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Single-junction a-Si solar cells with over 13% efficiency

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Abstract

Single junction hydrogenated amorphous silicon solar cells having a high conversion efficiency of 13.2% were developed by combining three approaches. First, a new type of p-layer, such as $(a\text{-}Si/a\text{-}C)_n$ multilayers, was investigated. The high open-circuit voltage was obtained without lowering the short-circuit current and the fill factor. Second, alternately repeating deposition and hydrogen plasma treatment method was applied to the fabrication of an a-SiC or wide gap a-Si:H films for p/i interface layer. High photoconductive and wide bandgap materials were obtained applicable to the p/i buffer layers. Third, the relationships between defect density of films or fill factors of solar cells and hydrogen radical in plasma were investigated. It was suggested that the H^*/SiH^* ratio was an effective parameter to improve the defect and fill factor, and the excess hydrogen radical deteriorated quality of films and cells.

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1. Introduction

Amorphous silicon (a-Si:H) solar cell is a candidate for electric power generators, and has, therefore, been investigated extensively to improve the conversion efficiencies and reliability of the cells. Recently, conversion efficiencies of more than 12.5% have been reported for a-Si single-junction cell [1,2]. To progress the efficiencies of single-junction a-Si solar cells, we mainly have investigated the improvement of film properties of the p-layer, p/i interface layer and i-layer, because their film qualities and the interface properties are most effective to the efficiency of solar cells, which has been simulated by Tasaki et al. [3]. However, it is considered to be difficult to realize these items by optimizing the conventional materials and deposition method.

In this paper, in order to attain an efficiency of more than 13%, the development of a new type of p-layer, such as $(a\text{-}Si/a\text{-}C)_n$, the novel deposition method of p/i interface layer, and i-layer are reported.

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2. Experimental

The deposition system in this paper was a conventional plasma system with a conventional capacitively coupled electrode and the glow discharge was produced by a 13.56 MHz rf power source through a matching network. The novel deposition method of alternately repeating deposition and hydrogen plasma treatment (ADHT) method has been explained in other reports [4,5]. The typical cell structure used in this study was glass/SnO2/p/p-i interface /i/n/metal whose area was 1 cm^2. The p, p/i interface, i, and n layers were fabricated in a separated chamber deposition system. The detailed fabrication conditions of the p and p/i interface layers have been shown in literature [6,7]. The i-layer was deposited from pure Si_2H_6 or SiH_4, whose thickness was about 550 nm. The n-layer was a micro-crystalline silicon that was deposited from a $SiH_4/PH_3/H_2$ mixed gas (thickness about 40 nm). An anti-reflective coating layer, ITO, Ag, and Al were prepared by an electron beam evaporation method. The photovoltaic properties of the solar cells were measured under the insolation of AM-1.5, 100 mW/cm^2 using a solar simulator. Absorption coefficients, reflectance, and transmittance of films were measured by a spectrophotometer. The hydrogen content and hydrogen bonding configuration were estimated by infrared absorption spectroscopy.

3. Results and discussion

3.1. New p-type $(a\text{-}Si/a\text{-}C)_n$ multilayers

We have reported a high conversion efficiency of 12.0% using p-type $(a\text{-}SiC_x/a\text{-}SiC_y)_n$ multilayers [8]. However, it was difficult to reduce the optical absorption loss and to improve the doping efficiency at the same time in the case of conventional a-SiC alloy films. So, we have developed new p-type $(a\text{-}Si/a\text{-}C)_n$ multilayers to control the doping efficiency in the a-Si or a-C layer. The a-Si layers and a-C layers were deposited by a glow discharge method from $SiH_4/B_2H_6/H_2$ and $CH_4/B_2H_6/H_2$ as source gases, respectively. Typical conditions are listed in Table 1. The existence of well-defined layers for periodic $(a\text{-}Si/a\text{-}C)_n$ multilayers was confirmed by X-ray diffraction. The layer spacing determined from the Bragg's

Table 1
Typical condition of p-type $(a\text{-}Si/a\text{-}C)_n$ multilayers

Gas flow rate (cc/min)	SiH_4 3 B_2H_6 0.3	CH_4 17 B_2H_6 3 H_2 12
Pressure (mTorr)	60	180
RF power density (mW/cm^2)	32	45
Deposition time (s)	10	3
T_s (°C)	220	220

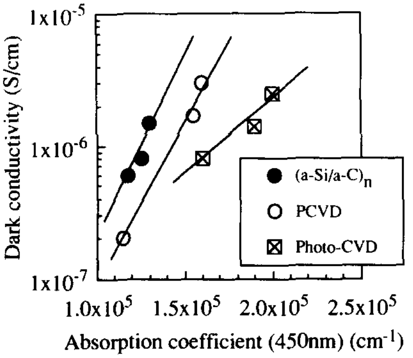

Fig. 1. Dark conductivity plotted against the absorption coefficient for various p-type films.

equation was in agreement with the layer thickness determined from the deposition rates of each layer. The relation between the absorption coefficients (at a wavelength of 450 nm) and the dark conductivities of the resulting films is shown in Fig. 1. The dark conductivities of new p-type multilayers were about five times higher than those of a conventional p-type a-SiC film at the same absorption coefficient. These results show that the new p-type multilayers are more useful to the window layer of solar cells. Fig. 2 shows the dependence of solar cell performance on the cycle number of p-type $(a\text{-}Si/a\text{-}C)_n$ multilayers. Open-circuit voltage and fill factor were improved, as compared with the case of uniform p-type a-SiC layer. Especially, V_{oc} increased with the cycle number of $(a\text{-}Si/a\text{-}C)_n$ multilayer. This is attributed to the increase of the optical bandgap and the lowering of the resistance of the p-layer. Fig. 3 shows the dependence of solar cells performance on the B_2H_6 doping ratio in the a-Si layers. In the case of undoped a-C

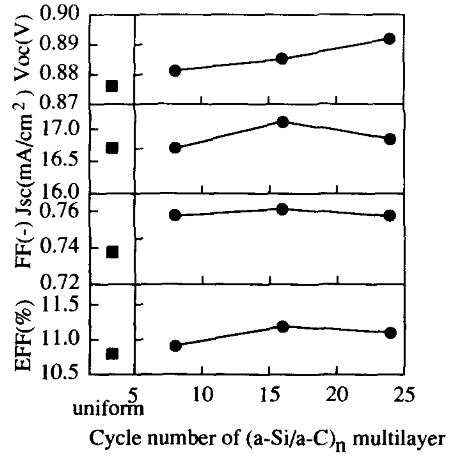

Fig. 2. Dependence of solar cell performance on cycle number of p-type $(a\text{-}Si/a\text{-}C)_n$ multilayers.

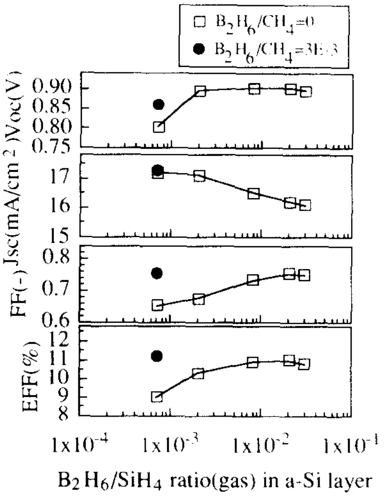

Fig. 3. Dependence of solar cell performance on B_2H_6 doping in a-Si layer of p-type (a-Si/a-C)$_n$ multilayers.

layer, with increasing the B_2H_6 doping ratio, the open-circuit voltage and the fill factor were increased, but the short-circuit current was decreased. However, in the case of very small B_2H_6 doping in a-C layer, a high open-circuit voltage and a high fill factor were obtained without decreasing the short-circuit current. The dependence of the cell characteristics on the diborane doping ratio in the a-C layers is shown in Fig. 4. V_{oc} and FF were increased by slightly diborane doping to a-C layer compared with undoped a-C layer. However, J_{sc} was decreased. From these results, we also found that the doping in a-C layer was very important to improve the cell performance, and the doping level for a-C layer was highly different from the one for a-Si layers. Further, higher open-circuit voltages over 0.93 V were obtained by optimizing boron doping in a-Si and a-C layers, independently. This is attributed to the improvement in the conductivities of these layers with separate optimization of boron doping in each layer. This could be done because the boron level in each layer can be controlled independently by using the (a-Si/a-C)$_n$ multilayers and because there is no intermixing of Si atom and C atom such as in homogeneous p-type a-SiC films.

3.2. Improvement of p / i interface layer properties

Alternately repeating deposition and hydrogen plasma treatment (ADHT method [4,5]) were applied to the p/i interface layers which were a-SiC films or a-Si:H films. The typical preparing conditions and ADHT method of the a-SiC and a-Si:H p/i interface layers are reported elsewhere in detail [6,7]. In the case of a-SiC films prepared by the ADHT method, the absorption coefficients were lowered and the optical bandgaps were increased with the treatment time, while the ratio of $SiH_2/(SiH + SiH_2)$ had a minimum in the range of the particular

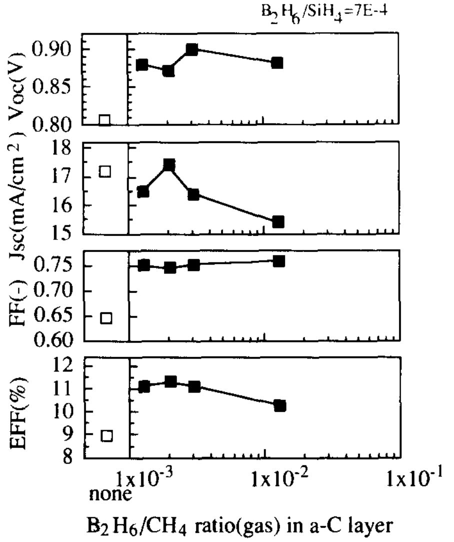

Fig. 4. Dependence of solar cell performance on B_2H_6 doping in a-C layer of p-type (a-Si/a-C)$_n$ multilayers.

treatment time, and then the photoconductivities were improved (shown in Fig. 5). Also, in the case of a-Si:H films deposited by the ADHT method, the bonded hydrogen content increased with the treatment time, and, as a result, the absorp-

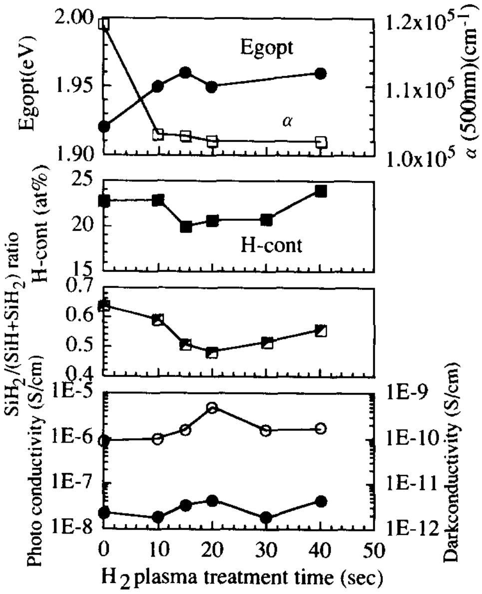

Fig. 5. Film properties as a function of H_2 plasma treatment time.

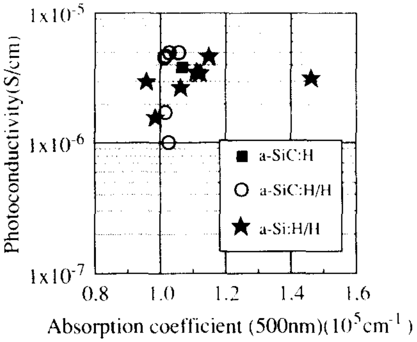

Fig. 6. Photoconductivity plotted against absorption coefficient for various p/i buffer layers.

tion coefficients were lowered and the optical bandgaps were increased. On the other hand, the ratio of $SiH_2/(SiH + SiH_2)$ was slightly increased [6,7]. Concerning various films obtained by these ways, the photoconductivity of these films plotted against the absorption coefficients are shown in Fig. 6, where a-SiC films and a-Si:H films by ADHT method are denoted as a-SiC/H and a-Si:H/H, respectively. The photoconductivities of these films were almost same at the same absorption coefficients. It is clear that by using the ADHT method, hydrogenated amorphous silicon films without carbon were obtained with a wide optical bandgap of more than 1.9 eV and high photoconductivity.

Fig. 7 shows the relationship between $SiH_2/(SiH + SiH_2)$ and the bonded hydrogen content in the films. the ratio of $SiH_2/(SiH + SiH_2)$ increased with the hydrogen content for all kinds of films. However, the ratios of the a-SiC/H(ADHT) films and the conventional a-Si:H films were larger compared to the a-Si:H/H(ADHT) films. So, we had measured the absorption spectra within the bandgap, using CPM (constant photocurrent method) for high quality wide gap a-Si:H/H(ADHT) films containing no carbon atoms and a-SiC/H(ADHT) films. Fig. 8 represents the CPM spectra of a-Si:H/H and a-SiC/H films. The Urbach

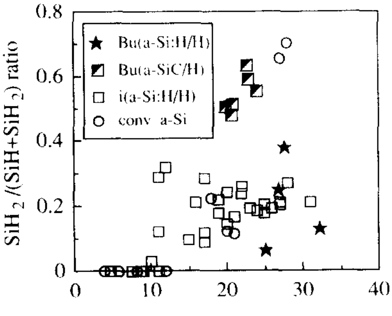

Fig. 7. $SiH_2/(SiH + SiH_2)$ ratio versus hydrogen content.

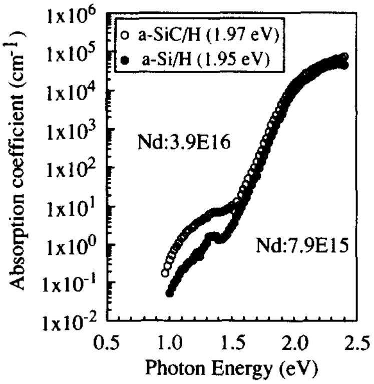

Fig. 8. CPM spectra of wide gap materials for p/i buffer layers.

energies were almost the same, but the absorption coefficient of the a-Si:H/H film was smaller than that of the a-SiC/H film, which suggests that a-Si:H/H films have a low defect density compared to the a-SiC/H films. This suggests that the density of state within the bandgap for a-Si:H/H films is smaller than that of a-Si alloy containing hetero-atoms of carbon. Fig. 9 shows the solar cell characteristics as a function of the hydrogen plasma treatment time for the a-Si solar cells used a-SiC/H films or a-Si:H/H films as a p/i interface layer. The open-circuit voltage and the short-circuit current were initially increased corresponding to the dependence of the optical bandgap, photoconductivity, and hydrogen bonding configuration on the treatment time. However, at longer time of hydrogen plasma

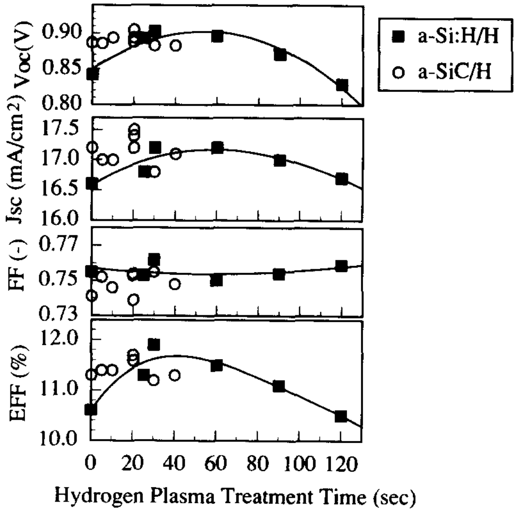

Fig. 9. Cell performance versus H_2 plasma treatment time for cell with buffer layer of a-Si:H/H and a-SiC/H film.

treatment, the open-circuit voltage and the short-circuit current were fallen down remarkably, which was not consistent with the tendency of the films properties. These are due to damage of the p-layer and the p/i interface properties by hydrogen radical treatment, which is thought to create the defect in the films and interface of p-layer and i-layer. The fill factor of cells with a-Si : H/H p/i interface layer were slightly larger than that of cells with a-SiC/H p/i interface layer. This arises from the low defect density of a-Si : H/H films. These results suggest that the alternately repeating deposition and hydrogen plasma treatment (ADHT) method is effective to improve not only the film properties, but also the solar cell performances.

3.3. Improvement of intrinsic a-Si layer

The efficiency of a-Si single junction solar cells is primarily determined by the quality of the intrinsic a-Si layer. So, we have investigated the deposition process and the system to improve the i-layer film quality and fill factor of solar cells [9]. In this section, we focus on the correlation between the hydrogen radical in plasma for a-Si deposition and the defect density of films or fill factors of solar cells. Fig. 10 shows the relationship between the intensity ratio of the emissive species of hydrogen (H*) and monohydride (SiH*), and the space charge density (N_d) in the films and fill factor of solar cells. The space charge density was measured from low frequency C–V characteristic of Au/a-Si/n$^+$ c-Si/Al type Schottky barrier diodes. N_d, which was correlative with defect density of near the Fermi level, had strong relation to the ratio of H*/SiH*. The H* emission intensity is equivalent to the hydrogen radical flux reached to the a-Si film growing surface and the SiH* emission intensity is related to the Si related radical density, namely the a-Si deposition rate. It appeared that excess hydrogen radicals induced the defect in the a-Si films and the hydrogen radical flux per Si deposition rate is a key factor for suppressing the defect in the films. The relationship between H*/SiH* emission intensity ratio and fill factor of solar cells was similar to the case of space charge density, as indicated in Fig. 10. So, it is found that the hydrogen radical is

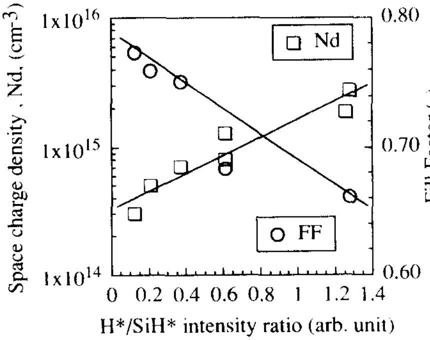

Fig. 10. Relationship between H*/SiH* intensity ratio and space charge density and fill factor.

important for improving the fill factor of cells, which depends on the defect density of a-Si films, and excess hydrogen radical lowers the cell performance. Moreover, to clarify the role of hydrogen radicals to solar cell performance, the hydrogen addition effect to the characteristics of a-Si solar cells with intrinsic a-Si layer deposited at various substrate temperatures was investigated. The results are shown in Fig. 11, which indicates the dependence of a-Si solar cells performance on deposition temperature with and without hydrogen gas addition. From this experiment, at a range of lower temperature, FF of a-Si solar cells with H_2 addition was higher than that of cells without H_2 addition. On the other hand, in the case of no H_2 addition, higher fill factors were obtained in the region of higher temperature. These results were supported by the results of the dependence of the fill factor on the deposition rate of the i-layer, where i-layers of a-Si solar cells were deposited by various hydrogen gas flow rates and at lower substrate temperatures (under 100°C). These resulted that the fill factors were improved by the addition of H_2, but there was the optimum H_2 addition ratio. These suggest that the energy transfer from hydrogen radical to Si growing surface or the reaction of hydrogen radical with Si atoms at growing surface (the interaction between the hydrogen radical and silicon growing surface) caused the relaxation or the restructuring of a-Si network at growing surface, at lower temperature. As a result, defects in the films were suppressed and fill factors were increased. However, the interaction of the excess hydrogen radical had created defects at the Si growing surface. Accordingly, lowering the deposition temperature and rf power density for glow discharge of deposition of intrinsic a-Si layer were investigated to improve the fill factor. The aim of lowering the temperature was the suppression of the hydrogen radical effect to the properties of deposited films, and of thermal damage to p-layer, p/i interface layer and interfacial properties such as p/i and

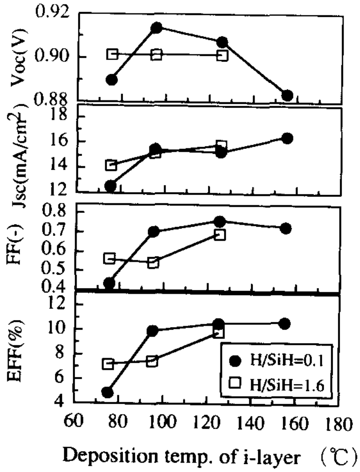

Fig. 11. Cell performance as a function of substrate temperature of i-layer for pure and H_2 dilution deposition.

TCO/p-layer interface. Also, the object of lowering the rf power density was the depreciation of hydrogen radicals occurred in the glow discharge. To establish these aims, we had used disilane (Si_2H_6) as a source gas for a-Si deposition. Fig. 12 shows that the dependence of the performance of a-Si solar cells on the substrate temperature at three kinds of rf power densities. The open-circuit voltage was increased with decreasing temperature and was almost the same at same temperature, not depending on the rf power density. As for short-circuit current, the complicated behavior was explained as follows. For the case of high rf power density (24 mW/cm^2), the remarked decrease of J_{sc} is observed with decreasing temperature. For the medium power density (16 mW/cm^2), high J_{sc} is sustained in the wide range and for the lower power density (11 mW/cm^2), drop of J_{sc} in the higher temperature is large. The tendency for higher rf power density is thought to be because the relaxation of Si network is not accomplished enough at lower temperatures due to the higher deposition rate, so that a-Si films have wide bandgap and higher defect density, resulting in low J_{sc} and FF. Therefore, the optimum temperature for obtaining high efficiency is higher. For lower power density, the exposure time of process temperature during i-layer deposition is longer than for higher power density because of lower deposition rate. So, the heat stress damages the p-layer, p/i interface layer and i-layer during the i-layer deposition, and, consequently, the defect in the cell is created. Therefore, the performance of solar cells is constant at lower temperature and has remarked decline at higher temperature. Accordingly, the optimum temperature for getting the high efficiency could be decreased by 30° by lowering the rf power density.

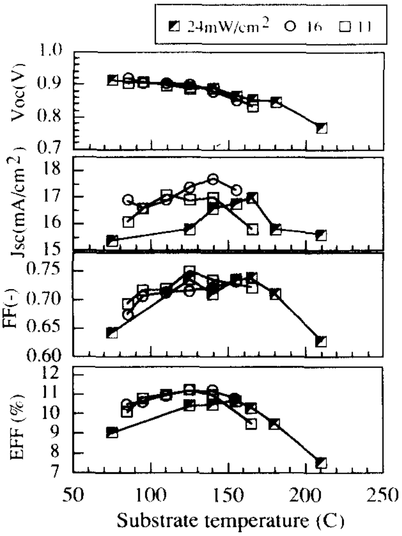

Fig. 12. Temperature dependence of a-Si solar cells with i-layer using disilane for various rf power densities.

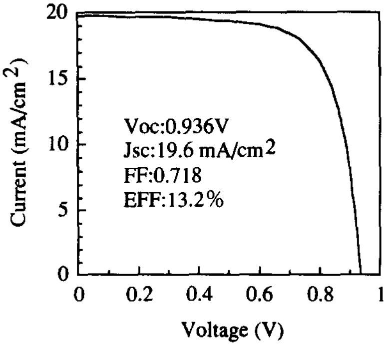

Fig. 13. $I-V$ characteristics of single-junction a-Si solar cell with p-type (a-Si/a-C)$_n$ multilayers and p/i buffer layer of ADHT a-SiC/H film.

It is recognized that the high performance of a-Si solar cells were obtained by the use of disilane and lower rf power density at lower temperature, and the optimum temperature could be lowered. These are attributed to the decrease in deposition rate and the lowering of hydrogen radicals in plasma by use of lower rf power density and disilane as a source gas.

Combining the high reflection back electrode such as ITO/Ag double layer [10], i/n interface layer [9], highly textured SnO2, anti reflection multicoating on glass surface to the above mentioned materials and technology, a high conversion efficiency of 13.2% was obtained for the solar cell structure of ARC/glass/texture SnO_2/p-type (a-Si/a-C)$_n$ multilayers/p-i interface ADHT a-SiC layer/i-layer/i-n interface layer/ITO/Ag (Fig. 13).

4. Conclusion

To improve the conversion efficiencies of a-Si single junction cells, new p-type multilayers, such as (a-Si/a-C)n multilayers, and new type fabrication of p/i interface layer were developed, and the key parameter for high quality intrinsic a-Si layer was proposed. Significantly high open-circuit voltage ($>$ 0.93 V) was attained for a-Si solar cells with p-type (a-Si/a-C)$_n$ multilayer. The fabrication of a-SiC and new wide gap a-Si : H (without carbon) p/i interface layer by alternately repeating deposition and hydrogen plasma treatment (ADHT) method resulted in improving the film properties and the solar cell performance. It was revealed that hydrogen radical per Si deposition rate, which was monitored by H*/SiH*, was a key parameter to obtain low defect density in films and high fill factor of solar cells. As a result, the highest conversion efficiency of 13.2% was achieved for the single junction type a-Si solar cell, whose structure was ARC/glass/texture SnO_2/p-type (a-Si/a-C)$_n$ multilayers/p-i interface ADHT a-SiC layer/i-layer/i-n interface layer/ITO/Ag.

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