

SILICON NITRIDE ARC THIN FILMS BY NEW PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION SOURCE TECHNOLOGY

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ABSTRACT: Hydrogenated silicon nitride thin films are an important technology for improving the efficiency and economics of crystalline silicon solar cells. Our group at General Plasma has developed an innovative new plasma technology for plasma enhanced chemical vapor deposition (PECVD) of hydrogenated silicon nitride. This PECVD technology overcomes problems with electrode coating, poor uniformity and slow deposition rates associated with other PECVD platforms. The uniformity of deposited silicon nitride using our PECVD technology is +/- 3% over substrate widths exceeding 1 meter which is ideal for economical production of crystalline solar cells. In addition to uniform deposition over large area, our PECVD technology enables the control of refractive index, hydrogen bond density and Si-N bond density which are important for passivating defects as well as optical matching to n-type emitters of crystalline silicon solar cells [1]. In this work, we present an overview of the plasma source and thin film analysis of hydrogenated silicon nitride thin films that include FTIR, SIMS and UV-VIS-IR spectroscopic data and dielectric properties. The Resonant Coupled Photoconductivity Decay (RCPCD) technique is used to correlate carrier recombination lifetime to these properties [2].

Keywords: Passivation, Silicon-Nitride, Lifetime

1 INTRODUCTION

PECVD silicon nitride films were recognized several decades ago by researchers in semiconductor technology as an important diffusion barrier and dielectric material [3]. Recently hydrogenated silicon nitride (SiN) thin films have found an important functional role in modern crystalline solar cell manufacturing. The refractive index of the SiN films can be matched to the underlying substrate as an anti-reflecting layer to maximize transmitted light to the active layers. The silicon nitride is superior to other optical matching materials such as SiO₂ and TiO₂. The SiN is an excellent encapsulant to prevent contamination from making its way into the active layers which compromises device long term performance. Hydrogen contained in the as-deposited silicon nitride thin films is released during subsequent thermal processing and effectively passivates defects in the underlying active layer.

Here at General Plasma we have developed a large area thin film coating platform for solar cell manufacturing utilizing an innovative patented linear source for plasma enhanced chemical vapor deposition (PECVD) [4]. The Dual Plasma Beam Source™ technology overcomes technical hurdles that limit the effectiveness of other PECVD platforms used for deposition of hydrogenated silicon nitride. The advantages of this new PECVD technology include exceptional deposition rates, high precursor utilization, high quality thin films deposited at temperatures significantly below those of competing PECVD platforms.

Existing PECVD technologies suffer from excessive coating of reactor electrodes. For instance, in a parallel plate RF reactor, the powered electrode is exposed to the PECVD process and receives a large portion of the deposition. In semiconductor and flat panel display applications this is countered by routine plasma etch back cycles. A similar problem exists for recently developed linear microwave (MW) PECVD technology. The microwave waveguide surface, where the plasma

intensity is the highest, receives substantially more coating than the substrate. Frequent removal of the waveguide tubes is required which is not satisfactory for manufacturing platforms. Beyond electrode coating, the ability of this new PECVD technology to operate at lower pressures is a powerful process advantage because operation in the pressure regime of 10's of millitorr avoids gas phase particle generation [5].

It is common for the uniformity requirements to be better than $\pm 5\%$ over the substrate for ARC layers in solar cell manufacturing. Conventional RF and linear microwave PECVD sources struggle to meet this demanding requirement for source widths exceeding several hundred millimeters. This new PECVD platform easily meets this demanding requirement demonstrating uniformity better than $\pm 3\%$ for silicon nitride thin films.

2 PLASMA SOURCE DESCRIPTION

The Plasma Beam Source™ (PBS™) for PECVD technology was introduced in 2002 [4] and applied to plasma cleaning in 2003 [6]. This patented plasma source is a linear source that implements an internal magnetron cathode in a discharge cavity. Figure 1 shows a section view of the PECVD source arrangement highlighting discharge cavity, plasma beam, location of reactive and precursor gas delivery and the substrate.

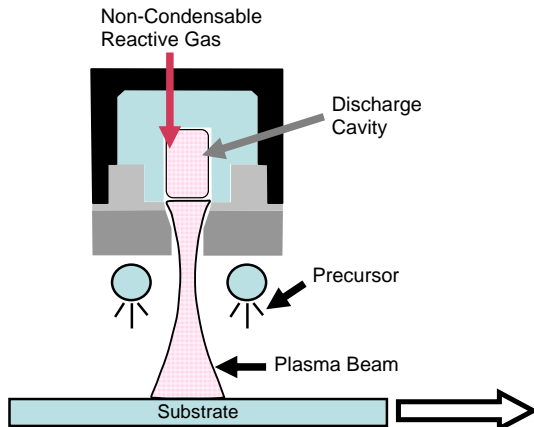


Figure 1. Section view of PBS™ showing discharge cavity, precursor manifold, plasma beam and substrate.

Inside the discharge cavity the magnetron cathode forms a linear, uniform high density electron source where non-condensable reactive gas is introduced. Here, the high density plasma efficiently dissociates the reactive gas into radicals and ions. As electrons leave the discharge cavity they encounter a divergent magnetic field. This magnetic field confines the electrons and forms a hall current that flows the length of the source. The hall current electrons aid in the efficient dissociation of gases outside the discharge cavity.

The SiH₄ precursor is delivered outside the discharge cavity in the presence of the plasma beam. This has two advantages; first the silane is dissociated outside the discharge cavity eliminating contamination of the source electrodes. Second, the reaction zone is in the chamber volume where there is high pumping speed. Silane fragments generated by the plasma chemistry will have a low residence time in the reaction volume reducing possible particulate contamination of the growing thin film. The uniform, collimated nature of the emanating plasma beam is clearly seen for one of these sources in Figure 2.



Figure 2. Section view of PBS™ in operation. The confined plasma beam is clearly observed.

3 SILICON NITRIDE THIN FILM PROPERTIES

3.1 Refractive Index

The refractive index of the hydrogenated silicon nitride is controlled in our PECVD process by adjusting the ratio of ammonia (NH₃) to silane (SiH₄) that are used as the chemical precursors. As the ratio of the NH₃ is increased the refractive index decreases owing to more Si-N bond formation in the thin film. A testament to the effectiveness of this new PECVD source technology is found in this ratio. For our PECVD source we find that we operate our processes with a lower ratio of NH₃:SiH₄ than either radio-frequency (RF) or microwave (MW) PECVD technologies.

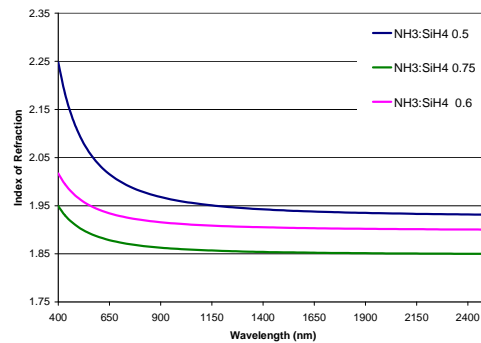


Figure 3. Optical dispersion data for select hydrogenated silicon nitride thin films deposited by our new PECVD platform.

As shown in Figure 3 the NH₃:SiH₄ ratio for our process is less than one to cover the index range between 2.2 and 1.95. Where as competing RF and MW PECVD technologies utilize ratios in excess of five or more to achieve similar refractive indices [7,8].

3.2 SiN Bond Density

Weeber et al., have correlated Si defect passivation effectiveness with Si-N bond density from the MW PECVD technology and we use this as a target for our thin film material development [9]. We utilize Fourier transform infrared spectroscopy (FTIR) to characterize our thin films. The Si-N bond density is calculated by multiplying integrated area of Si-N vibrational modes at 790 cm⁻¹, 850 cm⁻¹ and 1020 cm⁻¹ with their respective calibration constants [10]. In Figure 4 we show an example spectra of a SiN:H deposited at two different NH₃:SiH₄ ratios. The spectra indicate that as the ammonia ratio increases, the Si-N bond density increases and the proportion of N-H bonding decreases as Si-H bonds increase. The Si-H bonds are thought to be responsible for the release of hydrogen that passivates the underlying silicon as discussed below [11].

The optimum process conditions for passivation will typically require Si-N bond densities in excess of 10²³ bonds/cc. Figure 5 shows a composite summary of our thin film silicon nitride refractive index and Si-N bond densities. The process space for our PBS technology is quite large providing a large range of refractive indices

and bond densities. Our data is collected over a range of process parameters that have been modified over temperatures from 80 to 325 °C, pressures from 30 to 90 millitorr and $\text{NH}_3:\text{SiH}_4$ ratios from 0.3 to 2. We demonstrate the ability to manipulate process parameters to achieve different refractive index and Si-N bond density which is important to produce SiN films with excellent defect passivation properties.

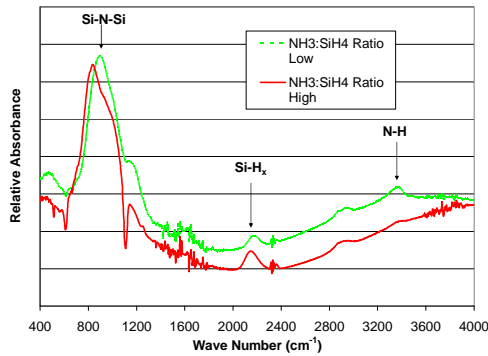


Figure 4. FTIR spectra for two different $\text{NH}_3:\text{SiH}_4$ ratios. Temperature, pressure, power and gas ratios control the Si-N, Si-H and N-H bond densities

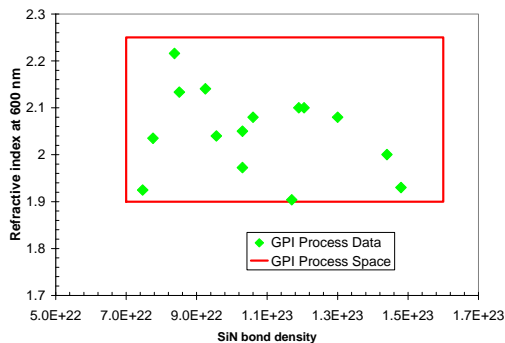


Figure 5. Summary of thin film properties of index of refraction and SiN bond density for a variety of processes from our new PECVD platform.

3.3 Hydrogen Release

The release of hydrogen from the silicon nitride layer during the thermal process of firing contacts remains disputed as the improvement mechanism for the carrier lifetime [12]. There however is agreement with the change of the hydrogen profile before and after firing. In Figure 6 we show the hydrogen profile for two thin films of silicon nitride deposited on high quality high resistivity FZ Si, one prior to anneal and the other after anneal. Also shown in the depth profile is the background hydrogen concentration of the substrate. The high quality FZ material has minimal defect sites so the hydrogen concentration falls to the background level of the wafer. It has been shown in the literature that the hydrogen profile will follow the defect density of the underlying silicon.

The hydrogen depth profile in Figure 6 compares favorably with the data reported by Bragagnolo et. al.

[13]. We do not observe blistering of the SiN:H films caused by the evolution of the hydrogen.

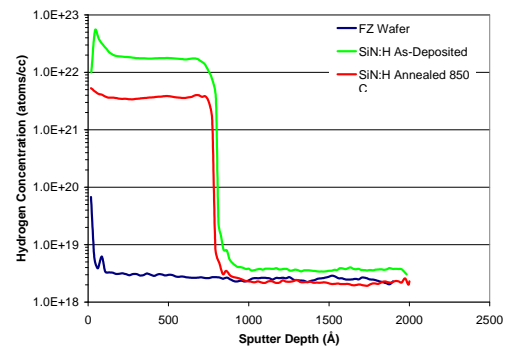


Figure 6. Hydrogen concentration in silicon nitride thin film before and after anneal. The blue line is the base line for the Float Zone wafer coated with the silicon nitride.

3.4 Carrier Recombination Lifetime

Carrier lifetime is strongly influenced by the quality of the interface between the SiN:H thin film and the crystalline Silicon interface. Our films have been measured for lifetime by the resonant couple photoconductivity decay (RCPCD) method developed by Ahrenkiel at NREL. This technique is capable of measuring the transient decay of the carriers over many orders of magnitude of charge injection and lifetime [14]. For analysis of our thin films we have selected a very low level of light injection to enhance the sensitivity of the technique to interface defects. The injection level is adjusted to $24 \mu\text{j}/\text{cm}^2/\text{pulse}$, with a pulse width of 5 nanoseconds and an excitation wavelength of 532 nm giving an injection of 1.9×10^{15} carriers/ cm^3 . Figure 7 shows the lifetime for three different SiN:H thin films deposited on high resistivity FZ wafers.

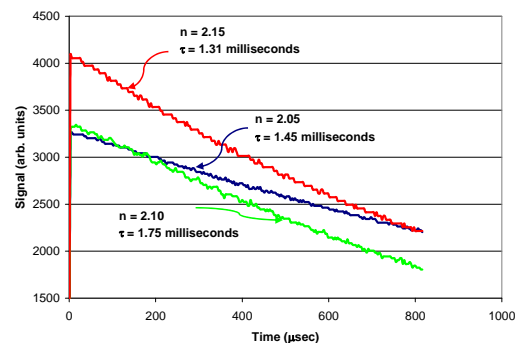


Figure 7. Recombination lifetime for three different SiN:H thin films. Substrates are high resistivity n-type FZ Si wafers. Lifetime measured from the Resonant Coupled Photoconductivity Decay method.

In order to test for the presence of deep level traps or shallow traps we have measured the dependence of the lifetime for one sample over 4 decades of charge injection. As shown in Figure 8 there is no indication of shallow traps or deep level traps up to the Auger recombination limit. This is confirmation that the SiN:H interface quality is excellent.

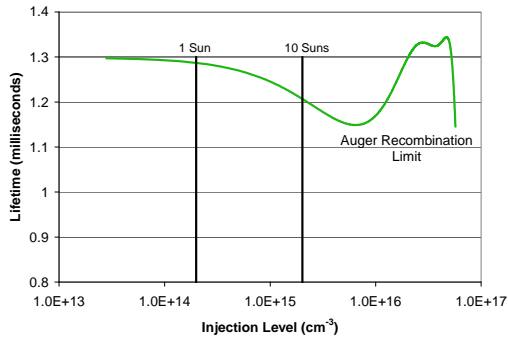


Figure 8 Carrier recombination lifetime measured as a function of the charge injection level up to the Auger recombination limit. The stability of the lifetime over almost four decades of injection indicate the absence of deep level or shallow traps.

3.5 Uniformity, Utilization & Deposition Rates

The new plasma source technology is capable of extremely high deposition rates. We have demonstrated dynamic deposition rates exceeding 150 nm-m/min at a flow rate of silane of 240 sccm for a 400 mm wide source. This rate has been matched with excellent thin film thickness uniformity and optical properties. The thickness uniformity is $\pm 3.4\%$ and uniform film properties are demonstrated by a refractive index at 632.8 nm that varies by an ellipsometer limited resolution of 0.004 over the 300 mm useful source width. Figure 9 shows these impressive results.

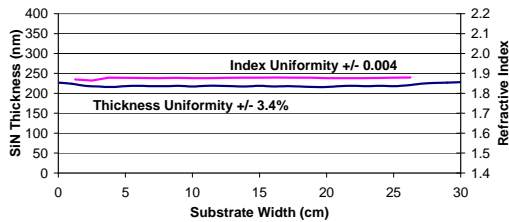


Figure 9. Thickness and index uniformity of SiN:H thin film

Efficient use of the precursor is a key factor in reducing frequency of maintenance. Spurious deposits away from the substrate lead to a build up of coating in the deposition chamber leading to flaking and particle generation. With a precursor utilization in excess of 15% compared to less than 5% for other PECVD technologies, the build up of these spurious deposits is greatly reduced.

The avoidance of coating on the discharge electrodes extends the maintenance period. Electrodes with 50 hours of operational time are shown in Figure 9, as they were pulled from the source.

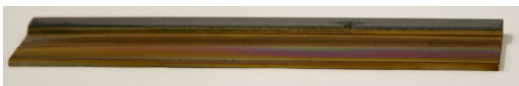


Figure 9. PBS™ discharge cavity electrode pulled from source after 50 hours of operation. Minimal coating build-up on the surface of the electrode.

The absence of coating build-up is due to a plasma source design that permits the precursor being injected external to the discharge cavity. Extended operation of the plasma source is a key element to economical in-line solar cell manufacturing processes.

4. CONCLUSIONS

General Plasma's PBS™ promises to provide a disruptive technology for large area coating of solar cells with hydrogenated silicon nitride thin films. The high throughput advantage, high precursor utilization, reduced maintenance, high carrier lifetimes and uniform thin film properties make this a compelling process technology for the demanding challenges of economical silicon solar cell production.

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