

Effect of p-layer properties on nanocrystalline absorber layer and thin film silicon solar cells

Amartya Chowdhury, Koel Adhikary, Sumita Mukhopadhyay and Swati Ray

Energy Research Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

E-mail: ray_swati2004@yahoo.co.in

Received 1 March 2008, in final form 9 May 2008

Published 10 June 2008

Online at stacks.iop.org/JPhysD/41/135104

Abstract

The influence of the p-layer on the crystallinity of the absorber layer and nanocrystalline silicon thin film solar cells has been studied. Boron doped Si : H p-layers of different crystallinities have been prepared under different power pressure conditions using the plasma enhanced chemical vapour deposition method. The crystalline volume fraction of p-layers increases with the increase in deposition power. Optical absorption of the p-layer reduces as the crystalline volume fraction increases. Structural studies at the p/i interface have been done by Raman scattering studies. The crystalline volume fraction of the i-layer increases as that of the p-layer increases, the effect being more prominent near the p/i interface. Grain sizes of the absorber layer decrease from 9.2 to 7.2 nm and the density of crystallites increases as the crystalline volume fraction of the p-layer increases and its grain size decreases. With increasing crystalline volume fraction of the p-layer solar cell efficiency increases.

1. Introduction

Hydrogenated microcrystalline and nanocrystalline silicon solar cells developed by plasma enhanced chemical vapour deposition (PECVD) have attracted greater attention due to their high stabilized efficiency. In the case of a nanocrystalline silicon p-i-n single junction solar cell, the nanocrystalline i-layer (nc-i-layer) is deposited on the nanocrystalline p-layer (nc-p-layer). Therefore, the properties of the nc-i-layer depend on the p-layer properties. On the whole p-layer properties affect the solar cell performances. So in order to improve the efficiency of the solar cell it is necessary to understand the effect of properties of the p-layer on the i-layer and on the solar cell. The increase in i-layer crystalline volume fraction decreases the open circuit voltage and increases the short circuit current. The use of a buffer layer at the p/i interface also improves the performance of a solar cell. Mai *et al* [1, 2] deposited a 100 nm thick interface layer of lower defect density by the hot wire chemical vapour deposition (HWCVD) method and the other layers of a solar cell by the PECVD method and reported improvement in solar cell performance. However, large area homogeneous deposition of such solar cells is complicated.

The effect of the nc-p-layer on the structural and optoelectronic properties of the incubation zone of the absorber layer and the overall effect on the nanocrystalline solar cell have not been studied in detail. In this paper p-layers with different crystallinities have been used as substrates for the i-layer and their effects on i-layer structure and solar cell performance have been studied.

2. Experimental

For the characterization of p-layers, three different boron doped nanocrystalline silicon p-layers and an amorphous silicon-carbon alloy p-layer (P_a) were fabricated on glass substrates by radio frequency PECVD (RF-PECVD) at a different chamber pressures (P_r) and plasma power densities (P_w). The ratio of diborane (B_2H_6), silane (SiH_4) and hydrogen flow rate were kept constant for all the p-layers. The nanocrystalline silicon p-layers were deposited at three different conditions; (1) $P_1 : P_r = 1.4$ Torr, $P_w = 0.1$ W cm⁻², (2) $P_2 : P_r = 3$ Torr, $P_w = 0.25$ W cm⁻² and (3) $P_3 : P_r = 4$ Torr, $P_w = 0.4$ W cm⁻² keeping other conditions fixed. In order to avoid damage in the film, simultaneous increase

Table 1. Properties of thin p-layers.

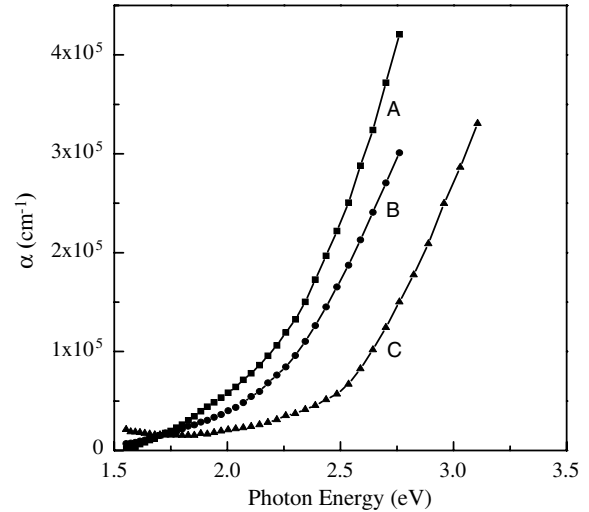
| Sample name | P_w (W cm ⁻²) | P_r (Torr) | X_c (%) | σ_d (S cm ⁻¹) |
|----------------|--------------------------------|-----------------|--------------|-------------------------------------|
| P ₁ | 0.1 | 1.4 | 2.3 | 0.12 |
| P ₂ | 0.25 | 3.0 | 25.2 | 2.44 |
| P ₃ | 0.4 | 4.0 | 40.1 | 4.1 |
| P _a | 0.044 | 1.4 | — | 6.3×10^{-7} |

in power density and pressure has been made. Structural properties of these p-layers were analysed by Raman scattering study, x-ray diffraction study and transmission electron microscopy (TEM). The crystalline volume fraction (X_c) of the films has been investigated by Raman spectroscopy with a 514.5 nm Ar laser. Each of these spectra was deconvoluted into three Gaussian peaks around 520 cm⁻¹, 510 cm⁻¹ and 480 cm⁻¹ corresponding to the crystalline, grain boundary and amorphous components in the films. X_c was calculated from the simplified empirical relation $X_c = (I_c + I_b)/(I_c + I_b + I_a)$, where I_c , I_b and I_a are the integrated intensities of the crystalline, grain boundary and amorphous components, respectively [3,4]. XRD studies were done by Cu K α radiation. The grain sizes of the films were calculated from the full width at half maxima of the (220) peak using Scherrer's formula [5,6]. The film thicknesses were measured by a Dektak type profilometer. Optical absorption coefficients were evaluated using a UV-NIR-VIS spectrophotometer. The dark conductivity (σ_d) was measured in a cryostat under vacuum ($\sim 10^{-6}$ Torr). To study the effect of p-layer on i-layer, i-layers of two different thicknesses (55 and 775 nm) were deposited on these nc-p-layers and an amorphous p-layer. The thicknesses of these p-layers are about 25 nm. The deposition conditions of these nc-i-layers were kept constant. About 80 nm thick p/i samples were taken for Raman scattering study from the sample side and the TEM study. Thick samples were used for XRD study and for Raman scattering study. These thick p/i samples were also deposited on SnO₂ coated glass substrate to simulate the actual p-i-n solar cell structure. Ultimately, p-i-n solar cells were fabricated using these p-layers on SnO₂ coated glass substrates. An aluminium electrode of 1 cm² area was used as a back reflector. The current-voltage characterizations of the solar cells were done under 100 mW cm⁻² AM1.5 illumination at 28 °C.

3. Results and discussions

3.1. Doped layer

Table 1 shows the crystalline volume fraction and dark conductivity of p-type silicon films deposited at different power densities and chamber pressures. The thicknesses of the films are about 40 nm. A minimum X_c of 2.3% is obtained for the P₁ sample deposited at 0.1 W cm⁻². X_c increases to 40.1% as power density and pressure increase to 0.4 W cm⁻² and 4 Torr, respectively for the P₃ film. As X_c of the samples increases dark conductivity also increases. P_a is an amorphous p-layer consisting of silicon and carbon. The conductivity of this film is $\sim 10^{-7}$ S cm⁻¹. The low value of conductivity

**Figure 1.** Variation of optical absorption coefficient with incident photon energy of different p-layers. A: P₁, B: P₂, C: P₃.

may be due to the incorporation of carbon atom in Si:H, which increases the band gap depending on the fraction of carbon and Si-C bond configuration [7]. The nc-Si film is a mixed phase material comprising amorphous and crystalline phases, the films grow initially as a-Si:H and crystallites begin to nucleate from the amorphous phase and evolve as a nanocrystalline film. The values shown in table 1 are for thin p-layer. X_c increases with increase in thickness of the film and saturates after a certain value as reported elsewhere [8]. For application in solar cells, a thin p-layer is used and so structures of ~ 40 nm films have been investigated. In order to study the orientations of nc-p-layers x-ray studies have been performed and films with thickness of 300 nm have been used. A minimum grain size of 6.6 nm is obtained for P₃ film and a maximum grain size of 11.3 nm is obtained for P₁ film. The ion bombardment on the film-forming surface is higher in the former case. Therefore, X_c is higher and the grain size is smaller for P₃ [8]. Usually at higher power density, chamber pressure is kept higher to avoid damage in the film and thus to obtain better film properties [9,10].

Figure 1 shows the variation of the absorption coefficient (α) of p-type nc-Si:H films for incident photons in the energy range from 1.5 to 3.5 eV. The absorption coefficient is higher for the P₁ film than for the P₃ film for $h\nu > 1.7$ eV. This can be correlated with X_c of the films, i.e. the absorption coefficient decreases as the fraction of crystalline volume fraction increases. This also indicates that the response of the solar cell to higher frequency of light will be higher when X_c of the p-layer increases, i.e. absorption of light in the p-layer decreases.

3.2. Absorber layer on p-layer

3.2.1. Raman scattering study. Raman scattering studies have been done to learn the crystalline volume fraction of the i-layer (absorber layer) deposited on the two nc-p-layers P₁, P₃ and the amorphous p-layer P_a. The p/i samples were deposited on glass and TCO substrates. Two sets of p/i samples having different i-layer thicknesses of 55 and 775 nm were deposited

on glass. The thicker p/i layers on glass substrates are studied from the sample side as well as from the glass side. The laser light of wavelength 514.5 nm is used, which can penetrate a depth of about 50 nm in the nanocrystalline silicon film [11]. Figure 2 shows the Raman spectra of the i-layers deposited on different p-layers in the range 420–560 cm^{-1} and table 2 shows the values of X_c .

Raman spectra of thick p/i layers measured from the sample side are shown in figure 2(a). It is observed that X_c of the i-layer increases from 79.8% to 82.4% with increase in deposition power of the p-layer i.e. with increase in X_c of the p-layer. When a-SiC p-layer was used, the X_c of the i-layer is 78.7%. Here X_c of the i-layer increases with the increase in X_c of the p-layer but the variation is not so significant. For the p/i samples deposited on textured SnO_2 coated glass (figure 2(b)) X_c of the i-layer increases from 75.0% to 79.6% for increase in X_c of the p-layer. This shows that X_c decreases by 3–4% when textured SnO_2 coated glass is used in place of Corning glass substrate. The texture of the substrate may cause obstacles in initial crystalline orientation of the nc-Si film growth. Finally, a slight decrease in X_c is observed when textured TCO is used instead of smooth glass as the substrate. As the 514.5 nm laser can penetrate about 50 nm thickness, these values of X_c indicate crystallinities in the bulk of the materials and here X_c does not change with increase in film thickness [12, 13]. So Raman scattering studies have also been done from the substrate (Corning glass) side in order to study the X_c near the interface (figure 2(c)). It is observed that X_c of the i-layer is 37% when deposited on P_1 and it is 62% when deposited on P_3 . It may be mentioned here that X_c of the thin P_3 layer is only 40% (table 1). This shows that near the interface, X_c of the i-layer depends very strongly on the X_c of the p-layer. In the case of a-SiC p-layer X_c is only 5.2% as measured from the glass side. This indicates very little nanocrystalline growth near the interface.

Raman spectra of a thin i-layer (~ 55 nm) on a p-layer (~ 25 nm) were taken from the sample side (figure 2(d)) to confirm the above observations. Here the maximum X_c obtained for the i-layer is 65% when deposited on P_3 and it is 49.5% when deposited on P_1 . In the case of an i-layer deposited on a-SiC p-layer the X_c obtained is 18.5% when measured from the sample side. Compared with the previous case where penetration of laser light was through the p-layer (figure 2(c)), here values of X_c are slightly higher (table 2). It may be mentioned here that X_c of a thin i-layer on glass is 36%. However when it is deposited on an amorphous p-layer it is only 18.5%. It may be noted that X_c is very low when measured from the back side as scattering is from the P_a layer and a portion of initial absorber layer. Thus the observations suggest that X_c of an i-layer near the p/i interface very sensitively depends on the substrate and is highest when a nc-i-layer is deposited on a highly crystalline p-layer.

It may be mentioned here that the total crystalline volume fraction of i-layers deposited on different p-layers is higher than that of a thick i-layer ($X_c = 74.5\%$) deposited on glass. This indicates that X_c of a p-layer still has an effect on an i-layer of about 775 nm thick. It can be noted from the earlier section that the thin P_1 layer has very low crystalline volume fraction.

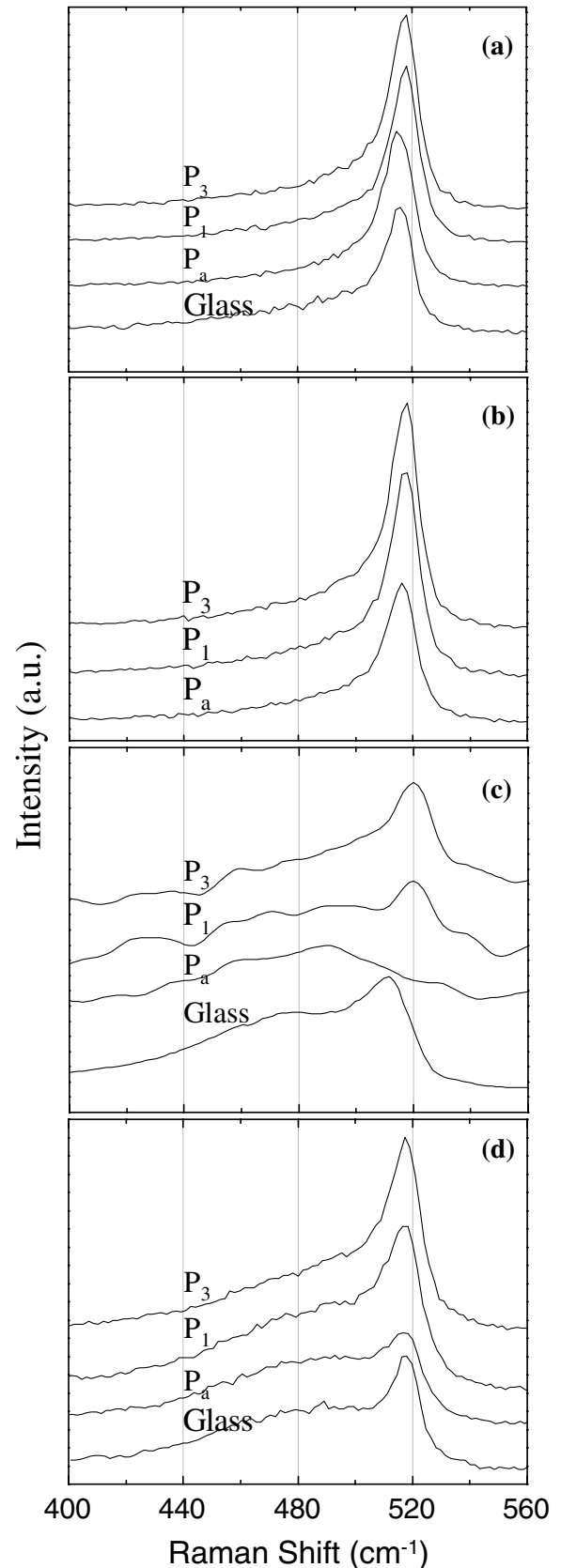
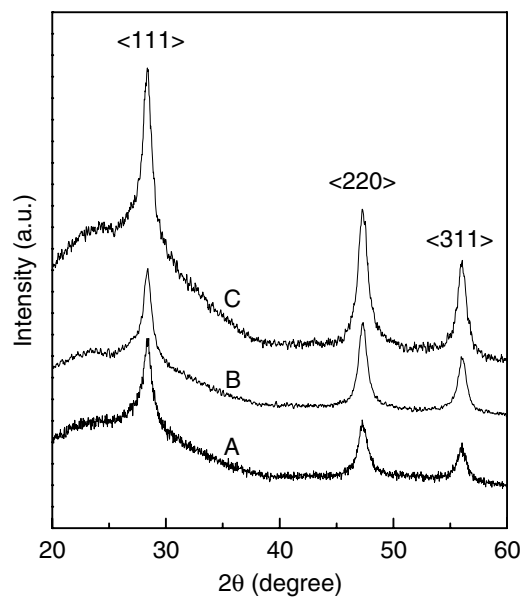


Figure 2. Raman spectra of p/i samples using different p- and i-layers deposited at 54.24 MHz. (a) Thick p/i on glass from the sample side, (b) thick p/i on SnO_2 coated glass from the sample side, (c) thick p/i, studied from the glass side and (d) thin p/i, studied from the sample side.

Table 2. Variation of X_c of the films with thickness and substrate.

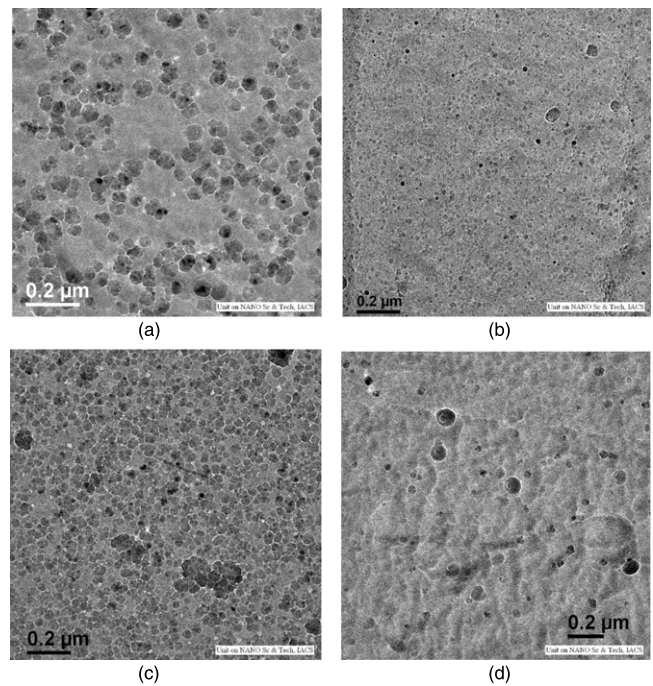
| Substrate specification | X_c (%) | | |
|-------------------------|--------------------------|-------------------------|--------------------------|
| | Thick sample | | Thin sample |
| | Studied from sample side | Studied from glass side | Studied from sample side |
| Glass | 74.5 | 27 | 36 |
| g/P ₃ | 82.4 | 62 | 65 |
| g/P ₁ | 79.8 | 37 | 49.5 |
| g/P _a | 78.7 | 5.2 | 18.5 |
| TCO/P ₃ | 79.6 | — | — |
| TCO/P ₁ | 76.9 | — | — |
| TCO/P _a | 75 | — | — |

**Figure 3.** XRD spectra of i-layers deposited on different p-layers. A: glass/P_a/nc-Si : H, B: glass/P₁/nc-Si : H, C: glass/P₃/nc-Si : H.

However, when thin i-layers are deposited on an amorphous p-layer and on a P₁ layer they have remarkable differences in X_c .

When the Raman scattering studies were performed on thick samples but from the glass side of the sample (figure 2(c)) X_c of i-layer deposited on P_a decreases to 5.2%. This indicates the fact that nanocrystalline growth is absent in the i-layer for about 25 nm from the p/i interface. It is also observed that X_c of the i-layer is 37% when a P₁ layer is used and it is 62% when a P₃ layer is used. X_c is 27% when the i-layer is deposited without a p-layer, i.e. directly on glass. This fact suggests that higher X_c of the P₃ layer has a positive effect on the X_c of the i-layer even if the p-layer is 25 nm thick.

3.2.2. X-ray diffraction study. XRD spectra of thick p/i samples are shown in figure 3. Three orientations of c-Si, i.e. $\langle 111 \rangle$, $\langle 220 \rangle$ and $\langle 311 \rangle$, have been observed irrespective of the X_c of the p-layer. Intensities of the peaks increase slightly as X_c of the p-layer increases. The grain size as calculated from the $\langle 220 \rangle$ peak decreases from 9.2 to 7.2 nm as the P₃ layer is used instead of the P₁ layer. Similar variation is also observed for other orientations. The grain size of the i-layer deposited

**Figure 4.** Transmission electron micrographs of i-layers deposited (a) without p-layer, (b) on P₁, (c) on P₃ and (d) on P_a.

on glass is 10.2 nm (not shown here). So with the increase in X_c of the p-layer the grain sizes of the i-layer decrease. It is also mentioned that X_c of the i-layer increases with increase in X_c of the p-layers. This is possible only if the number density of crystalline grains increases with the increase in X_c of the p-layer.

From Raman scattering study it is observed that X_c of a thick i-layer varies a little when deposited on different p-layers having different X_c as scattering is from the top 50 nm of the film. However, from XRD study it is observed that the intensity of the peaks indicating X_c of samples increases considerably as the X_c of the p-layers increases. This may be due to x-rays penetrating the full depth of the samples and intensity of the peaks indicates average crystalline volume fraction of samples.

3.2.3. Transmission electron microscope study. Figure 4(a) shows the transmission electron micrograph of an i-layer without a p-layer. Many dark spots of about 50 nm diameter are observed in the low resolution TEM image. Orientations of crystalline silicon can be observed inside these dark spots in a high resolution TEM image (not shown here). When an i-layer is deposited on a nanocrystalline P₁ layer (figure 4(b)) the number density of these dark spots significantly increases. The number density of crystallites increases further as more crystalline P₃ layer is used (figure 4(c)). These indicate that the crystalline volume fraction of a thin i-layer increases with that of the p-layer. When an i-layer is deposited on an amorphous p-layer (figure 4(d)) very few of these dark spots are observed indicating a drastic drop of X_c in the film. Raman scattering study of this film revealed only 18.5% crystalline volume fraction.

Table 3. Performance of p-i-n solar cell using different p-layers.

| p-layer | Solar cell performance | | | |
|---------------------------------|------------------------|------------------------------------|------|---------------|
| | V_{oc} (V) | J_{sc} (mA cm ⁻²) | FF | η (%) |
| P ₁ | 0.52 | 19.8 | 0.54 | 5.55 |
| P ₂ | 0.48 | 20.6 | 0.60 | 5.93 |
| P ₃ | 0.45 | 21.8 | 0.64 | 6.28 |
| P ₂ + P ₃ | 0.45 | 22.0 | 0.64 | 6.34 |
| P _a | 0.9 | 9.3 | 0.5 | 4.2 |

3.3. Solar cell

Single junction p-i-n silicon solar cells are fabricated using these different p-layers, nc-i-layer and a phosphorus doped amorphous n-layer. Results are shown in table 3. A maximum solar cell efficiency (η) of 6.3% has been obtained using P₃ layer. High open-circuit voltage (V_{oc}) of 0.9 V has been obtained using an amorphous p-layer and a minimum V_{oc} of 0.45 V has been found when a P₃ layer was used. This variation of V_{oc} of solar cells can be correlated with the change in crystalline volume fraction of p-layers. In nc-Si:H based thin film solar cells the doped layers provide the built-in field and thus are important in determining the open-circuit voltage. The built-in potential depends on the acceptor and donor concentrations in the p- and n-type layers that determine the position of the quasi-Fermi levels relative to the valence and conduction bands of the two layers, respectively. The V_{oc} also depends on the position of these bands relative to those of the intrinsic layer. Therefore, a high V_{oc} of 0.9 V is obtained using an amorphous silicon-carbon alloy p-layer that has an optical band gap of 2.6 eV.

As X_c of p-layers increases, the X_c of the i-layer also increases. Therefore, the short circuit current density increases and maximum short circuit current density (J_{sc}) of 21.8 mA cm⁻² is obtained when the P₃ layer is used. It is also observed that fill factor (FF) increases with increase in X_c of the p-layer. The lowest FF of 0.5 is obtained using carbon doped a-Si p-layer. The P₁ layer also has a very low value of X_c . However, a solar cell fabricated using the P₁ layer shows a higher FF of 0.54. So the drop in FF can be explained by mismatch of band gaps in the p/i interface as the optical band gap of the P_a layer is 2.6 eV and for the i-layer it is below 1.9 eV. Higher values of J_{sc} and FF of solar cells were achieved when the P₃ layer is used instead of the P₁ layer. It can be explained by higher conductivity of the P₃ layer and thinner incubation zone in the i-layer due to the better seeding effect of the p-layer with higher X_c . It is observed that the incubation zone for the crystalline structure of the i-layer is much smaller when the P₃ layer is used. As this portion of the solar cell absorbs a high fraction of incoming photon flux, a less defective structure of the i-layer near the p/i interface improves the short circuit current density. Although the cell on the P₃ layer shows highest efficiency, the cell is sometimes found dead. This may be due to damage of the SnO₂ substrate by high plasma power density.

Short circuit current density, efficiency as well as reproducibility of a solar cell improves further when the p-layer consists of 10 nm thick P₂ layer and 15 nm thick P₃ layer deposited consecutively before i-layer deposition. This may be due to decrease in the damage of the SnO₂ substrate by high plasma power density of 0.4 W cm⁻².

4. Conclusions

At the beginning of nc-i-layer growth, the number density of nucleation centres and the crystalline volume fraction strongly depend on X_c of the p-layer and increase with increase in X_c of the p-layer. Multiple orientations of c-Si have been observed in the i-layer irrespective of the type of p-layer used. The grain sizes of the i-layer slightly decrease as X_c of the p-layer increases. The thickness of the incubation zone in the i-layer near the p/i interface decreases as X_c of the p-layer increases. Electronic properties of the incubation zone in the i-layer have a strong influence on the performance of solar cells. In a p-i-n silicon solar cell J_{sc} and FF improve significantly as X_c of the p-layer improves. The highest efficiency achieved so far with the single junction nanocrystalline silicon solar cell is 6.34% using two p-layers deposited consecutively at low and then at high power densities.

Acknowledgments

The XRD studies have been done under a project entitled 'High resolution x-ray studies' funded by the Department of Science and Technology (DST), Government of India. TEM studies were done under the Nano Science and Technology Initiative programme, DST, Government of India.

References

- [1] Mai Y, Klein S, Carius R, Stiebig H, Geng X and Finger F 2005 *Appl. Phys. Lett.* **87** 073503
- [2] Mai Y, Klein S, Carius R, Stiebig H, Houben L, Geng X and Finger F 2006 *J. Non-Cryst. Solids* **352** 1859
- [3] Houben L, Carius R, Lundszen D, Folsch J, Finger F, Luysberg M and Wagner H 1998 *Phil. Mag.* **A77** 1447
- [4] Chowdhury A, Mukhopadhyay S and Ray S 2007 *J. Cryst. Growth* **304** 352
- [5] Klug H P and Alexander L E 1974 *X-Ray Diffraction Procedures* (New York: Wiley)
- [6] Bardet E, Bouree J E, Cuniot M, Dixmier J, Elkaim P, Le Duigou J, Middy A R and Perrin J 1996 *J. Non-Cryst. Solids* **198–200** 867
- [7] Losurdo M, Giangregorio M, Capezzuto P, Bruno G and Giorgis F 2005 *J. Appl. Phys.* **97** 103504
- [8] Adhikary K and Ray S 2007 *J. Non-Cryst. Solids* **353** 2289
- [9] Kondo M, Fukawa M, Guo L and Matsuda A 2000 *J. Non-Cryst. Solids* **266–269** 84
- [10] Guo L, Kondo M, Fukawa M, Saitoh K and Matsuda A 1998 *Japan. J. Appl. Phys. (Part 2)* **37** L1116
- [11] Danesh P, Pantchev B, Antonova K, Liarakis E, Schmidt B, Grambole D and Baran J 2004 *J. Phys. D: Appl. Phys.* **37** 249
- [12] Cabarrocas P 2000 *J. Non-Cryst. Solids* **266–269** 31
- [13] Cabarrocas P 2002 *Curr. Opin. Solid State Mater. Sci.* **6** 439