

*Full Length Research Paper*

# Sensitivity of thin film nanocrystalline silicon properties to radio frequency plasma-enhanced chemical vapor deposition (rf PECVD) parameters

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**Hydrogenated nanocrystalline silicon (nc-Si:H) films for efficient nc-Si:H solar cells are made at the transition to the nanocrystalline regime during radio frequency plasma-enhanced chemical vapor deposition (rf PECVD). This transition occurs within a sensitive process window and is affected by various deposition parameters. This paper reports an investigation into the material properties of nc-Si:H films as affected by the following rf PECVD parameters: deposition power, deposition pressure, substrate temperature and silane concentration. The aim was to verify the sensitivity of nc-Si:H material properties to rf PECVD parameters. Our results showed that i-layer deposition pressure and the silane concentration mainly affected the blue response of nc-Si:H solar cells. The a-Si:H/nc-Si:H transition can be attained by manipulating any of deposition pressure, deposition power and silane concentration while keeping all other deposition conditions constant.**

**Keywords:** Nanocrystalline, vapor deposition, thin film, parameters.

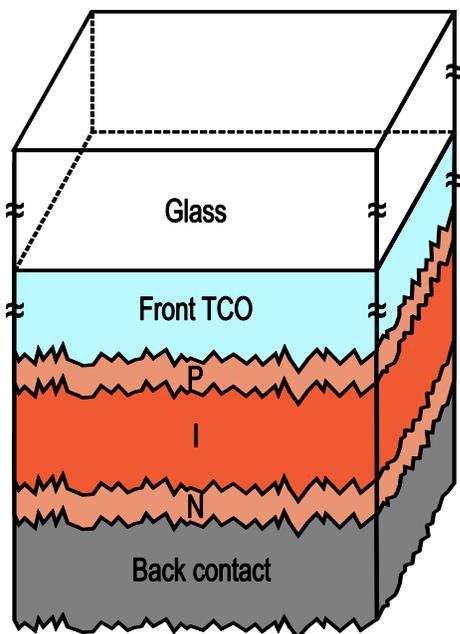
## INTRODUCTION

Solar energy is one of the renewable energy sources that have long been explored for energy generation. The increasing energy demand and the current high crude oil prices have made solar energy an attractive energy option. This energy from the sun is exploited either as heat energy using solar collectors or as electrical energy using solar cells. Hydrogenated nanocrystalline silicon (nc-Si:H) is an interesting solar cell material which was used for the first time in the 90s (Torres et al., 1996; Faraji et al., 1992). One of its main features is its stability against light-induced degradation. Nc-Si:H is applied in the so-called micromorph tandem as bottom cell. In the tandem structure, the band gap of nc-Si:H and that of a-Si:H result in an almost-perfect match for effective utilization of the solar spectrum. Stabilized efficiencies up to 12% have been reported for such double-junction devices (Meier et al., 1994; Green et al., 2011). Thin film nanocrystalline silicon is a complex mixed-phase material;

the makeup of which depends on the deposition conditions. For radio frequency plasma enhanced chemical vapour deposition (rf PECVD) films, the general properties of the films are affected by the deposition conditions.

Key challenges in the current effort towards optimizing and utilizing nc-Si:H include the sensitivity of its properties to defects and to the deposition conditions (Kamei et al., 1998). In conventional rf PECVD, device-quality nc-Si:H is made around the amorphous-to-nanocrystalline transition. This transition regime is usually found within a sensitive process window and is influenced by a number of deposition parameters (Rech et al., 2005). For a variation in any of the deposition parameters, the transition tends to shift, hence making the process difficult to control. For instance, at a constant rf power and deposition pressure, varying the silane concentration affects the transition with the amorphous fraction increasing with increasing silane flow. For depositions at high gas flows, the challenge of flow control and process stability is critical and affects material properties of the film. Deposition parameters such as gas flow ratio, deposition power and deposition pressure have been

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**Figure 1.** Structure of the p-i-n thin film nanocrystalline silicon solar cell as deposited in our rf PECVD set-up. The back contact was a stack of 100 nm thick Ag and 200 nm Al thick layer. P- and N- refer to the p-doped and n-doped layers, respectively.

reported to affect the crystalline mass fraction, and the optical and electrical properties of nc-Si:H (Python et al., 2010; Bugnon et al., 2009; Amanatides et al., 2001; Miyahara et al., 2002). However, not much attention has been paid to how these deposition parameters affect the material properties of films grown at the amorphous-to-nanocrystalline transition. Amorphous-to-nanocrystalline transition is important in nc-Si:H growth because devices with highest performance are believed to be made at this transition (Amanatides et al., 2005).

In this contribution, we reported on the effect of rf PECVD parameters on the material properties of nc-Si:H grown before, at and after the amorphous-to-nanocrystalline transition. We further investigated these effects on the performance of nc-Si:H solar cells.

## EXPERIMENTAL DETAILS

The films whose properties are presented here were deposited using radio frequency plasma enhanced chemical vapor deposition. The procedure followed is as follows: First, the intrinsic nc-Si:H films were deposited using a given deposition condition. Then, one of the deposition variables for example, substrate temperature, is varied such that nc-Si:H of varying properties are deposited. In a similar way, the other deposition parameters were investigated. The following deposition parameters were investigated: silane concentration, deposition power, deposition pressure, and substrate temperature. These parameters were varied such that a wide range of material compositions were obtained. These materials were

grown before the transition, at the transition and after the transition. We compare the properties of these films obtained by a systematic variation of different deposition parameters. We carefully varied a combination of pressure, power, and silane concentration while keeping all the other deposition conditions constant. The deposition pressure varied between 7 to 11 mbar while the deposition power was maintained in between 60 and 100 W. The silane concentration,  $S_c$ , defined as  $[\text{SiH}_4]/([\text{SiH}_4 + [\text{H}_2]])$  (with  $[\text{SiH}_4]$  and  $[\text{H}_2]$  the silane and hydrogen flow, respectively) used to obtain transition material depended on the pressure-power combination and varied between 1.2 and 2.4%. Here, the hydrogen was fixed at 150 sccm while the silane flow varied between 1.8 and 3.7 sccm. In complete nc-Si:H solar cells, the effect of different flow and pressure regime on the solar cell performance were investigated. Typical structure of the nc-Si:H device is as shown in Figure 1.

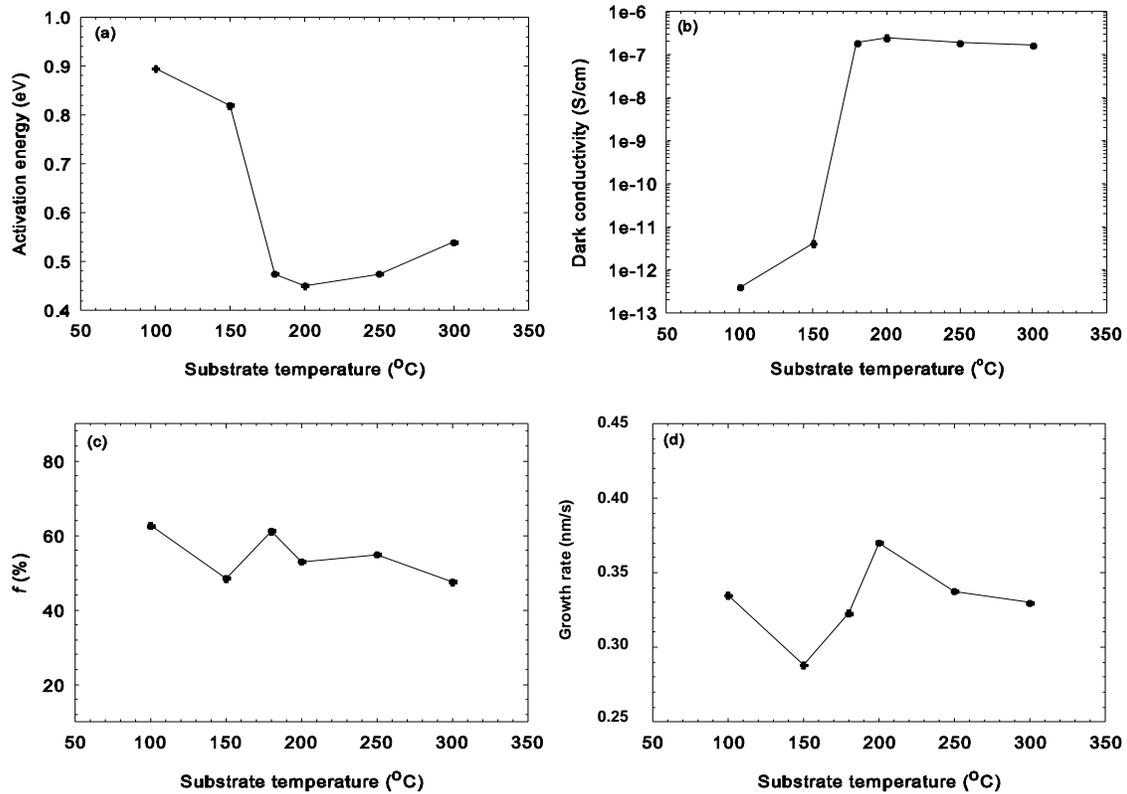
To characterize the films, dark conductivity measurements were taken. For this, 300 nm thick Al bars were deposited on the layers and annealed in oven for 30 min at 130°C in order to secure Ohmic contact. The activation energy of the dark conductivity of the films was obtained from a temperature-dependent measurement of the dark conductivity. The crystalline mass fraction,  $f$  which simply refers to the fraction of the entire mass of the nc-Si:H film that are in the crystalline phase was extracted from the Raman spectroscopy measurement by using the peak-fitting approach to the model of Smit et al. (2003). First, the complete amorphous contribution in the Raman spectrum of nc-Si:H is fitted to three Gaussians in the range from 220 to 480  $\text{cm}^{-1}$ . This amorphous contribution is subtracted afterwards from the Raman spectrum. The crystalline contribution which has only TO peaks at 510 and 520  $\text{cm}^{-1}$  is fitted with two Lorentzian distributions. After subtracting the fitted amorphous part of the film from the spectrum, the cross-sectional area of the crystalline part is divided by the sum of the integrated areas of the crystalline and amorphous parts to obtain  $f$ . The crystalline mass fraction,  $f$ , was chosen as bases for comparison of the transition materials, because nc-Si:H material properties are very sensitive to this fraction (Klein et al., 2005).

The solar cells were characterized by carrying out current-voltage measurements under AM1.5 Oriel illumination and external quantum-efficiency (EQE) measurements. The solar cells had the following structure (Figure 1): 25 nm thick p-type nc-Si:H layer, 1100 nm thick intrinsic nc-Si:H layer, 20 nm n-type a-Si:H layer. ZnO:Al-coated corning glass (E2000) served as the substrate. The ZnO:Al front transparent conductive oxide (TCO) was sputtered in our lab and thereafter a chemical wet etching for 40 s in 0.5% HCl was applied in order to roughen the surface for light scattering. Ag/Al layer was used as the back contact. The solar cells were not annealed before the measurements.

## RESULTS AND DISCUSSION

### Effect of rf PECVD parameters on the properties of nc-Si:H films

In this article, we based our analysis of the effects of i-layer deposition parameters on the following properties: growth rate, crystalline mass fraction, dark conductivity, and activation energy. The deposition parameters were varied such that films spanning from amorphous materials through the transition materials to the nanocrystalline phase materials are obtained. However, the ranges covered in the deposition pressure were limited by the system configuration. The experiments were done with the following as reference deposition parameters: pressure (9 mbar), power (80 W), substrate



**Figure 2.** Effect of substrate temperature on the (a) activation energy; (b) dark conductivity; (c) crystalline mass fraction; and (d) growth rate of intrinsic thin film nc-Si:H.

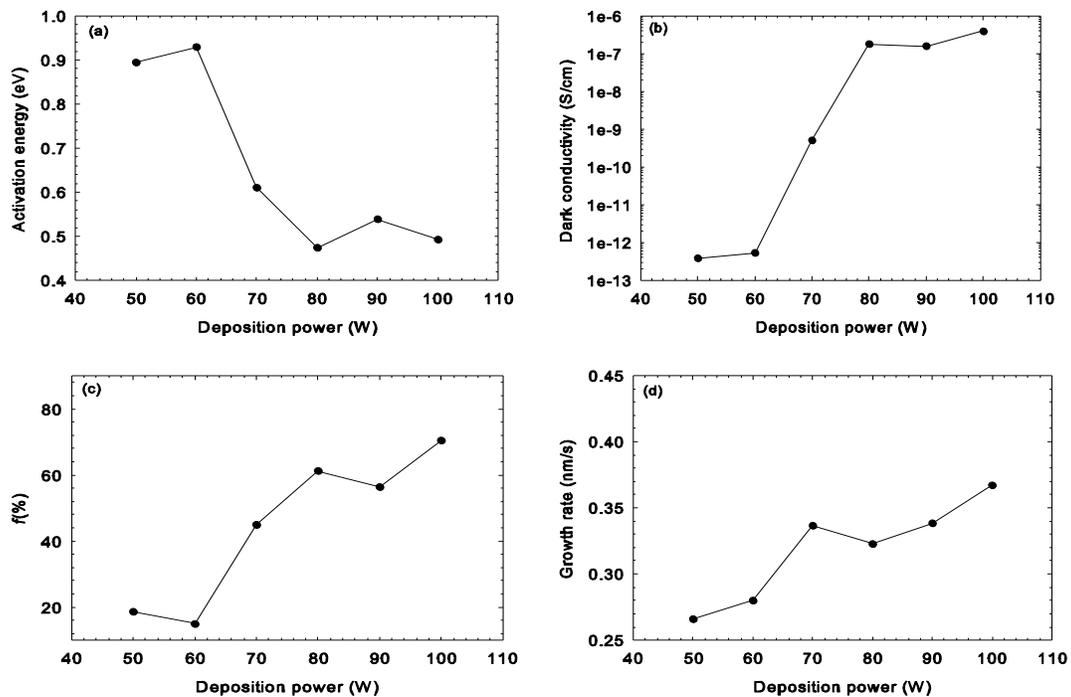
temperature (180 °C), silane concentration (1.32%) and electrode distance (8 mm). In Figure 2, the effect of substrate temperature on the material properties of nc-Si:H is presented. Here, the crystalline mass fraction only slightly decreases with increase in temperature in the range of 100 to 300 °C.

Low effect of substrate temperature on the crystallinity of nc-Si:H has also been previously observed (Miyazaki et al., 1984). Surprisingly, at low deposition temperatures (100 and 150 °C) low dark conductivity and high activation energy values are obtained, typical of a-Si:H. The profile of both the activation energy and the dark conductivity suggest a shift in growth transition from one regime to another in the temperature range of 150 to 180 °C. Within this shift, the  $f$  changes from around 48% at 150 °C to around 62% at 180 °C. We speculate that this electrical effect can be due to a restructuring of the grain arrangement in the film at high temperature. Such restructuring probably re-aligns the crystals such that their surface area of contact is increased hence increasing charge carrier transport path within the material.

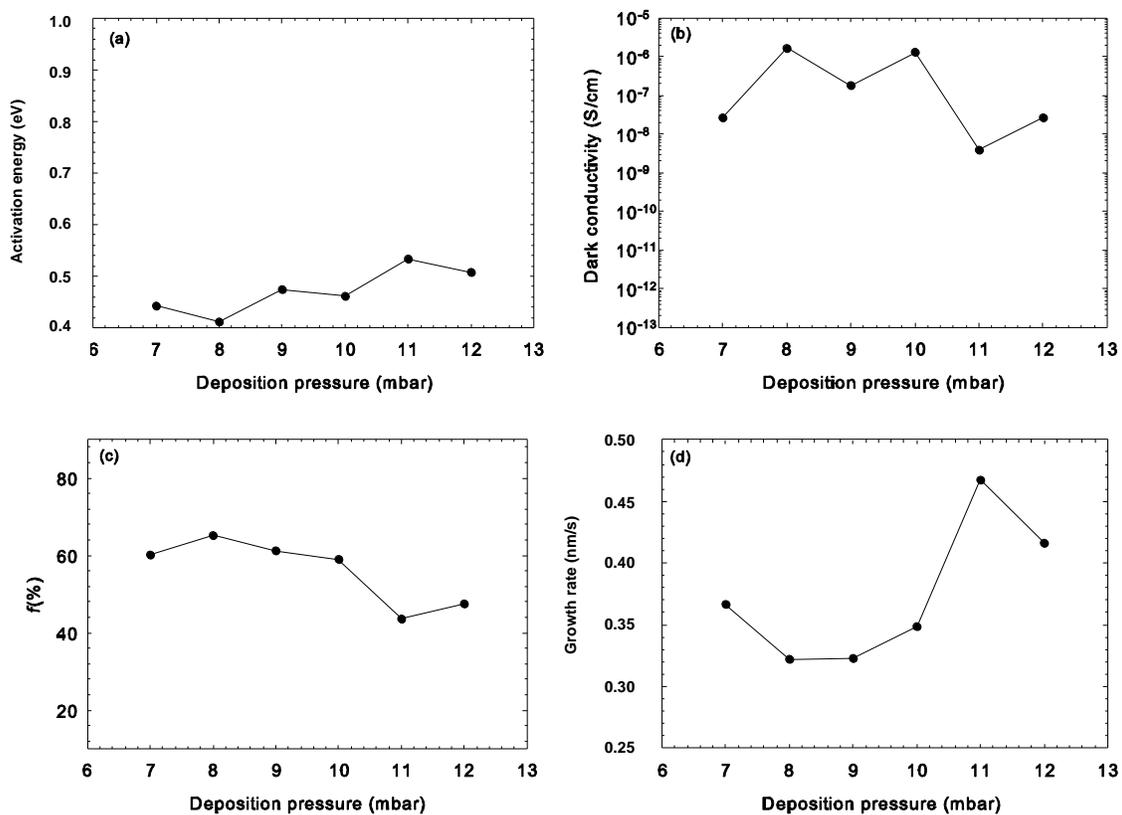
In Figure 3, the activation energy, dark conductivity, crystalline mass fraction, and growth rate are plotted as a function of the deposition power. Increasing the deposition power leads to increase in both the growth rate and  $f$ . As the power increases, the SiH<sub>4</sub> dissociation

rate increases, leading to increased growth rate. This SiH<sub>4</sub> dissociation also releases atomic hydrogen, which is essential for crystal formation (Rath et al., 2006; Matsuda, 2004), and hence increases  $f$ . The growth precursors of nc-Si:H films are generally believed to be SiH<sub>3</sub> radicals, which are formed by the hydrogen abstraction reaction between SiH<sub>4</sub> and H in the plasma (Rath et al., 2006). With increase in deposition power, the activation energy drops as the material becomes more crystalline. Notice that by varying the deposition power between 50 to 100 W, a phase transition takes place from the low (about 19%) to high (above 70%)  $f$ .

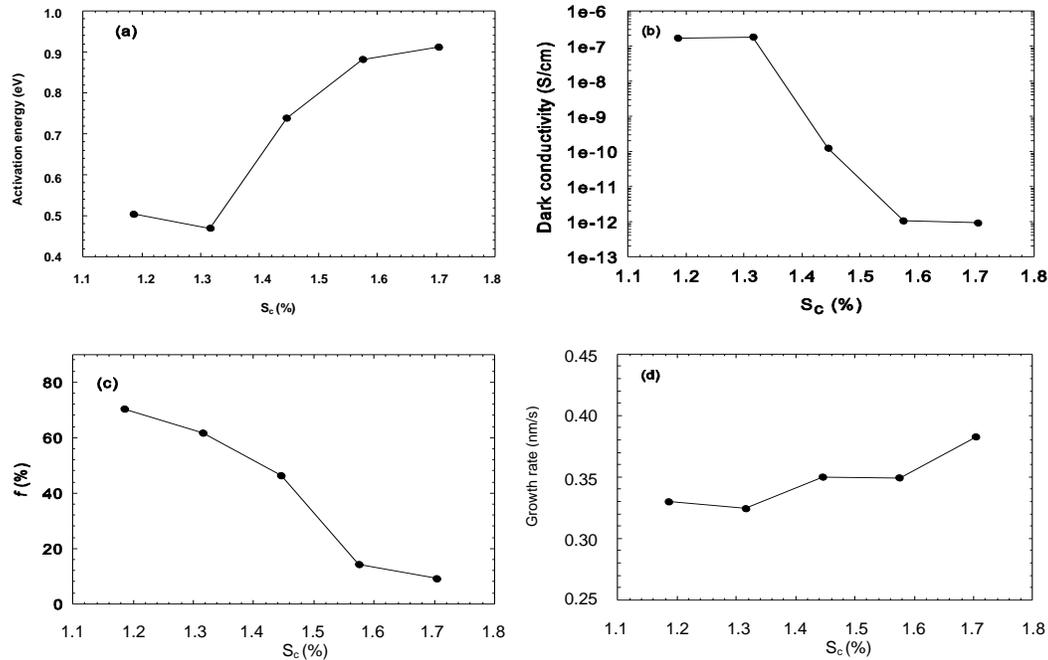
The effect of the deposition pressure on the material properties of nc-Si:H is presented in Figure 4. The growth rate decreases from about 0.37 nm/s at a pressure of 7 mbar to 0.32 nm/s at 9 mbar before increasing again to peak at 11 mbar. The crystalline mass fraction decreases gradually from around 60% at 7 mbar to 44% at 11 mbar. The activation energy changes by 18% in moving from 7 to 11 mbar. With deposition pressure increasing, the atomic hydrogen concentration in the reactor decreases (Mai et al., 2005; Vanderhaghen et al., 2004) thus, the ratio of atomic hydrogen flux to the SiH<sub>3</sub> radical flux also decreases. As a result,  $f$  decreases with increase in deposition pressure. It is noteworthy to observe that through the changes in deposition pressure from 7 to 11



**Figure 3.** Effect of deposition power on the (a) activation energy; (b) dark conductivity; (c) crystalline mass fraction; and (d) growth rate of intrinsic thin film nc-Si:H.



**Figure 4.** Effect of deposition pressure on the (a) activation energy, (b) dark conductivity, (c) crystalline mass fraction, and (d) growth rate of intrinsic thin film nc-Si:H.



**Figure 5.** Effect of silane concentration on the (a) activation energy; (b) dark conductivity; (c) crystalline mass fraction; and (d) growth rate of intrinsic thin film nc-Si:H.

mbar, nc-Si:H materials mainly remained crystalline in composition. The values of activation energy and the dark conductivity further corroborate this. With comparison to Figure 3, we observe that the deposition pressure affects nc-Si:H composition and growth regime less significantly than the deposition power.

Figure 5 shows the effect of  $S_c$  on nc-Si:H material properties. Increasing  $S_c$  implies increasing the amount of silane relative to that of hydrogen in the flow ratio. This reduces the ratio of H atoms to the  $\text{SiH}_3$  radical and in turn favors amorphization, hence  $f$  drops as shown. The values of  $f$  indicate that within the  $S_c$  values covered, various phase materials ranging from amorphous to highly crystalline phase materials are obtained. The growth rate increases from 0.33 nm/s for the highly crystalline film ( $f$  around 70%) to about 0.38 nm/s for the amorphous ( $f$  around 10%). The increase in activation energy from 0.5 eV (for device grade nc-Si:H) to above 0.9 eV (for a-Si:H) with increase in  $S_c$  are in agreement with the changing film composition from the crystalline to amorphous material.

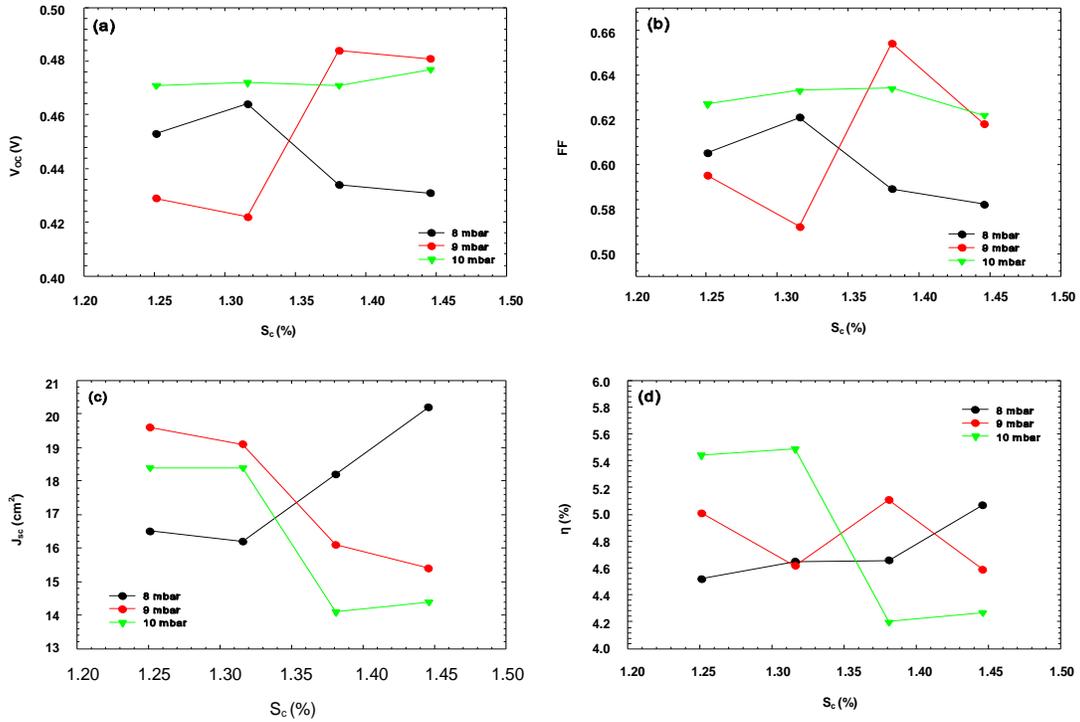
### Effect of rf PECVD parameters on nc-Si:H solar cell performance

Based on the results of the above investigation of rf PECVD parameters effect on nc-Si:H material properties, three series of nc-Si:H solar cells were deposited. The series include one  $S_c$  series for each of 8, 9 and 10 mbar pressure. We limited  $S_c$  to values that will yield nc-Si:H

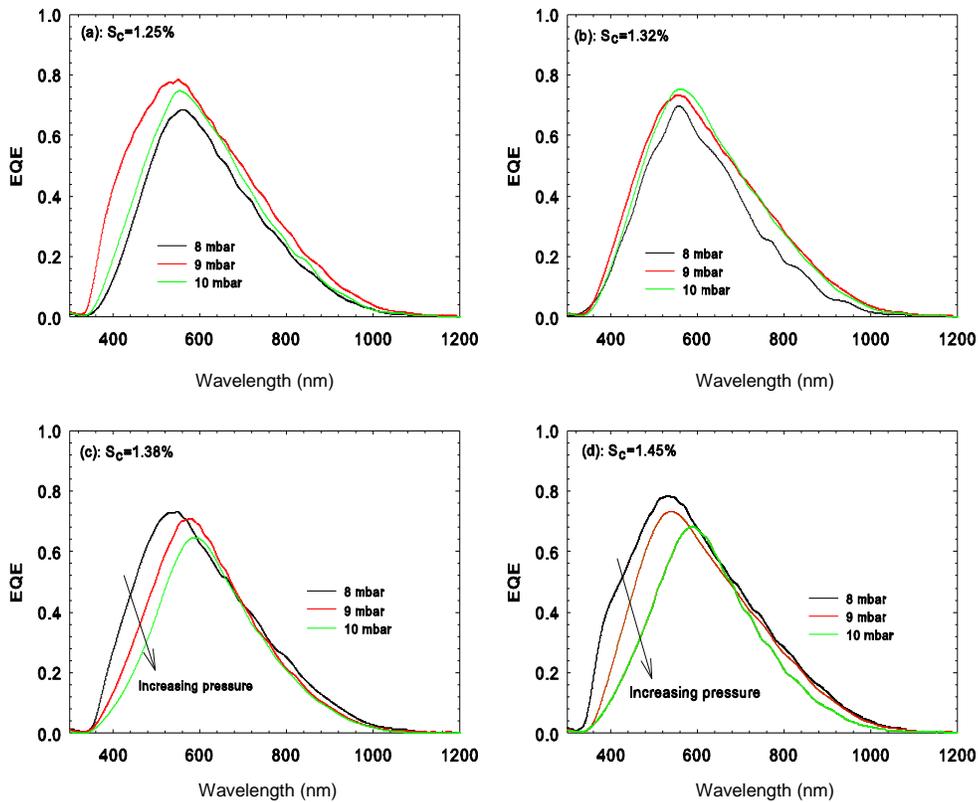
( $f \geq 50\%$ ). For the substrate temperature and deposition power, 180°C and 80 W, respectively were used for i-layer deposition following from the sensitivity study results above. These values are judged to have resulted in material with crystalline mass fraction intermediate between amorphous and nanocrystalline silicon.

Figure 6 shows the external parameters of nc-Si:H solar cells deposited under varying pressure- $S_c$  conditions. We observe that the  $V_{oc}$  varies with  $S_c$  depending on the pressure regime. At 8 mbar, the  $V_{oc}$  drops as  $S_c$  increases while at 9 mbar, the trend is almost reversed. The  $V_{oc}$  for the 10 mbar series indicates no significant dependence on  $S_c$ . A similar trend is also observed for the FF. The  $J_{sc}$  follows an inverse trend to the  $V_{oc}$  for 8 and 9 mbar. At 10 mbar, the  $J_{sc}$  decreases in going to higher  $S_c$ . Increasing  $S_c$  at higher pressure (9 and 10 mbar) leads to lowering of  $J_{sc}$ . This can be linked to the fact that at high pressure, amorphous growth is favored because of the decrease in the atomic hydrogen flux in the plasma (Mai et al., 2005). Overall, the efficiencies of the solar cells (Figure 6d) also fluctuate for the different growth regimes and seem to be mainly affected by  $J_{sc}$  given their similar trend.

In Figure 7, the EQE of all nc-Si:H solar cells deposited at 8, 9, and 10 mbar is presented for different values of  $S_c$ . Here, we observe a strong dependence of the EQE on pressure- $S_c$  combination. At low  $S_c$  (1.25%), increasing pressure from 8 to 9 mbar results in significant increase in the EQE especially around the short wavelength region before dropping significantly again for 10 mbar. At  $S_c$  of 1.32%, a similar but less-pronounced



**Figure 6.** Effect of silane concentration on the (a) open circuit voltage; (b) fill factor; (c) short circuit current density; and (d) efficiency of p-i-n thin film nc-Si:H solar cells.



**Figure 7.** Effect of varying deposition pressure at silane concentration values of (a) 1.25% (b) 1.32% (c) 1.38% and (d) 1.45% on the external quantum efficiency (EQE) of p-i-n thin film nc-Si:H solar cells.

effect of pressure is observed on the EQE. We speculate that at these low  $S_c$  flow values, the process window for the growth of nc-Si:H narrows, hence making process control and stability difficult. The fluctuations in EQE for the different pressure can be related to the fluctuations in the nc-Si:H growth regime at these low flows. At higher silane flow ( $S_c = 1.38$  and  $1.45\%$ ), the effect of deposition pressure is more pronounced and is mainly observed within the blue (short-wavelength) response of the solar cells. At these high silane flow regime, the blue spectral response significantly decreases as the deposition pressure increases. Increase in pressure leads to a drop in the blue spectral response because of the associated amorphous growth which dominates onset of growth and leads to an amorphous-rich and defective p-i interface. Charge carrier extraction losses at this interface results in the low blue response.

## Conclusion

The rf PECVD growth of nc-Si:H have been investigated with particular attention paid to how some selected deposition parameters affect their material properties and the performance of nc-Si:H solar cell. The material properties are strongly dependent on deposition conditions. These material properties include the crystalline mass fraction, the growth rate, activation energy and the dark conductivity and have been shown to be affected by such parameters as deposition power, deposition pressure, substrate temperature, and silane concentration. Each of the various deposition parameters affects the material properties at varying degrees. It has been demonstrated that using any of the above deposition parameters as a deposition variable, it is possible to grow device grade nc-Si:H. Device grade films are made within a sensitive process window. In solar cells, we found that the effect of deposition pressure and silane concentration are mainly manifested at the short wavelength spectral response of nc-Si:H solar cells. Hence, these deposition parameters have dominant effect mainly at the onset of growth.

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