Dominant Effect of p/i Interface on Dark J-V Characteristics in p-i-n Nano-crystalline Si Solar Cells

U. Das, A. Bozsa¹ and A. Madan

MVSystems Inc., 17301 West Colfax Ave, Suite 305, Golden, Colorado 80401 USA ¹ Institut für Physikalische Elektronik, Universität Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany

ABSTRACT

Nanocrystalline silicon (nc-Si) based p-i-n solar cells were fabricated onto various substrates using *modified* pulsed PECVD technique. Dark J-V characteristics of nc-Si p-i-n solar cells were found to depend strongly on the substrates and are studied at different i-layer thickness and varying the p/i interface structures. In this work, we report an almost constant diode quality factor (n = 1.2 - 1.3) up to the thickness of $3.8 \,\mu$ m for the devices grown on "suitably textured" ZnO substrates. The rather insensitive variation of n with i-layer thickness suggests that the dark J-V characteristics are not dominated by bulk recombination for the devices grown on textured ZnO, which prevents grain collision in the i-layer. In contrast to that, a significant change of n (1.8 - 1.3) was found while changing the p/i interface using various duration of H₂ plasma treatment of nc-p surface (ST). The p/i interface structure in nc-Si p-i-n device plays the crucial role either by changing the p/i interface defects or the film structure at p/i interface determines the quality of subsequently grown nc-i layer and hence the whole device performance.

INTRODUCTION

The nc-Si:H p-i-n solar cells grown by plasma enhanced chemical vapor deposition (PECVD) / hot wire chemical vapor deposition (HWCVD) techniques have demonstrated device efficiency of > 9% [1,2]. Apart from the structural properties of nc-Si:H films such as the crystal orientation and passivation of grains, oxygen concentration, voids, crystalline fraction etc., there are some other critical issues from a device point of view, such as the minimization of the incubation layer, control of interfaces, effect of texture, etc.

The p/i interface in a superstrate-type (p-i-n) amorphous silicon solar cells plays a crucial role in device performance and has been studied extensively in the past. Its role in nc-Si:H p-i-n type solar cells is even more critical for solar cells. The formation of p/i interface defects due to enhanced boron diffusion into the i-layer was found for p-i-n type nc-Si:H solar cells [3]. The film structure at p/i interface is made more complicated due to an additional fact that the nc-Si:H grown by PECVD technique often starts with an amorphous incubation phase (typically >10 nm), the extent of which sensitively varies with the film growth conditions and on the substrate material. Numerous efforts have been made to reduce / eliminate such an incubation layer for the films deposited on glass by various techniques like layer-by-layer deposition [4], flow modulation methods [5], triode type RF PECVD with high H₂ dilution etc. [6]. From p-i-n device point of view, it is often believed that the nc-p layer with a sufficient amount of crystallinity would serve as a seed layer to facilitate an epitaxial-like growth with no incubation for the overlying nc-i layer. However, our present results exhibit that the nc-i layer starts to grow with an incubation layer even when it is grown on well-crystallized nc-p surface. The usual pulsed PECVD technique was modified (*modified* Pulsed PECVD) for nc-i layer growth, to provide

extra degrees of freedom to manipulate the growth surface reactions, and hence control the initial film growth via altering the density and energy of various radicals (like H, SiH₃ etc.) and ions, which leads to a much improved p/i interface and hence better p-i-n device performances.

EXPERIMENTAL METHODS

Different layers of p-i-n devices were deposited in a commercially available PECVD cluster tool system specifically designed for the thin film semiconductor market and manufactured by MVSystems Inc. We used conventional RF PECVD technique to deposit the doped [nc-p and amorphous (a-) n] layers of p-i-n devices. A proprietary *modified* pulsed PECVD technique was used to deposit nc-Si:H absorber layer in "superstrate" type p-i-n solar cells on ZnO coated Ashai TCO and textured ZnO substrate. The pulsed PECVD technique allows an increase in the electron density during 'ON' cycle, while in the 'OFF' cycle neutralizing the ions responsible for dust formation in the plasma. A H₂ plasma treatment (ST) at p/i interface using *modified* pulsed PECVD method facilitates improved (quick) nucleation of overlying nc-i layer, leading to a better device performance. The crystalline fraction in thin nc-p layer and the film structure at the p/i interface were investigated using UV reflectance spectra. The UV reflectance spectroscopy gives information about the near-surface film structure and hence allows closer examination of the structure of very thin films.

RESULTS AND DISCUSSIONS

Apart from the p/i interface defects and boron in-diffusion in the overlying i-layer, a careful examination of the film structure at the p/i interface is necessary for superstrate type nc-Si:H p-i-n devices. A simple and useful technique to investigate the structure of very thin film is UV reflectance measurement where, additional reflections (at 365 nm and 275 nm) appear due to the presence of any crystalline phase in the film. Such an additional reflectance in nc-Si:H films arise due to the specific values of pseudo dielectric constant of crystalline Si, which is often studied by ellipsometric measurements. The reflectance at such a low wavelength is highly sensitive to the near surface structure and therefore provides structural information for very thin films (~ 30 nm).



Fig. 1: Reflectance spectra of (i) nc-p, (ii) nc-p/7 nm nc-i, (iii) nc-p/ST/7 nm nc-i. Two arrows indicate the location of shoulder in reflection due to crystallinity.

To gain an insight into the structure of the film at p/i interface (initial growth of nc-i layer on fully nucleated nc-p), we studied the reflectance spectra at UV region. The reflectance spectra for (i) nc-p layer, (ii) 7 nm nc-i layer on top of nc-p, (iii) 1 min ST using *modified* pulsed PECVD method of nc-p followed by 7 nm nc-i layer are compared in Fig. 1. The curve (i) in Fig. 1 shows the shoulders in reflectance spectra at 365 nm and 275 nm, which confirms a good crystallinity in nc-p layer (well nucleated). However, 7 nm nc-i layer directly grown on a well-nucleated nc-p surface appear amorphous [curve (ii)]. Even 1 min of ST of nc-p layer results in an elimination of amorphous incubation layer at p/i interface [curve (iii)].

Figure 2 shows the illuminated J-V characteristics of nc-Si:H p-i-n devices with and without ST on nc-p layer. The performance of the device without the ST at p/i interface is very poor with a low fill factor (0.47). However, the FF improved dramatically (0.66) for the device with ST at p/i interface, primarily due to the reduction or elimination of the amorphous incubation layer at the p/i interface as was revealed from the UV reflectance spectra in Fig. 1. Therefore, an overall improvement in the device performance is evident due to the elimination of amorphous incubation layer at p/i interface.

The analysis of dark J-V characteristics provides important information about the quality of nanocrystalline i-layer and the p/i interface. Figure 3 exhibits a typical dark J-V characteristics of a nc-Si:H device with ST using *modified* pulsed PECVD method at the p/i interface. The diode quality factor (*n*) and the dark saturation current density (J_0) were estimated from the shaded region (region "b") of forward voltage in Fig. 3. The dark current density (J_{dark}) under forward voltage (*V*) is given by,

$$\mathbf{J}_{\text{dark}} = \mathbf{J}_0 \left[\exp\left(\frac{eV}{nkT}\right) - 1 \right]$$
(1)

where, e, k, and T are the electronic charge, Boltzmann constant and temperature respectively. The value of diode quality factor, n is 2 if the current is dominated by carrier generation and recombination in the deep localized defects.



Fig. 2: Illuminated I-V curves for nanocrystalline Si p-i-n devices with and without surface treatment at p/i interface.



Fig. 3: Typical dark J-V characterictics for nanocrystalline p-i-n device. The diode quality factor (n) and dark saturation current density (J_0) was estimated from the shaded region (b) in forward voltage.



Fig. 4: Variation of diode quality factor (*n*) and dark saturation current density (J_0) as a function of i-layer thickness for nc-Si:H p-i-n solar cells deposited on three different substrate (20 nm ZnO coated Asahi "U"-type TCO, AIST supplied textured ZnO and MVS developed textured ZnO).

The figure 4 shows the variation of n and J_0 as a function of i-layer thickness of nc-Si:H p-i-n devices grown on three different substrate, namely Asahi "U"-type TCO (coated with 30 nm ZnO to protect SnO_2 from H₂ plasma), AIST ZnO (textured ZnO supplied by AIST, Japan), and MVS ZnO (textured ZnO developed at MVSystems Inc.). Interestingly, we observed that the values of n and J_0 for the devices grown on Asahi "U"-type TCO decreases as the device thickness increase from 0.7 μ m up to 2 μ m. In a previous paper, we argued that the decrease of n for the thicker i-layer is indicative of lower recombination in the bulk and the nc-Si:H material properties is in fact improving with thickness [7,8]. Also, we have shown from the cross sectional TEM picture that the texture of Asahi "U"-type TCO is not optimal for nc-Si:H film growth, because it leads to grain collision and hence a void rich and defective region at the collision area. However, the AIST ZnO and MVS ZnO show a better texturing (the cross sectional TEM picture will be reported elsewhere) with minimum grain collision and results in a higher current from the similar device on TCO. The figure 4 shows an insignificant variation of n and J_0 with device thickness from 0.7 μ m to 3.8 μ m for the device grown on "suitably textured" ZnO substrates. The rather insignificant change in n suggests that the dark J-V characteristics are not dominated by bulk recombination and hence ensures a good nanocrystalline i-layer quality.

On the contrary to the insignificant variation of n with i-layer thickness, a large variation of n values (from 1.8 to 1.2) has been observed with the ST time at p/i interface. Figure 5 shows the variation of open circuit voltage (V_{oc}) and *n* values as a function of ST time at p/i interface. The device without any ST at p/i interface shows a high V_{oc} (>600 mV) and a high n value of 1.8. Such a high Voc may arise due to the fact that the nc-i layer starts to grow with an amorphous incubation layer (which is evident from the UV reflectance spectra as shown in Fig.1) and the subsequent i-layer has less crystallinity in it. The high value of n indicates a defective i-layer quality and/or a very defective p/i interface, which eventually leads to an effective carrier recombination during their transport. Even a short time (30 s) ST at p/i interface improves the light and dark device characteristics dramatically, the value of n reduces from 1.8 to 1.3 and



Fig. 5: Variation of open circuit voltage (V_{oc}) and the diode quality factor (*n*) as a function of surface treatment time at p/i interface for the nc-Si:H p-i-n solar cells deposited on to MVS developed textured ZnO.

remains almost constant up to the ST time of ~ 5 mins. At a longer ST time (6 mins), the Voc drops sharply and n increases significantly, which essentially suggest that a long time ST damages the underlying nc-p layer and affects the device performances. Therefore, the structure and the defect states of p/i interface in nc-Si:H based solar cells dictates the overall device performance. The structure of the film at p/i interface is more critical because it can change the whole i-layer structure and properties. To get a better insight about what is happening in the plasma at the beginning of nc-i layer deposition, we studied optical emission spectroscopy (OES) duirng nc-i layer growth.

Figure 6 shows the ratio (SiH^*/H^*) of 414.2 nm emission peak (due to SiH^{*}) to 656 nm emission peak (due to H^{*}) as a function deposition time. It should be noted that we start the nc-i layer deposition at time, t=0. Interestingly, the OES study shows that when we start the plasma for nc-i layer deposition without ST, the SiH^{*}/H^{*} ratio starts with a high value of 1 and tends to



Fig. 6: Ratio (SiH^*/H^*) of 414.2 nm emission peak (due to SiH^{*}) to 656 nm emission peak (due to H^{*}) observed by OES as a function of deposition time.

stabilize at a value of ~ 0.7 over the deposition time of ~ 250 s. On the contrary, when we start deposition of nc-i layer with ST at p/i interface, the SiH^{*}/H^{*} value starts with a low value of 0.4 and stabilizes at ~ 0.6 in ~ 250 s. Therefore the OES study reveals that there is a basic difference in the plasma conditions and hence the type of radicals and growth precursors at the initial 250 s of nc-i layer growth. Initial high value of SiH^{*}/H^{*} without ST leads to the growth of a-Si:H layer at the p/i interface, which corroborates well with the UV reflectance measurement (Fig.1) and the device performances with and without ST (Fig.2 and Fig.5). Therefore, the ST at p/i interface is a crucial step to achieve a good nucleation and eliminate amorphous incubation layer for nc-i layer, even while it is grown on a well-crystallized and nucleated nc-p layer. We have achieved 8% efficiency in single junction nc-Si:H p-i-n devices by improving p/i interface and optimizing i-layer thickness.

CONCLUSIONS

The p/i interface in a superstrate-type (p-i-n) solar cells is very important and it plays a critical role in nc-Si:H device performance due to the fact that the nc-Si:H films often starts to grow with an amorphous incubation layer. OES studies reveal that nc-i layer starts with a higher ratio of SiH^{*}/H^{*} at the initial stage of nc-i layer growth and leads to an incubation layer. However, a short time H₂ plasma followed by the nc-i layer deposition (addition of SiH₄, without interrupting plasma) prevents initial increase of SiH^{*}/H^{*} ratio and hence the incubation layer.

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