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Double amorphous silicon-carbide *p*-layer structures producing highly stabilized *pin*-type protocrystalline silicon multilayer solar cells

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We have applied double *p*-type amorphous silicon-carbide (*p*-*a*-SiC:H) layer structures to *pin*-type protocrystalline silicon (*pc*-Si:H) multilayer solar cells. The less-pronounced initial short-wavelength quantum efficiency variation against the biased voltage and the wide overlap of dark current—voltage (J_D - V) and short-circuit current—open-circuit voltage (J_{sc} - V_{oc}) characteristics prove that the double *p*-*a*-SiC:H layer structure successfully reduces recombination at the *p/i* interface. Therefore, we achieved highly stabilized efficiency of 9.0% without any backreflector. © 2005 American Institute of Physics. [DOI: 10.1063/1.2126802]

In recent years, the hydrogen dilution has been a useful deposition technique to change the phase of Si-based thin films. With an increase in the hydrogen dilution ratio (H_2/SiH_4), we can monitor the phase transition from an amorphous silicon (*a*-Si:H)-based film to a microcrystalline silicon (μ c-Si:H)-based film. The latter film contains columnar growth of crystalline silicon (*c*-Si) grains in an *a*-Si:H matrix. We proposed a double hydrogenated boron-doped amorphous silicon-carbide (*p*-*a*-SiC:H) layer structure consisting of a conventional undiluted *p*-*a*-SiC:H window layer and a H_2 -diluted *p*-*a*-SiC:H buffer layer in order to effectively improve *p/i* interfaces of amorphous silicon *a*-Si:H solar cells.¹ The preparation technique of this buffer material is based on that of a highly conductive and wide bandgap hydrogenated boron-doped nanocrystalline silicon—silicon-carbide alloy (*p*-*nc*-Si-SiC:H) film containing nanocrystalline silicon (*nc*-Si) grains (*c*-Si grains with a size of a few nm) embedded in an *a*-SiC:H tissue due to the hydrogen dilution.^{2–4} We reported that the natural hydrogen treatment (etching the defective undiluted *p*-*a*-SiC:H window layer and increasing dark conductivity of the window layer by improving structural order) occurred just before the highly conductive, low absorption, and well-ordered H_2 -diluted buffer layer deposition onto the window layer.^{1,5} Accordingly, we achieved a high initial conversion efficiency of 11.2% without any backreflector by successfully reducing the recombination loss at the *p/i* interface.

On the other hand, we developed alternately H_2 -diluted protocrystalline silicon (*pc*-Si:H) multilayer solar cells.^{6,7} The *pc*-Si:H is an edge material existing just below the threshold of the *a*-Si:H to μ c-Si:H transition. The *pc*-Si:H multilayer cells exhibit the excellent light-induced metastability. Based on the photoluminescent (PL) and Fourier Transform infrared (FTIR) spectroscopy measured at room temperature, we provided strong evidence that regularly arranged isolated *nc*-Si grains in *i*-*pc*-Si:H multilayer absorbers suppress the photocreation of dangling bonds.⁸ In this Letter, we investigated the optimized double *p*-*a*-SiC:H layer structure for *pc*-Si:H multilayer solar cells and its benefits.

Using the photoassisted chemical vapor deposition

(photo-CVD) system, we fabricated *pin*-type solar cells at 250 °C with a simple structure of glass/SnO₂:F/undiluted *p*-*a*-SiC:H/ H_2 -diluted *p*-*a*-SiC:H/*i*-*pc*-Si:H multilayer (640 nm)/*n*- μ c-Si:H(40 nm)/Al (cell area: 0.092 cm²). To dissociate the gases, we used a low-pressure mercury (Hg) lamp with resonance lines of 184.9 and 273.7 nm as an uv light source. The undiluted *p*-*a*-SiC:H films were grown by a direct photo-CVD method using a mixture of Si₂H₆, B₂H₆, and C₂H₄ reactant gases. The lightly doped (B₂H₆/SiH₄ = 1000 ppm) H_2 -diluted *p*-*a*-SiC:H films were prepared by a Hg-sensitized decomposition of a mixture of SiH₄, H_2 , B₂H₆, and C₂H₄ reactant gases.¹ The alternately H_2 -diluted *i*-*pc*-Si:H multilayer consists of low H_2 -diluted *a*-Si:H sublayers (S_L 's) and highly H_2 -diluted *a*-Si:H sublayers (S_H 's). This repeatedly layered structure is deposited by just modulating the mass flow control of H_2/SiH_4 between 0 (for the deposition of S_L) and 20 (for the deposition of S_H) under continuous uv light irradiation. Because we maintained the angle of the throttle valve in the reaction chamber at a constant value during the continuous process, the sublayers deposited under the condition of $H_2/SiH_4=0$ were indeed low H_2 -diluted *a*-Si:H layers and all interfaces were graded by hydrogen. In addition, the average deposition rate of the multilayer (7 nm/min) is comparable to that of conventional undiluted *i*-*a*-Si:H (10 nm/min). Details were provided in our previous report.^{7,8}

In order to obtain the thickness of the undiluted *p*-*a*-SiC:H window layer (d_w), thickness of the H_2 -diluted *p*-*a*-SiC:H buffer layer (d_b), and the thickness ratio of S_H to S_L for the *i*-*pc*-Si:H multilayer (S_H/S_L), we performed spectroscopic ellipsometry measurements of angles (Ψ, Δ) in the range of 1.5–4.0 eV with a phase-modulated spectroscopic ellipsometer (UVISSEL-Jobin Yvon).^{9,10} As a result, we achieve a S_H/S_L value of 32/10 (nm/nm). The cell characteristics were measured under 100 mW/cm² (AM 1.5) solar simulator irradiation. For spectral response measurements of solar cells, we calculated external quantum efficiencies (QE) in the wavelength region of 400–800 nm via a constant energy monochromator (light intensity: 50 μ W/cm²). We also measured external QE at a short wavelength of 400 nm by

FIG. 1. Initial performance dependence of *pc*-Si:H multilayer solar cells as a function of d_w . d_b is maintained at 2.2 nm.

varying the applied voltage from -1 to 0.4 V with the step increment of 0.2 V. The dark current—voltage (J_D - V) and short-circuit current—open-circuit voltage (J_{sc} - V_{oc}) characteristics were measured at room temperature. The latter was achieved by varying the illumination intensity in the range of 10^{-7} to 1 sun ($J_{sc}=10^{-9}$ – $\sim 10^{-2}$ A/cm 2).

Figure 1 shows the dependence of solar cell parameters on d_w . For clarity, d_b is maintained at 2.2 nm. The d_w value is the final thickness of the window layer after the buffer layer deposition: ~ 5.5 nm-thick defective surface of the window layer is etched just before the buffer layer deposition. V_{oc} increases up to 0.920 V with the increase in d_w , and then virtually saturated for $d_w \geq 12.5$ nm. J_{sc} shows its maximum value of 16.6 mA/cm 2 when d_w is 10.5 nm. This value is lower than that of the *a*-Si:H solar cell due to lower QE in the long-wavelength region of 600 – 800 nm.^{1,5} In the case of a fill factor (FF), it provides the maximum value of 0.725 when d_w is 18.5 nm. For $d_w \geq 18.5$ nm, FF declines because the electrical loss with the thicker window layer reduces the photogenerated voltage by diminishing the current to the window layer. Therefore, we obtained the maximum initial efficiency by using the 14.5 nm-thick *p*-*a*-SiC:H window layer.

Figure 2 displays the spectral response dependence on the variation of d_w . In the wide wavelength range of 400 – 640 nm, QE increases until d_w reaches 10.5 nm. However, QE decreases by a further increase in d_w .

We found that the dependence of initial cell performance upon the d_b value is less sensitive than its dependence on d_w like *a*-Si:H solar cells.^{1,5} Thus, we achieved $\sim 10\%$ initial efficiency by employing a 1.5 – 2.5 nm-thick *p*-*a*-SiC:H buffer layer. For $d_b=2.2$ nm, we obtained the optimized initial conversion efficiency of 10.4% ($V_{oc}=0.920$ V, $J_{sc}=15.6$ mA/cm 2 , and $FF=0.721$). If we do not use the H_2 -diluted *p*-*a*-SiC:H buffer layer, the initial efficiency severely reduces to 7.7% due to the decrease in all parameters

FIG. 2. Initial QE dependence of *pc*-Si:H multilayer solar cells as a function of d_w . d_b is maintained at 2.2 nm.

($V_{oc}=0.845$ V, $J_{sc}=13.6$ mA/cm 2 , and $FF=0.670$). The extent of the improvement for the multilayer cell is smaller than that of *a*-Si:H solar cells.^{1,5} Since the first layer of the *i*-*pc*-Si:H multilayer is ultrathin (~ 5 nm) S_H , the multilayer cell without the H_2 -diluted *p*-*a*-SiC:H buffer also has a weak natural hydrogen treatment during the *p/i* interface formation. Therefore, the improvement of the multilayer cell by the natural treatment effect during the formation of the double *p*-*a*-SiC:H layer structure diminishes.

Figure 3 depicts the QE (at a wavelength of 400 nm) dependence as a function of the bias voltage. The optimized multilayer cell with the H_2 -diluted *p*-*a*-SiC:H buffer layer exhibits less variation at the short wavelength than its bufferless analog. It can be attributed to a higher electric field and well-ordered structure formed by applying the H_2 -diluted *p*-*a*-SiC:H buffer layer at the *p/i* interface. We conclude that the lightly doped H_2 -diluted *p*-*a*-SiC:H buffer layer successfully reduces the recombination at the heterojunction interface by blocking the diffusion of boron into an *i*-*pc*-Si:H multilayer and relaxing the strain.¹¹ Compared to *a*-Si:H cells,^{1,5} the bufferless multilayer cell shows the smaller variation at 400 nm. It can be ascribed to the aforementioned weak natural hydrogen treatment effect during its *p/i* interface formation.

J_D - V characteristics of *pc*-Si:H multilayer cells are investigated to inspect the contribution of the *p/i* interface on

FIG. 3. Ratios of QE (V) to QE (0 V) at the short wavelength of 400 nm. These values are evaluated from an initial QE of the optimized *pc*-Si:H multilayer solar cell.

FIG. 4. Initial J_D - V characteristics of the optimized pc -Si:H multilayer solar cell superimposed on its J_{sc} - V_{oc} characteristics.

V_{oc} . The J_D of multilayer cells can be expressed as

$$J_D = J_0[\exp(qV/nkT) - 1], \quad (1)$$

where J_0 is the reverse saturation current density, n is the diode quality factor, q is the electric charge, k is Boltzmann's constant, and T is the absolute temperature. The effect of the p/i interface to V_{oc} can be identified from its dependence on the light illumination intensity. Applying a simplified model in which series and shunt resistance effects are negligible and the photocurrent density has no voltage dependence, we obtain the following equation by substituting J_{sc} and V_{oc} for J_D and V in Eq. (1), respectively:

$$J_{sc} = J_0[\exp(qV_{oc}/nkT) - 1]. \quad (2)$$

Initial J_D - V and J_{sc} - V_{oc} characteristics of the optimized pc -Si:H multilayer cell are shown in Fig. 4. Due to the reversible recovery of the multilayer cell by the thermal annealing,^{6,8} its initial characteristics are the same as those in the annealed state. For $V < 0.74$ V, J_D shows an exponential dependence on V . In this regime, the carrier transport with $n=1.53$ can be ascribed to the injection of electrons and holes from n - μc -Si:H layer and p - a -SiC:H layers, respectively, which is followed by their diffusion and ultimate recombination.¹² For $V \geq 0.74$ V, J_D limited by a series resistance¹³ and by a transition from diffusive to drift transport.¹⁴ We should note that J_D - V characteristics agree well with bulk recombination dominant J_{sc} - V_{oc} characteristics with $n=1.45$ except for $V_{oc} \geq 0.8$ V. The wide overlap means that our multilayer cell is free from the recombination at the p/i interface¹⁵ by the natural hydrogen treatment effect during the formation of the double p - a -SiC:H layer structure.

Because of the highly conductive H_2 -diluted p - a -SiC:H buffer layer, we improve the built-in potential (ΔV_{bi}) at the p/i interface, which can be expressed as⁵

$$\Delta V_{bi} = \Delta \phi_b + \Delta E_{va}. \quad (3)$$

We achieved optical bandgap values of p - a -SiC:H window (~ 2.0 eV) and buffer (~ 1.8 eV) layers via spectroscopic ellipsometry measurements.^{1,5} The optical bandgap of i - pc -Si:H is slightly wider than undiluted a -Si:H (~ 1.7 eV), because of the quantum confinement by the isolated nc -Si:H grains.^{7,8} It is considered that a high conductivity of the buffer improves the built-in potential of

the pc -Si:H multilayer solar cell: (i) by lowering a barrier potential ($\Delta \phi_b$) at the SnO_2 :F/undiluted p - a -SiC:H window interface due to the increase in the dark conductivity of the window layer, (ii) by the band lift arising from the Fermi level location of the buffer closer to the valence band edge of the i - pc -Si:H absorber (ΔE_{va}) due to the highly conductive H_2 -diluted p - a -SiC:H buffer layer. Due to the improvement of V_{bi} , the cell with the buffer shows the higher V_{oc} than its bufferless analog. This improvement of V_{bi} is also beneficial to prevent the electron backdiffusion. As mentioned earlier, the multilayer has the repeated layered structure consisting of S_L 's and S_H 's. In addition, all interfaces are graded by hydrogen. Isolated spherical nc -Si grains embedded in a well-ordered a -Si:H matrix of S_H 's.⁸ An a -Si:H grain boundary layer with a high hydrogen concentration wraps each nc -Si grain. This grain boundary layer is the most defective layer in the multilayer. S_L 's that hinder the columnar growth of μc -Si:H have a less-ordered a -Si:H matrix than that of S_H 's.

The optimized pc -Si:H multilayer solar cell exhibits a stabilized efficiency of 9.0% ($V_{oc}=0.919$ V, $J_{sc}=15.0$ mA/cm², FF=0.652, and a degradation ratio [efficiency ($t > 12$ h)/efficiency ($t=0$)] = 13.4%) after 12 h 1 sun (100 mW/cm², AM 1.5) light irradiation at 50 °C.^{7,8} Isolated nc -Si grains embedded in regularly arranged S_H 's suppress the photocreation of dangling bonds.^{8,16} Due to virtually invariant V_{oc} , the pc -Si:H multilayer solar cell has a low degradation behavior. Thus, the H_2 -diluted p - a -SiC:H buffer layer contributes to the improvement of the stabilized efficiency by enhancing initial V_{oc} .

We are currently trying to achieve a higher conversion efficiency via a highly stable and textured intentionally hydrogen-doped ZnO (ZnO:H)¹⁷ or ZnO:H/Ag backreflector.

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