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DEPOSITION PRESSURE AND HYDROGEN DILUTION EFFECTS ON THE SPECTRAL RESPONSE OF THIN FILM NANOCRYSTALLINE SILICON SOLAR CELLS

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The radio frequency plasma enhanced chemical vapor deposition (rf PECVD) is widely used for the growth of thin film nanocrystalline silicon (nc-Si:H) solar cells. The performance of the solar cell is largely affected by the different deposition parameters. It is therefore imperative to optimize growth conditions for different deposition parameters. In this work, we report on the investigation of the effect of hydrogen dilution and the deposition pressure on the performance of nc-Si:H solar cell. These rf PECVD parameters were for the growth of the nc-Si:H absorber layer. The results show that the blue response of the solar cell is sensitive to the hydrogen-to-silane dilution ratio and the deposition pressure of the absorber layer. The long wavelength response is minimally affected. We show that by using a regulated gas flow supply to avert the so-called transient depletion, the blue response is further enhanced.

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1. Introduction

Thin film based solar cells have generally received a lot of attention in recent times and have been considered the most widespread alternative to bulk crystalline solar cell [1]. This is judging from the low cost material consumption and large area deposition at relatively low substrate temperature which allows for the use of cost-effective substrate materials such as glass, stainless steel and plastic [1]-[3]. Bulk mono- and multi-crystalline silicon (c-Si) solar cells which represent the first generation solar cells though still populate the PV market [4], have their cost largely due to the bulk material usage in the production and the cost of other components namely the wafer, the glass cover plate and the encapsulant. A number of other semiconductors such as copper indium gallium diselenide, cadmium telluride, and cadmium sulphide have found application in thin film solar cells. These materials (except crystalline silicon) are characterized by direct energy band gap and consequently high optical absorption resulting in the need for a few microns of material for solar absorption. Materials such as gallium arsenide and indium phosphide and their alloys are still very expensive for large area application.

Thin film amorphous silicon has widely been used as an absorber material in solar cells since its emergence in the mid 70s based on its high absorption coefficient in the visible range of the solar spectrum and low processing temperature hence the possibility of using low cost substrates [3], [5]. The ability to hydrogenate and dope this material resulted in its application in other electronic technologies like transistors, sensors etc. Today, one of the greatest challenges of research and development in thin film amorphous silicon is the Staebler-Wronski effect [6] observed with a-Si:H solar cells. It is the degradation in performance of the cell upon illumination which is attributed to the creation of additional metastable defects acting as trap/recombination centres in the absorber layer [7].

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Research efforts in this regard have geared towards improved understanding of the mechanism of the process in terms of the specific effects of hydrogen dilution, weak Si-Si bonds and Si-H bonds and complexes in the creation of the defects [5] as well as reducing the thickness of the film expected to result from improved light-trapping schemes into the solar cell [8].

Hydrogenated thin film nanocrystalline silicon evolved as an off-shut of research in amorphous silicon. By increasing the hydrogen dilution (for dangling bonds passivation) during deposition, the film growth evolves first from an amorphous layer to the formation of protocrystalline silicon on moderate hydrogen dilution. Increased hydrogen dilution beyond this point leads to transition to the crystalline regime. First, μc-Si:H layers were deposited by Vepřek and Marečeк [9] by a form of plasma deposition and in 1979, Usui and Kikichi [10], [11] doped the first nanocrystalline layer using strongly hydrogen-diluted silane in a plasma-induced microcrystalization at a deposition rate of less than 10^{-12} m/s. The first P-I-N and N-I-P type solar cells of entirely thin film nanocrystalline layers with efficiency above 7% were made at the Neuchatel University in 1996 [12]. Since then, several research efforts [13]-[15] have been put into utilizing and optimizing the inherent advantages of this cell such as its stability against light-induced degradation and the extension of its spectral response to the near infrared light region. nc-Si:Hsolar cells are used as single junction cell and in tandem and triple junction cells where they are particularly used as the bottom cell to collect the less energetic photons transmitted through the top cell and to aid tunnel/recombination junctions that form the connection between individual cells [11]. Being an indirect band gap material, nc-Si:H has a low absorption coefficient in the visible part of the solar spectrum hence requires a relatively thick absorber layer and an efficient light trapping mechanism for sufficient current generation within the solar cell.

For the growth of n-Si:H film, the evolution of the film, the structural and material properties of the film and the growth rate are dependent on a number of deposition conditions and process parameters. Some of these parameters include the total gas flow and the gas dilution ratio, the gas pressure, plasma power, and electrode distance [16]. The film growth evolves first through the amorphous incubation layer, then the nucleation and the subsequent formation of nanocrystals which continues through the amorphous-to-nanocrystalline transition where the best quality films are made into the pure nanocrystalline regime. The total gas flows into the reaction chamber of the deposition system comprises the total volume of silane and hydrogen used for the process. For doping, the relevant dopant gas is introduced. Common trend involves large volume of process gas (mainly high volume of hydrogen and a low volume of silane) which implies a high dilution ratio [$R = \frac{[H_2]}{[SiH_4]}$]. The large hydrogen supply is believed to passivate the dangling bonds and as well etch the growing film surface both of which are pre-requisites for μ-Si:H growth. However, van den Donker *et al* [17] has argued that the high hydrogen dilution is rather necessarily needed for the suppression of silane back diffusion from the reaction chamber into the process zone due to its transient depletion which results in poor material quality. The author has therefore proposed a modification in the start-up process of the film growth as a remedy.

The amorphous to nanocrystalline transition regime is a narrow process window in time and flow scales that depends on a number of deposition variables. Finding this regime has attracted a lot of attention as best solar cells are made here. For each variation in any of the deposition and process parameters the transition tends to shift hence there has not been any defined general parameter values for film growth, instead research groups have optimized their material growth based on the peculiarities of their deposition system. Even though the process stability and the quality of the nc-Si:H films depend on the above parameters, the sensitivity of each of these parameters to the amorphous-to-nanocrystalline growth regime and then the solar cell spectral response has not been well established. As an important feature of hydrogenated nanocrystalline silicon (nc-Si:H) solar cells, the spectral response extends to the long wavelength region (up to 1100 nm). This behaviour has been exploited in tandem solar cells in which a nc-Si:H solar cell is used as the bottom cell in combination with hydrogenated amorphous silicon (a-Si:H) top solar cell for effective utilization of the solar spectrum. The quality of the p-i interface strongly affects the collection of photo-generated carriers in the solar cell, which is particularly visible in the blue response.

The work reported here is an investigation of the short wavelength (blue) response of nc-Si:H solar cells as affected by the deposition parameters during radio frequency plasma enhanced chemical vapour deposition (rf PECVD) of the nc-Si:H absorber layer. Particularly, the deposition pressure and the hydrogen-to-silane ratio were the experimental variables. The so-called transient depletion experiment was carried out to optimize the gains of the hydrogen-to-silane flow and the deposition pressure series. The solar cells were characterized by the spectral response measurement and the current-voltage characteristics.

2. Experimental procedures

In order to investigate the effect of varying the hydrogen-to silane flow ratio of the absorber layer deposition (i.e. silane concentration which in our case is at fixed hydrogen flow and a varying silane flow), a series of P-I-N solar cells were deposited on Corning glass/etched ZnO substrate at a silane flow range: 1.9 – 2.2 sccm at 8 and 9 mbar deposition pressure. For the pressure series, the silane flow was fixed at 2.0 sccm while the pressure was varied between 8 to 10 mbar.

For the transient depletion experiment, the start-up of the conventional rf-PECVD deposition was modified as proposed by [17]. In the conventional rf PECVD, switching on plasma after simultaneous introduction of silane and hydrogen into the process chamber results in the variation of silane concentration in the plasma due to its initial depletion and later back diffusion from the reactor chamber; an effect that is associated with inhomogeneous nc-Si:H film growth. The transient depletion experiment therefore involves circumventing the effect of silane back diffusion by employing a delay between the silane introduction and plasma ignition and/or by profiling the silane supply into the process chamber. In this work, a delay time between 10 – 80 s was used with the deposition pressure and the silane flow fixed at 9 mbar and 2.0 sccm respectively. For all the experiments the rf power, the substrate temperature and the hydrogen flow for the deposition of the absorber layer were respectively maintained at 78 W, 180^{o}C and 150 sccm.

The solar cells were characterized by carrying out quantum efficiency measurements and current-voltage measurement under AM1.5 illumination.

3. Results and discussion

Fig. 1 shows the spectral response as a function of silane flow (SiH_4) at 9 mbar pressure. Varying the silane flow between 1.9 and 2.2 sccm results in shift in the short wavelength response of the solar cell. At 2.1 and 2.2 sccm, the blue response is lower compared to the response at lower values of 1.9 and 2.0 sccm. At 400 nm wavelength, the quantum efficiency of 40 % was obtained as the highest in the flow series. Increase in SiH_4 flow increases the amorphous component which in turn results in increased parasitic absorption and the attendant low blue response which is an indication of the quality of the p-i interface of the solar cell. At much higher SiH_4 flow, the film becomes completely amorphous as the open circuit voltage, V_{oc} of the solar cell exceeds 0.6 V and are therefore not included in this report.

In order to optimize the gains of the earlier flow series, a pressure series of nanocrystalline solar cells were deposited for 8, 9 and 10 mbar pressure at a fixed silane flow of 2.0 sccm. The spectral response as shown in Figure 2 indicates that a pressure change from 10 to 9 mbar shifts the spectral response at 400 nm from 10 to about 40 %. Figure 3 shows the spectral response of the solar cells deposited at 8 mbar pressure for varying silane flow. As indicated, for the entire pressure regime investigated, the spectral response in the blue region of the solar spectrum is more sensitive to the silane flow variation than the long wavelength region. At 8 mbar, the spectral response improves as the silane flow is increased from 2.0 to 2.2 sccm. However, at 2.4 sccm, the spectral response dropped sharply (not shown) as the growth has metamorphosed into the amorphous regime as also indicated by the 0.7 V value of the V_{oc} obtained. This trend is similar to that observed for 9 mbar series as in Figure 2, where the short wavelength spectral response of the solar cell improved progressively as the silane value is reduced from 2.2 to 2.0 sccm. In both cases, the spectral response in the near infra red region show no significant variation with change in both pressure and silane flow. The blue response shows an optimum at 2.2 sccm of silane for depositions at 8 mbar and at a higher pressure of 9 mbar, a lower silane value of 2.0 sccm yielded the best response. The sensitivity of the solar cell to the blue region of the solar spectrum as shown can be attributed to the changes in the evolving amorphous incubation layer near the p-i interface as either or both of deposition pressure and silane flow changes. This interdependence of silane flow and deposition pressure implies that contrary to assertions as in [18] where lower pressures are claimed to result in disordered grain boundaries which induce post-oxidation by impurity diffusion resulting in low current, device quality films can as well be made at lower pressure if the complementing silane flow is optimized.

Figure 4 presents a plot of the V_{oc} as a function of silane flow at 8, 9 and 10 mbar pressure. The V_{oc} also shows a significant sensitivity to the silane flow given the inconsistencies in the trend for the different pressures. This may be due to changes in the crystallinity of the bulk of the absorber material which affects the transport properties of the film as the growth evolves for varying silane flow. Just like in earlier reports by other authors [19], [20], at higher silane concentration, the open circuit voltage seems to improve, however, the short-circuit current drops due to the increasing amorphous component. At each deposition pressure, the solar cell characteristics vary and are optimized for different silane flow.

In figure 5, the fill factor (FF) is shown to follow the same trend as the V_{oc} indicating its sensitivity to silane flow.

In figure 6, the result of the transient depletion experiment is shown as a plot of spectral response for varying delay time between the silane introduction into the process chamber and plasma ignition. The plot indicates a significant increase in the blue response of the solar cell beyond the values obtained for both the pressure and silane flow series. The result shows that at 60 and 70 s delay time, the highest blue spectral response is observed. At 60 s delay, the spectral response at 400 nm was 60 % resulting in 200 A/m^2 short-circuit current for a solar cell of one micrometer thick absorber layer. On further delay after 70 s, the blue response dropped which can mean a mismatch in the timing of the silane back diffusion and the ignition of the plasma. The gains of the transient depletion experiment can be attributed to the relative suppression of the amorphous incubation layer by the experimental approach and the subsequent homogeneous material growth. The amorphous incubation layer parasitically absorbs energy of the blue part of the solar spectrum which should instead be absorbed in the active layer of the solar cell. The initial depletion of silane which affects the start-up growth of the film majorly influences the p-i interface as there is no observable change in the long wavelength region for all the delay time employed.

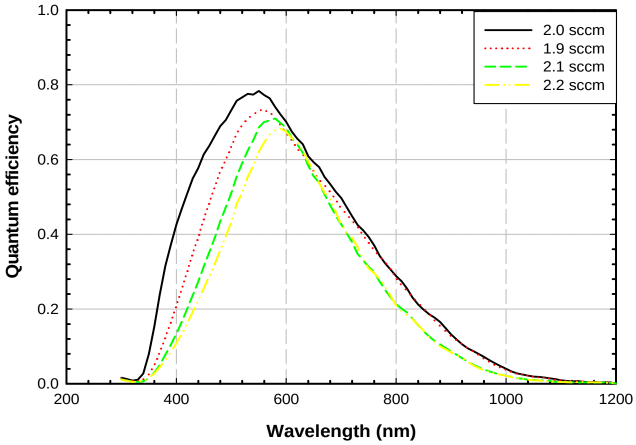

Fig. 1. Spectral response as a function of silane flow at 9 mbar deposition pressure.

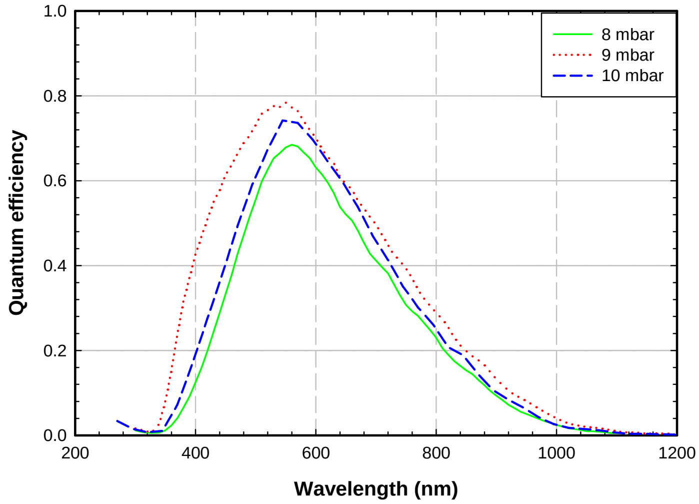

Fig. 2. Spectral response of nc-Si:Hsolar cell as influenced by deposition pressure at fixed silane flow

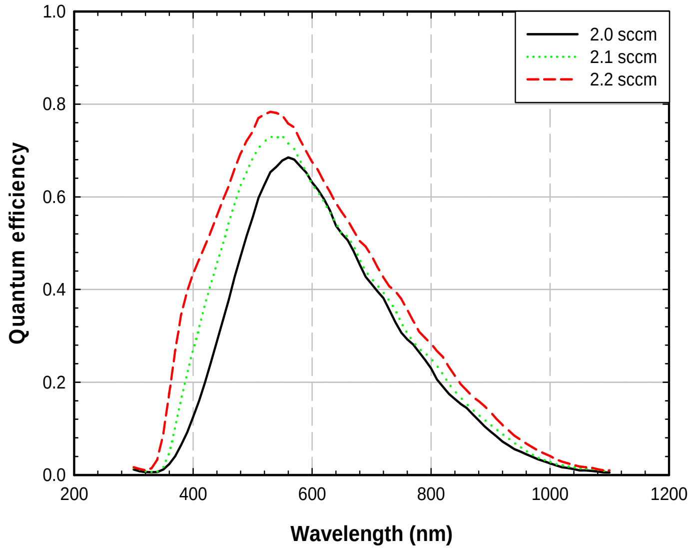

Fig. 3. Spectral response at 8 mbar for 2.0, 2.1 and 2.2 sccm flow of silane.

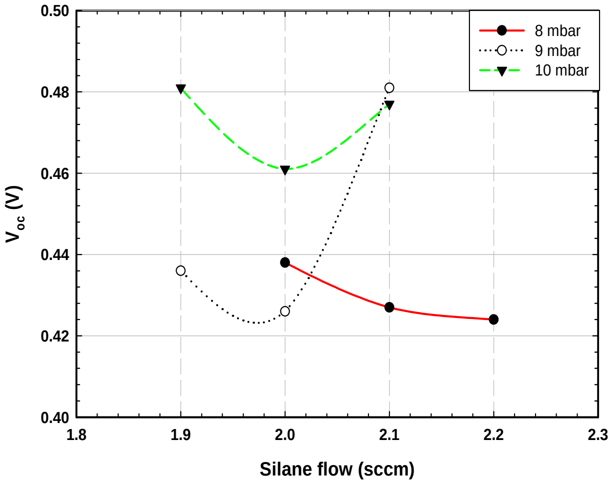

Fig. 4. Indication of variation of Voc with silane flow for different deposition pressure.

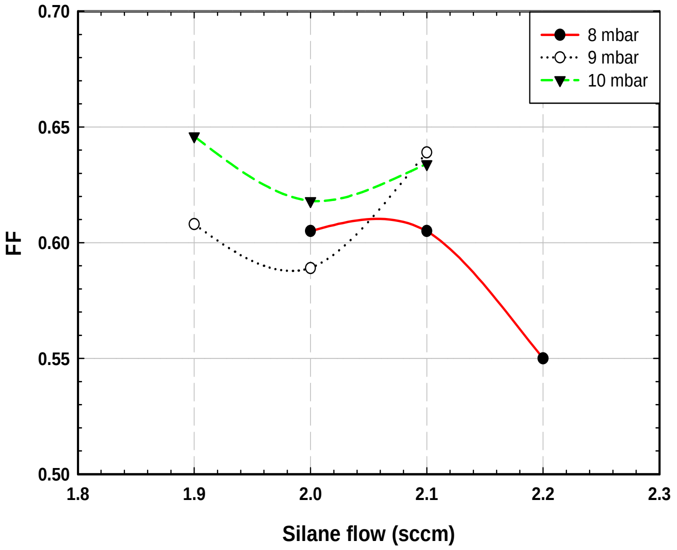

Fig. 5. Variation of FF with silane flow for different deposition pressure.

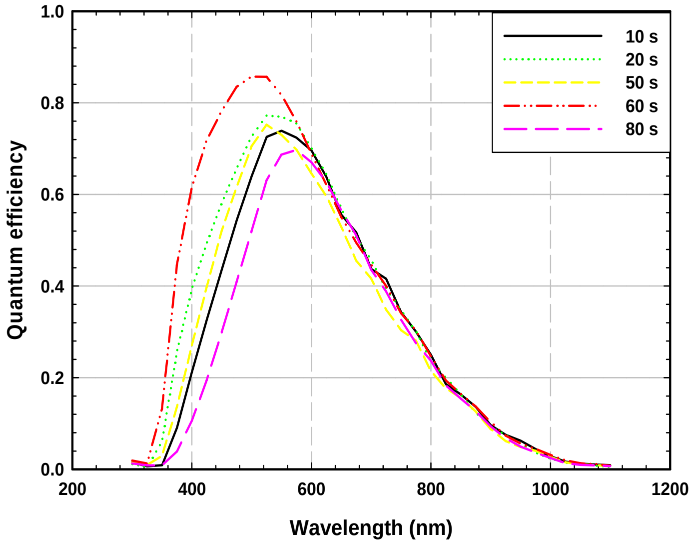

Fig. 6. Result of the transient depletion experiment showing the effects of the delay time on spectral response.

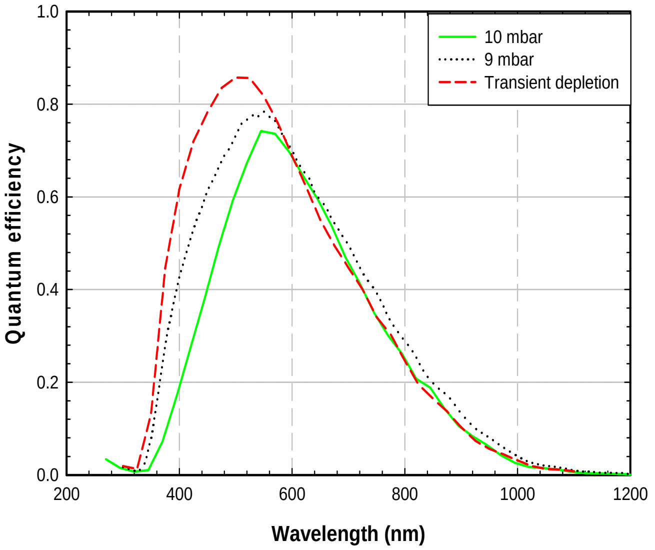

Fig. 7. Comparison of spectral response for deposition at 9 and 10 mbar by conventional RF PECVD and by transient depletion.

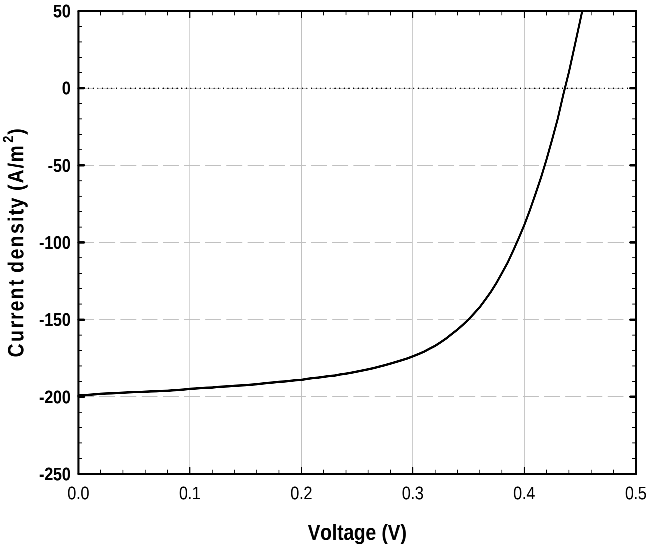

Fig. 8. JV plot of transient depletion solar cell with external parameters as: FF = 0.62, V_{oc} *= 0.44 V,* J_{sc} *= 200 A/m*^{2} *and* η *= 5.5%.*

Fig. 7 shows the progressive gain in the short wavelength response of the solar cell as the different growth approaches are followed. It typically portrays an improvement in the short wavelength response. Adjusting the deposition pressure from 10 to 9 mbar and then following the transient depletion, the spectral response increased from 20 % nm to 60 % at 400 nm. The corresponding JV plot is presented in Fig. 8.

4. Conclusion

The effect of hydrogen dilution and deposition pressure on rf PECVD thin film nanocrystalline silicon solar cell has been investigated. These deposition parameters show their effects mainly at the blue spectral response of the solar cells. A tremendous increase in the blue response has been attained by applying the transient depletion procedure in the deposition of the absorber layer. This enhancement has been attributed to the improved p-i interface owing to the reduced effect of the induced amorphous incubation layer and the inhomogeneous nc-Si:H growth due to silane back diffusion. The deposition pressure and the transient depletion of silane have been shown to particularly affect the spectral response of nc-Si:H solar cell within the short-wavelength region of the solar spectrum as no change in the long wavelength spectral response was observed. At optimum delay time between introduction of silane into the process chamber and ignition of the plasma, the transient depletion effect is suppressed. Over 100 % gain in the spectral response at 400 nm was obtained in adjusting the film growth approach from the conventional rf PECVD to that incorporating transient depletion.

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