



This item was submitted to Loughborough's Institutional Repository (<https://dspace.lboro.ac.uk/>) by the author and is made available under the following Creative Commons Licence conditions.



**CC creative commons**  
COMMONS DEED

**Attribution-NonCommercial-NoDerivs 2.5**

**You are free:**

- to copy, distribute, display, and perform the work

**Under the following conditions:**

**BY:** **Attribution.** You must attribute the work in the manner specified by the author or licensor.

**Noncommercial.** You may not use this work for commercial purposes.

**No Derivative Works.** You may not alter, transform, or build upon this work.

- For any reuse or distribution, you must make clear to others the license terms of this work.
- Any of these conditions can be waived if you get permission from the copyright holder.

**Your fair use and other rights are in no way affected by the above.**

This is a human-readable summary of the [Legal Code \(the full license\)](#).

[Disclaimer](#) 

For the full text of this licence, please go to:  
<https://creativecommons.org/licenses/by-nc-nd/2.5/>

## SILICON CARBON-NITRIDE ( $\text{SiC}_x\text{N}_y\text{:H}$ ) BY HIGH TARGET UTILISATION SYSTEM (HiTUS) FOR CRYSTALLINE SILICON SOLAR CELL ANTI-REFLECTIVE COATING AND PASSIVATION

P.M.Kaminski<sup>1</sup>, K.Bass<sup>1</sup>, B. Maniscalco<sup>1</sup>, J.M.Walls<sup>1</sup> and G.Claudio<sup>1</sup>

<sup>1</sup>Centre for Renewable Energy Systems Technology (CREST), School of Electronic, Electrical and Systems Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom  
Tel.: +44 (0)1509 635304, Fax: +44 (0)1509 635301, Email: P.M.Kaminski@lboro.ac.uk

**ABSTRACT:**  $\text{SiC}_x\text{N}_y\text{:H}$  films were deposited as anti-reflective (ARC)– passivation layers on crystalline silicon photovoltaics. The thin films were deposited using a remote plasma sputtering system HiTUS (High Target Utilisation Sputtering). The HiTUS allows the deposition of  $\text{SiC}_x\text{N}_y\text{:H}$  avoiding the use of pyrophoric silane precursor. Minority carrier lifetime was monitored, the effective minority carrier lifetime increased up to 40.7  $\mu\text{s}$ , which corresponds to an implied Voc of 640mV. Film roughness and thickness of the films were measured using coherence correlation interferometry (CCI) using a Taylor Hobson “Sunstar”. Deposited films were found to have rms roughness values below 2nm and the film roughness was found to be proportional to passivation quality but inversely proportional to deposition rates. Films were also characterised using Horiba UVISEL spectroscopic ellipsometer, which provided refractive index dispersion. The deposited films exhibited refractive indexes in the range of 2-2.5. Measured deposition rates were in range 1-25nm/min.

Keywords: antireflection coating, deposition, passivation, c-Si,

### 1 INTRODUCTION

With the recent dynamic growth of the Photovoltaic industry, efficiencies of modules are now exceeding 20%[1]. Wafer thickness reduction is one of the strategies for cost improvement of first generation PV. Regardless of the strategy chosen, thickness reduction implies the necessity of improved passivation of the silicon surfaces on both the front and back of the cell[2]. For 100 $\mu\text{m}$  devices the standard aluminium back surface field (Al BSF) is not an efficient way of passivation and a dielectric layer is required. Al BSF provides surface recombination velocity (SRV) of around 1000cm/s[2-3] but this needs to be reduced to at least 300cm/s to maintain the efficiency in these thinner cells.

Silicon Nitride ( $\text{a-SiN}_x\text{:H}$ ) deposited by Plasma Enhanced Vapour Deposition (PECVD) is a standard method of producing coatings for solar cells[4]. The technique delivers films of excellent quality[4,5] providing good ARC and surface passivation. The drawback of the technique is the usage of pyrophoric silane[6]. Sputtering can be an alternative technique for producing the thin film coating for c-Si solar cells[6,7] where silane gas is replaced by a silicon target and less hazardous gases. The HiTUS system was used to deposit thin layers of Silicon Carbon – Nitride films ( $\text{SiC}_x\text{N}_y\text{:H}$ ) for Si ARC.  $\text{SiC}_x\text{N}_y\text{:H}$  deposited by PECVD method has previously been successfully used for c-Si solar cell[8].

### 2 EXPERIMENTAL

The thin film layers of  $\text{SiC}_x\text{N}_y\text{:H}$  were deposited on Si substrates. Cz-Si  $\langle 100 \rangle$  p-type, boron doped photovoltaic grade wafers were used for experiments. Prior to deposition, wafers were saw damaged etched in 10% NaOH solution at 90°C for 5minutes, followed by 15minutes texture etch in NaOH/ isopropyl alcohol (IPA) at 90°C, resulting in a random pyramidal surface texture. After the texturing the wafer was 230 $\mu\text{m}$  thick. The samples were then loaded into  $\text{POCl}_3$  doping furnace where at 850°C phosphorus was diffused in two steps: 5minutes deposition and 15 minutes drive in time resulting in 100 $\Omega/\square$  n-type emitter. Samples were next deglazed by etching in 5% HF to remove phosphosilicate

glass grown during the doping, rinsed in DI water, dried in nitrogen and then loaded into the deposition chamber. Films were deposited also on polished silicon samples for optical characterisation.

Films were deposited using PlasmaQuest HiTUS system by a reactive sputtering process from a mixed silicon/graphite target in an atmosphere of argon, nitrogen and hydrogen. The target was 4” round 99.999% purity p-type polycrystalline silicon, covered by graphite strips(99.999%). The silicon area covered by graphite was varied in the 25-40% range. Other parameters investigated, and optimised, included plasma launch RF power, RF target bias, Ar/N<sub>2</sub>/H<sub>2</sub> gas flow and deposition temperature. A schematic of the deposition system is given in Figure 1. The system has a remote plasma source –a plasma launch source(PLS) where plasma is created by an inductive RF coil powered by 13.64MHz 3kW power supply. The plasma is then directed into the chamber and on to the target by two electromagnets (launch magnet and steering magnet). The configuration of the system ensures that plasma is dense and consists of low energy ions~10eV. In order to initiate sputtering of the target, bias has to be applied with a second RF power supply (1kW, 13.64MHz).

The refractive index and thickness of deposited films was monitored by spectroscopic ellipsometer(Horiba Jobin Yvon UVISEL iHR320FGAS). Surface quality and thickness were measured by coherence correlation interferometry CCI ( Taylor Hobson “Sunstar”). A Varian 5000 UV-Vis-IR spectrophotometer was used to measure reflection from the sample surface. Minority carrier lifetime and implied Voc of deposited samples was tested using Sinton WTC-100 lifetime tester.

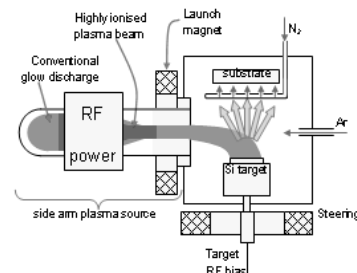


Figure 1 HiTUS schematic[9]

### 3 RESULTS

Deposition conditions were optimised to achieve high effective minority carrier lifetime. Minority carrier lifetime in the range 18-41 $\mu$ s were obtained which compares to 20 $\mu$ s prior to deposition. The optimal conditions found were 2.7kW RF plasma launch power, 0.5kW target bias(RF), 50sccm Ar/10sccm N<sub>2</sub>/4 sccm H<sub>2</sub> atmosphere, 300°C substrate temperature and 25% target coverage by graphite.

Temperature is known to be an essential parameter for depositing high quality thin films and passivation[4,5,7,8]. Influence of the deposition temperature is presented in Figure 1. The minority carrier lifetime at first increased with increased substrate temperature until the threshold value of 300°C where it then decreased.

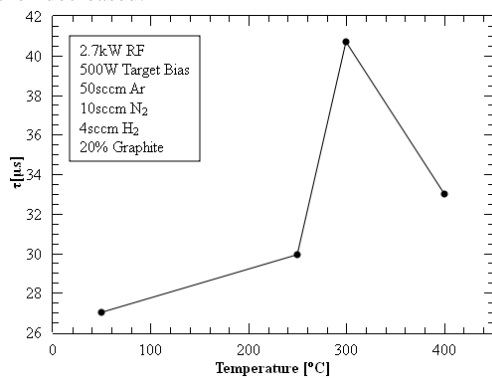


Figure 2 Influence of deposition temperature on minority carrier lifetime

Influence of target bias on minority carrier lifetime and deposition rates is presented in Figure 3. Increasing the target bias resulted in a decrease in minority carrier lifetime but it was found essential to obtain higher deposition rates Table II.

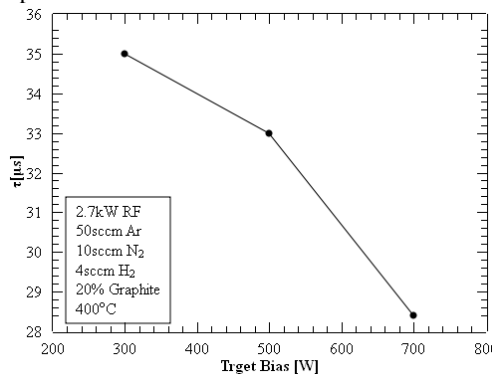


Figure 3 Influence of Target Bias on effective minority carrier lifetime and deposition rates

Hydrogen is known to be important addition to obtain good effective minority carrier lifetime. The effect of hydrogen on minority carrier lifetime is shown in Figure 4. Maximum lifetime was found to occur at 4sccm hydrogen flow. The occurrence of this maximum is also observed for other nitrides such as SiN<sub>x</sub>:H prepared by HiTUS[10] and other methods[7,11]. Passivation of a silicon surface can be obtained by two mechanisms, the reduction of trapping states near the surface and/or repelling charge carriers from the surface by band bending and fixed charge in dielectric layer[12]. The maximum in τ vs. H<sub>2</sub> characteristics is a result of

competition between these two phenomena. The passivation of the silicon surface improves as dangling bonds are passivated by hydrogen atoms and decreases by smaller band bending at Si/dielectric interface as the Fermi level in the dielectric lowers with increased hydrogen concentration[7,11].

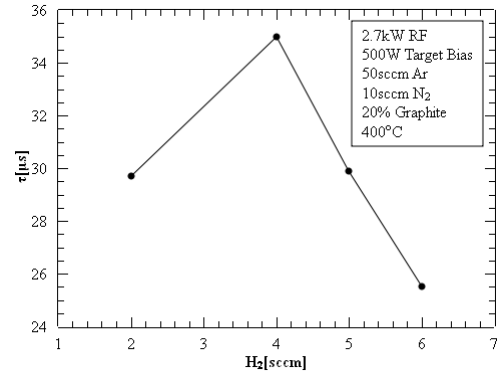


Figure 4 Influence of hydrogen on minority carrier lifetime of deposited films

The main disadvantage of the conditions which gave the highest effective minority carrier lifetime was the low deposition rate of ~1nm/min. A higher deposition rate of ~20nm/min was achieved by altering some of the parameters, viz: 0.9kW Target Bias, 5sccm flow of Nitrogen and without substrate heating. However this led to poorer minority carrier lifetime of 24 $\mu$ s. By optimising the conditions it was possible to obtain good passivation with a deposition rate of 7nm (by increasing the target bias, lowering N<sub>2</sub> flow and increasing the temperature to 400°C). The sputter rate increased with higher target bias. Also increasing the relative amount of Ar<sup>+</sup> ions and lower deposition pressure contributed to an increase in deposition rate[13,14]. When the Si/C sputter rate was increased more atoms arrive at the surface of substrate and hence Si/C adatoms have less time to nitride at the surface of substrate before being incorporated into the film growth[15]. Elevating the temperature of the substrate increases the mobility of adatoms[16]. It seems that increased mobility compensated for the effect of higher sputter rate.

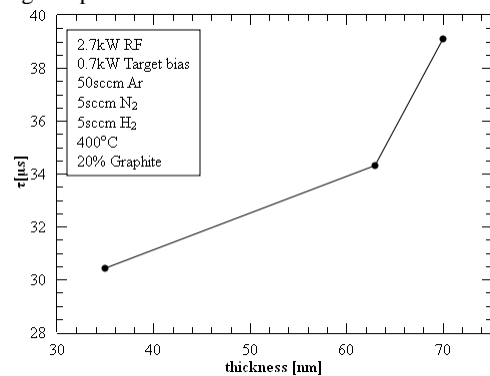


Figure 5 Minority carrier lifetime as a function of film thickness

The effective minority carrier lifetime reached 39 $\mu$ s for 70nm thick film (compared to the 10nm which yielded the 41 $\mu$ s). Influence of minority carrier lifetime with film thickness is given in Figure 5 and it showed that an increase in effective carrier lifetime corresponded with film thickness. Efficiency of surface passivation depends

on film thickness as there is critical thickness for accumulation of fixed charge which repels carriers from surface and decreases recombination[12].

The refractive index of the deposited films varied between 1.9 and 2.5 depending on deposition conditions. For optimised conditions the index was equal to 2 at 550nm with little sensitivity to deposition conditions. The dispersion of the refractive index is plotted in Figure 6. There is no absorption present in the film above 350nm which ensures no loss of light in ARC. The band gap of the film is ~5eV.

Anti reflective properties of  $\text{SiC}_x\text{N}_y\text{:H}$  were tested by depositing ~65nm layer on a textured Si sample. Reflection was measured using a Varian 5000 UV-Vis-IR spectrophotometer. The measured spectrum is plotted in Figure 7. Reflection is reduced below 5% for the spectral range 400-1040nm the minimum of 1.25% at 512nm, indicates that the actual film thickness was ~64nm.

The surface roughness of SiCN films deposited on polished silicon samples was measured using Coherence Correlation Interferometry (CCI) [17]. An example of a surface roughness map is given in Figure 8. Roughness of deposited films was measured for square areas of 0.325 x 0.325mm, using x50 lens. The RMS (root mean square) is expressed as the three-dimensional Sq value and was found to be below 5nm for measured samples.

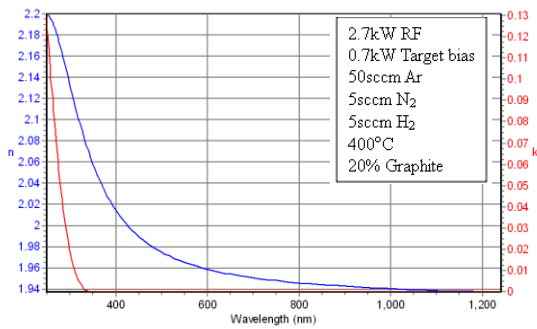


Figure 6 The dispersion of the refractive index

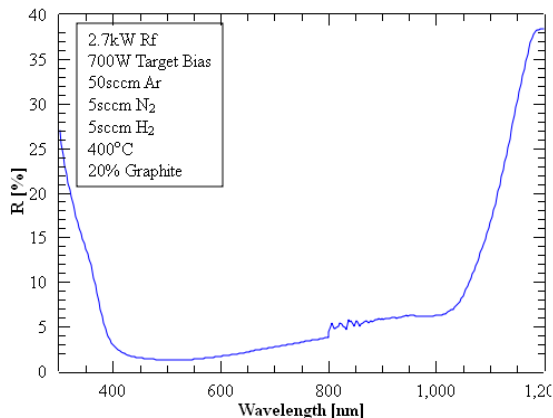


Figure 7 Reflectance from textured Si coated with ~70nm of  $\text{SiC}_x\text{N}_y\text{:H}$ .

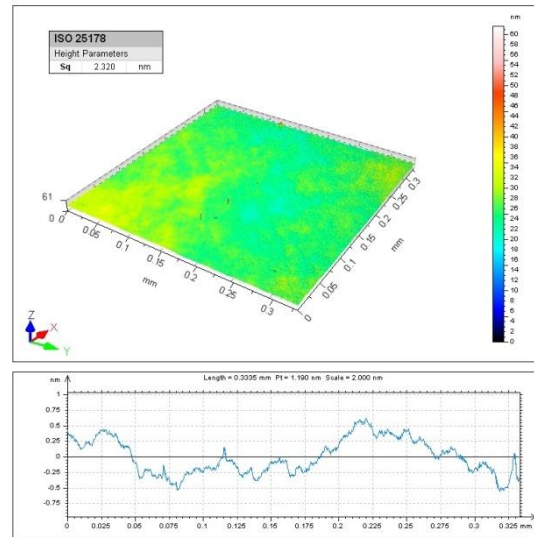


Figure 8 CCI surface roughness map of a deposited  $\text{SiC}_x\text{N}_y\text{:H}$  film

Variation of roughness and deposition rates for films deposited at different temperatures is given in Table I. It was observed that the RMS roughness improved when substrate temperature was increased during the deposition. Also minority carrier lifetime improves with the temperature. The deposition rate decreases with increasing temperature.

Surface roughness and deposition rate measured for different target bias levels are summarised in Table II. The RMS roughness decreases with increased bias level. In both experiments as the roughness improves the minority carrier lifetime also improves and decreases when the deposition rate increases.

Table I Roughness and deposition rate at different temperatures

Deposition Temp.[°C]	RMS roughness[nm]	Deposition rate [nm/min]
No heating	3.015	11.5
200	2.3	11
300	2.85	10.5
400	2.12	7

Table II Roughness and deposition rate at different target bias

Target Bias [W]	RMS roughness[nm]	Deposition rate [nm/min]
500	1.8	5
700	2.12	7
900	3.8	10

Thickness measurements obtained by CCI and ellipsometry are listed in Table III. Both techniques provided very similar results. The small difference may be the result of changes to the measurement spot location. CCI can provide accurate thin film thickness measurements, using a particular approach called ‘helical complex field’ (HCF) [18,19], which is able to extract the thickness through a complex algorithm, depending on the dispersive index of the material. The measurement is very fast and non-destructive.

Table III Thickness of deposited films measured by CCI and ellipsometer

Ellipsometer	Thickness measured [nm]	
	CCI	Difference[%]
69	67	-2.8
49	51	4.0
69	67	-2.8
97	99	3.0
110	116	5.4
105	104.5	-0.5
115	119	3.5

#### 4 SUMMARY

SiCN sputtered films provided effective minority carrier lifetime of 39 $\mu$ s, corresponding to 640mV implied Voc and 325cm/s SRV.

Deposition rates obtained were in 1-20nm/min range. However, for good quality films the deposition rate was 7nm/min rate.

Refractive index was measured to be 2 at 550nm which is the desired value for c-Si cell's ARC. SiC<sub>x</sub>N<sub>y</sub>:H ARC – 64nm thick was deposited on textured Si, the coating reduced reflection below 5% through most of the spectra and minimum reflection of 1.25% at 512 nm.

A new PV characterisation technique, CCI White light coherence interferometry was used to monitor the surface roughness and film thickness. Deposited films were smooth, typically <5nm RMS roughness and as low as 1.3nm for the smoothest films. The RMS roughness changes with deposition temperature and reflected changes in effective minority carrier lifetime.

The temperature increase leads to increased smoothness and minority carrier lifetime.

Target bias decreases minority carrier lifetime but increases deposition rates and roughness of deposited films.

Very good agreement between CCI and ellipsometer was found for thin film thickness measurements.

#### 5 REFERENCES

[1] M.A. Green, Keith Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Prog. Photovolt: Res. Appl. Vol.19 (2011) 565.

[2] L. Janßen, M. Rinio, D. Borchert, H. Windgassen, D. L. Bätzner and H. Kurz, Prog. Photovolt: Res. Appl. Vol. 15 (2007) 469.

[3] J. Dupuis, E. Fourmond, V. Mong-The Yen, O. Nichiporuk, M. Greffioz, N. Le Quang, M. Lemit, Proceedings 24<sup>th</sup> European Photovoltaic Solar Energy Conference (2009).

[4] A.G.Aberle, R.Hezel, Prog. Photovolt: Res. Appl. Vol. 5 (1997) 29.

[5] T. Lauinger, J. Schmidt, A.G. Aberle, R. Hezel, Appl. Phys. A-Mater Vol.68 (1996) 1231.

[6] M. Ruske, J. Liu, S. Wieder, R. Preu, W. Wolke, Proceedings 20<sup>th</sup> European Photovoltaic Solar Energy

Conference (2005) 1470.

[7] M.Vetter, Thin Solid Films Vol.337 (1999) 118.

[8] M. Vetter, I. Martin, A. Orpella, J. Puigdollers, C. Voz, R. Alcubilla, Thin Solid Films Vol.451-452 (2004) 340.

[9] G.Claudio, M. Thwaites, M. Boreland, Proceedings PV-SAT2 (2005) 121.

[10] P.M. Kaminski, K. Bass, G. Claudio, Proceedings PV-SAT7 (2011) 157.

[11] M.Vetter, Mater. Sco. Eng. B, Vol.71 (2000) 321.

[12] A.G. Aberle, Prog. Photovolt: Res. Appl. Vol. 8 (2000) 473.

[13] S. Mahieu, D. Depla, R.d. Gryse, J. Phys. Conf. Ser. Vol.100 (2008) 082003.

[14] H. Lee, G. Kim, S. Hong, K. Lee, Y. Yong, C. Chun, J. Lee, Thin Solid Films Vol. 261 (1995) 148.

[15] J.P Kar, G. Bose, S. Tuli, Scripta Mater. Vol.54 (2006) 1755.

[16] F. Medjani, R. Sanjines, g. Allidi, A. Karimi, Thin Solid Films Vol.515 (2006) 260.

[17] A. Bankhead, I. McDonnell, 'Interferometric Surface Profiling', GB2390676, 2004.

[18] D. Mansfield, Proceedings SPIE vol.6186, 2006.

[19] D. Mansfield, Proceedings SPIE vol.7101, 2008.