leads to more current generated. A graph of Auger corrected Inverse Lifetime vs. Carrier Density is shown in Figure

9[24]:

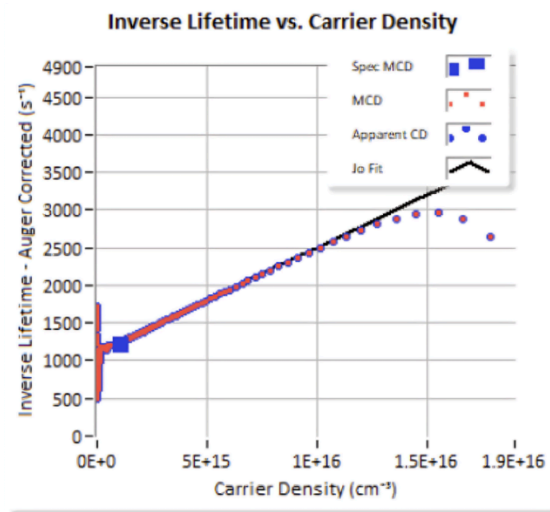


Figure 9: Inverse effective lifetime vs Carrier density

Generally speaking, in the case of good-quality surface passivation, the Auger corrected inverse lifetime should be linearly correlated with carrier density at the surface [3]. This is due to the decrease in defect states at the surface. We can observe towards the far right of the graph that as the carrier density goes beyond a certain threshold, the graph starts to exhibit non-linear behavior once again, leading to unwanted characteristics. This behavior suggests that beyond a certain threshold on carrier density, the mechanisms dictating recombination rates change, making surface passivation difficult. However, by analyzing the data, we can generate fairly accurate and optimized designs and models for solar cells.

4 Conclusion

In this study we have investigated the use of silicon nitride as a surface passivation layer for silicon solar cells. High quality surface passivation remains a key step in increasing the carrier lifetimes in solar cells, and hence increasing their overall efficiency. Silicon nitride was used because it has shown to be effective at reducing recombination rates at the surface by reducing defect states and excess carriers. The main SiN_x deposition was done via PECVD reactors.

However, the initial sample had to be prepared before any PECVD processing could be done it. First, the surface of the sample was cleaned with a combination of DI-O₃ water and HF etching. These 2 compounds helped clear the surface from metal and organic contaminants. Next, the sample was submerged into DI-O₃ water to facilitate the growth of a 2 nm native oxide layer. After this initial cleaning and oxide growth, PECVD reactors were used to deposit a thin film of SiN_x on the sample. Next, the sample was put through a rapid thermal annealing process to densify the film and release stress acquired during the PECVD process.

Through spectroscopic ellipsometry, the thickness of the deposited layers on the front and back of the sample were found to be 58 nm and 51 nm. This SiN_x layer helps reduce defect states on the surface of the sample, and also reduces the density of excess carriers. After ellipsometric characterization, PCD techniques were used to measure carrier lifetimes. Before the passivation layer was deposited, the sample showed a carrier lifetime of around 70 μ s. After depositing the SiN_x passivation layer, the carrier lifetimes were measured to be around 800 μ s, which is more than 10 times the lifetime without any passivation layers. This indicates that our deposited surface passivation layer of SiN_x was highly effective.

The more efficiently we can engineer solar cells to be able to convert light into electricity, the more competitive they will become as an energy source. To that extent, this is a small step in the quest to create high-efficiency silicon solar cells.

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