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Highly Stabilized Protocrystalline Silicon Multilayer Solar Cells

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Abstract: We have developed highly stabilized (p-i-n)-type protocrystalline silicon (pc-Si:H) multilayer solar cells. To achieve a high conversion efficiency, we applied a double-layer p-type amorphous silicon-carbon alloy (p-a-Si_{1-x}C_x:H) structure to the pc-Si:H multilayer solar cells. The less pronounced initial short wavelength quantum efficiency variation as a function of bias voltage proves that the double p-a-Si_{1-x}C_x:H layer structure successfully reduces recombination at the p/i interface. It was found that a natural hydrogen treatment involving an etch of the defective undiluted p-a-SiC:H window layer before the hydrogen-diluted p-a-SiC:H buffer layer deposition and an improvement of the order in the window layer. Thus, we achieved a highly stabilized efficiency of 9.0 % without any back reflector.

1. Introduction

Thin film silicon solar cells employing amorphous silicon (a-Si:H) based absorbers have attracted great interest in the industrial realm due to their easy optical band gap design, low-temperature, low-cost, and large-scale production. However, a-Si:H exhibits serious light-induced degradation called the Staebler-Wronski effect⁽¹⁾. The H₂ dilution of SiH₄ has attracted great interest in efforts to suppress the Staebler-Wronski effect in a-Si:H based material. Recently, so-called "edge" materials such as single layers of H₂-diluted protocrystalline silicon (pc-Si:H) or nanocrystalline silicon (nc-Si:H)⁽²⁻⁶⁾ were shown to be better absorbers than conventional H₂-diluted a-Si:H due to their higher stability and vertical photosensitivity (the ratio of photo- to dark-conductivity). Because the former is fabricated just below the threshold of an

amorphous-to-microcrystalline transition and the latter is fabricated just above the threshold of the transition, such depositions are very sensitive to the film thickness and H₂ dilution.

An a-Si:H/H₂-diluted microcrystalline silicon (μ c-Si:H) superlattice has been proposed as the most promising absorber due to its (i) isotropic transport properties achieved by perturbing the columnar growth of μ c-Si:H⁽⁷⁾ and (ii) lower sensitivity to the film thickness and H₂ dilution than single layers of edge materials. However, this

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structure is unsuitable for mass production because of the discrete deposition of its sublayers. Therefore, we have developed pc-Si:H multilayer absorbers that are prepared by alternate H₂ dilution under continuous ultraviolet (UV) light irradiation using a photoassisted chemical vapor deposition (photo-CVD) system⁽⁸⁻¹⁰⁾ as a practical simulation of the previous a-Si:H/ μ c-Si:H superlattice. The pc-Si:H multilayer absorbers have the advantages of excellent light-induced stability and fast annealing behavior. In this way, highly stabilized thin film solar cells were developed in our previous work⁽¹¹⁾. We observed faster stabilization and recovery by thermal annealing of the pc-Si:H multilayer solar cells compared with those of a-Si:H and pc-Si:H single layer solar cells^(8,11). In this paper, we demonstrate a quantum-size-effect (QSE) associated with nc-Si grains regularly distributed in an a-Si:H matrix and investigate its impact on the light-soaking behavior of the multilayer.

2. Experimental

Using a photo-CVD system, we fabricated i-pc-Si:H multilayers and (p-i-n)-type pc-Si:H multilayer solar cells at 250 °C with the following structure: glass/SnO₂/undiluted p-a-Si_{1-x}C_x:H/H₂-diluted p-a-Si_{1-x}C_x:H/i-pc-Si:H multilayer/n- μ c-Si:H/Al. To dissociate the reactant gases, we used a low-pressure mercury (Hg) lamp with resonance lines of 184.9 nm and 253.7 nm as a UV light source. For characterization, we deposited the i-pc-Si:H multilayers onto textured SnO₂ coated glass (Asahi U-type glass) and onto c-Si wafers by the Hg-sensitized photo-CVD technique, modulating a mixture of SiH₄ and H₂ gases. We prepared the widely-used undiluted p-a-Si_{1-x}C_x:H window layers of the solar cells by a direct photo-CVD technique with a mixture of Si₂H₆, B₂H₆, and C₂H₄ reactant gases. We prepared a H₂-diluted p-a-Si_{1-x}C_x:H buffer using the Hg-sensitized decomposition of a mixture of SiH₄, H₂, B₂H₆, and C₂H₄ reactant gases based on a previously-reported process for the deposition of H₂-diluted p-a-Si_{1-x}C_x:H that incorporated nc-Si grains⁽¹²⁻¹⁵⁾. This H₂-diluted p-a-Si_{1-x}C_x:H has a higher electrical

conductivity, optical transmittivity, carrier mobility, and doping efficiency than undiluted p-a-Si_{1-x}C_x:H.

Raman spectra were measured using a JASCO Corp., NRS-1000 system. The wavelength of the Ar laser is 532 nm. The cell characteristics were measured under 100 mW/cm² (AM 1.5) solar simulator irradiation. We also measured the initial quantum efficiency (QE) of the solar cells in the short wavelength region centered at 400 nm by varying the applied voltage from 1 to 0.4 V with a step increment of 0.2 V.

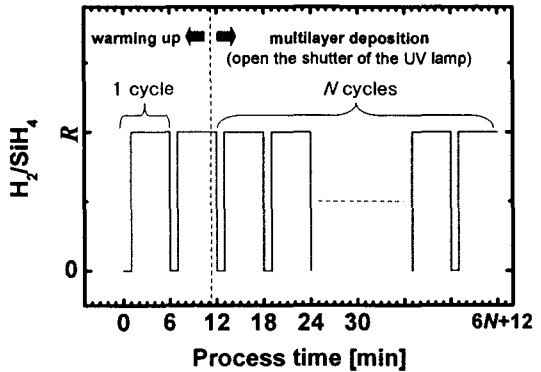


Figure 1. Schematic diagram of the hydrogen dilution (H_2/SiH_4) modulation for an i-pc-Si:H multilayer deposition.

Figure 1 shows a schematic diagram of alternating hydrogen dilution (H_2/SiH_4) for an i-pc-Si:H multilayer preparation performed using the photo-CVD technique. The i-pc-Si:H multilayer consists of low H_2 -dilution and high H_2 -dilution a-Si:H sublayers. This repetitively layered structure is deposited by simply toggling the mass flow control of H_2/SiH_4 between 0 and R under continuous UV light irradiation. Due to the continuous deposition, all interfaces are graded in H-content and the average deposition rate of the multilayer is comparable to that of conventional undiluted i-a-Si:H⁽¹¹⁾. During the deposition, however, the chamber pressure was also slightly toggled with the gas flow control because the angle of an automatic pressure controller (APC) was maintained at a constant value. To find an optimal layered structure, we deposited multilayers with R changing from 15 to 30. We also varied the total number of cycles of H_2/SiH_4 modulation

(N) in order to keep the thickness of the multilayers constant at ~ 550 nm. Thus, we increased N with the increase in R , because the hydrogen exposure near the growing surface increases during both the low H_2 -dilution and high H_2 -dilution a -Si:H sublayer depositions due to the continuous deposition while maintaining a constant angle of the APC.

3. Results and Discussions

Figure 2 displays Raman spectra of a series of i - pc -Si:H multilayers prepared at different R of the high H_2 -dilution sublayers and a single layer prepared at constant $R = 15$. We note that ~ 550 nm thick multilayers fail to show any distinct fraction of the μc -Si:H phase, whereas the 300 nm thick single layer indicates a μc -Si:H phase. We speculate that ~ 10 nm thick low H_2 -dilution sublayers⁽¹¹⁾ interrupt the columnar growth of μc -Si:H.

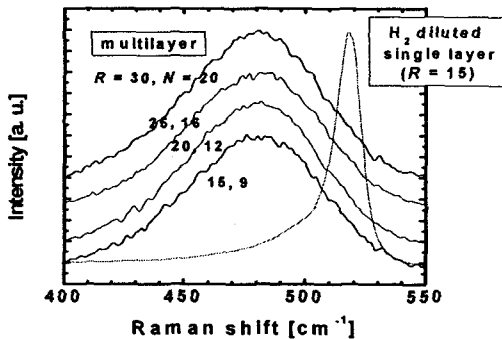


Figure 2. Raman spectra of a series of i - pc -Si:H multilayers prepared at different R for the high H_2 -dilution sublayers and a H_2 -diluted single layer (300 nm) prepared at $R = 15$.

To investigate the light-induced stability of the multilayers, we fabricated diodes with a structure of glass/SnO₂/ i - pc -Si:H multilayer (~ 550 nm)/Al. Figure 3 shows the R dependence of the initial quantum efficiency (QE). We found in Fig. 3 (a) that the initial QE declines with increasing R . All multilayers show their maximum values of the initial QE at a wavelength (λ) of 600 nm. In Fig. 3 (b) we found that all multilayers exhibit fast light-induced stabilization of the normalized QE at $\lambda = 600$ nm. From these figures, it is found that the optimum R for stable absorbers is 20.

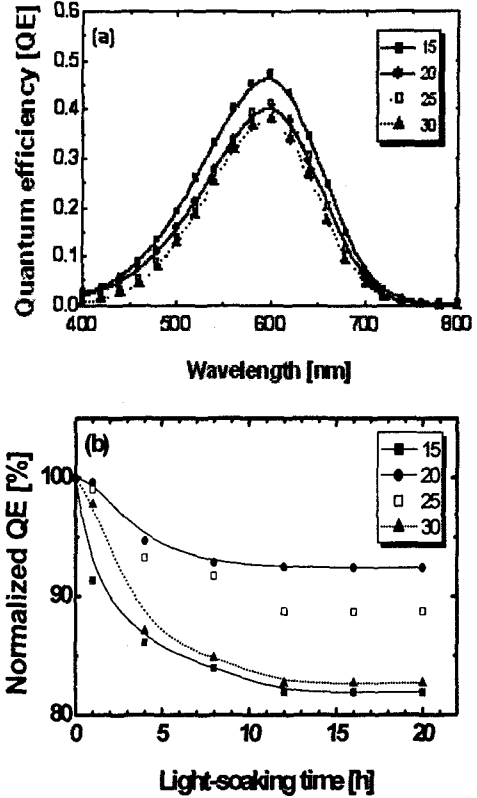


Figure 3. R dependence of the quantum efficiency (QE) of glass/SnO₂/ i - pc -Si:H multilayer (~ 550 nm)/Al structures. (a) initial QE (b) light-soaking behavior of normalized QE at the wavelength of 600 nm.

Figure 4 depicts the initial current-voltage (J-V) characteristics of a -Si:H based solar cells with and without a H_2 -diluted p - a -SiC:H buffer layer ($t_b = 12$ min). Compared to the bufferless analog, the a -Si:H based solar cell with the H_2 -diluted p - a -SiC:H buffer layer considerably increases the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), and the fill factor (FF). Consequently, it exhibits a drastic improvement of the initial conversion efficiency (Eff). The H_2 -diluted p - a -SiC:H buffer layer is very effective at improving the p/i interface. Hence, the high initial efficiency of 10.94 % ($V_{oc} = 0.904$ V, $J_{sc} = 17.5$ mA/cm², and FF = 0.692) was obtained while its bufferless analog shows a low initial efficiency of 8.59 % ($V_{oc} = 0.834$ V, $J_{sc} = 15.6$ mA/cm², and FF = 0.659). For $t_b = 15$ min, the

initial efficiency of solar cell is decreases to 10.37 % ($V_{oc} = 0.890$ V, $J_{sc} = 17.1$ mA/cm², and FF = 0.681). From the small decrease in FF, it can be speculated that the electrical loss with the thicker buffer reduces the photogenerated voltage by diminishing the current to the window layer. In addition, the increased absorption loss in the thicker buffer layer decreases J_{sc} .

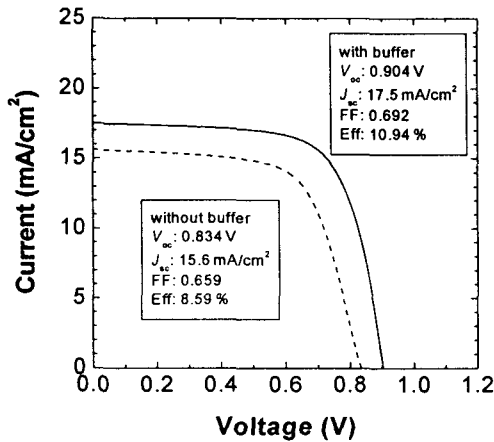


Figure 4. Photo current density-voltage (J-V) characteristics of solar cells with or without a H₂-diluted p-a-SiC:H buffer layer.

The spectral response of the cells without any bias is provided in Fig. 5. Compared to the bufferless analog, the QE of the cell with the H₂-diluted p-a-SiC:H buffer layer dramatically increases in the wide short wavelength region of 380 - 650 nm. Thus, the J_{sc} value of the cell significantly improves. The improvement of the QE in the short wavelength region of 380 - 500 nm can be ascribed to the reduced optical absorption at the double p-a-SiC:H layer structure due to the natural hydrogen treatment during the formation. Despite the decrease in the optical band gap after the buffer deposition, the QE considerably improves due to the significant etching and the increase in the structural order from the defective as-grown undiluted p-a-SiC:H window layer, as well as the good undiluted p-a-SiC:H/H₂-diluted p-a-SiC:H interface formation. The increase in the built-in potential due to the insertion of the highly conductive buffer layer contributes to the improvement of the QE in the region of 500

- 650 nm. The electron back diffusion to the undiluted p-a-SiC:H window layer is effectively diminished by employing the highly conductive buffer layer.

We performed a light-soaking test of the

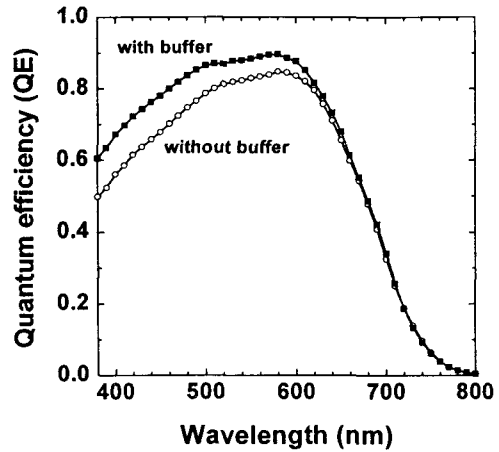


Figure 5. No biased spectral response of solar cells.

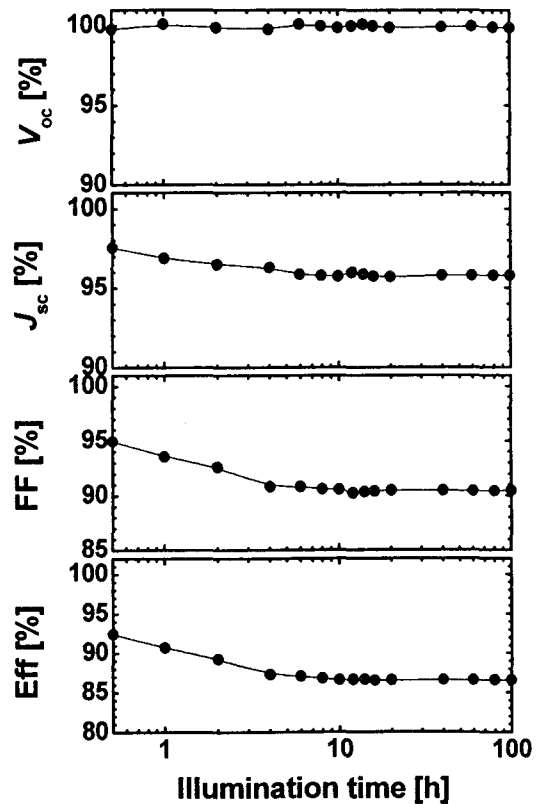


Figure 6. Normalized light-soaking behavior of a pc-Si:H multilayer solar cell.

multilayer cell via 100 h 1-sun light illumination. Figure 6 shows the normalized light-soaking behavior of a (p-i-n)-type pc-Si:H multilayer solar cell with the following structure: glass/SnO₂/undiluted p-a-Si_{1-x}C_x:H/H₂-diluted p-a-Si_{1-x}C_x:H / i-pc-Si:H multilayer (640 nm, $R = 20$)/n-c-Si:H/Al (cell area: 0.092 cm²). In order to determine the optical constants of the undiluted p-a-Si_{1-x}C_x:H window layer, we performed spectroscopic ellipsometry (SE) measurements with a phase-modulated spectroscopic ellipsometer (UVISEL-Jobin Yvon)⁽¹⁶⁻¹⁷⁾. From the SE analysis, we discovered a natural hydrogen treatment process that involves etching the defective undiluted p-a-Si_{1-x}C_x:H window layer and improving order in the window layer. This effect occurs in the initial stage when the highly conductive, low absorption, and well-ordered H₂-diluted buffer layer is deposited onto the window layer^(11, 18-19). Due to this natural hydrogen treatment effect, we can effectively reduce the recombination at the p/i interface, resulting in a dramatic improvement of all solar cell parameters including V_{oc} , J_{sc} , and fill factor (FF)⁽¹¹⁾. Consequently, we have achieved a considerable initial conversion efficiency of 10.4 ($V_{oc} = 0.920$ V, $J_{sc} = 15.6$ mA/cm², and FF = 0.721) without any back reflector. If we do not use the H₂-diluted p-a-Si_{1-x}C_x:H buffer layer, the initial efficiency is reduced significantly to 7.7 % due to the decrease in all parameters ($V_{oc} = 0.845$ V, $J_{sc} = 13.6$ mA/cm², and FF = 0.670). The extent of the improvement for the multilayer cell is smaller than that for a-Si:H solar cells⁽¹⁸⁻¹⁹⁾. Since the first layer of the i-pc-Si:H multilayer is an ultrathin (~5 nm) high H₂ dilution sublayer, the multilayer cell without the H₂-diluted p-a-Si_{1-x}C_x:H buffer also involves 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-Si_{1-x}C_x:H layer structure diminishes.

For the pc-Si:H multilayer solar cell, we have achieved a stabilized efficiency of 9.0 % ($V_{oc} = 0.919$ V, $J_{sc} = 15.0$ mA/cm², FF = 0.652,

and degradation ratio = 13.4 %) after 12 h 1-sun (100mW/cm², AM 1.5) light irradiation. Due to its stable V_{oc} , the pc-Si:H multilayer solar cell exhibits weak degradation behavior. Thus, the H₂-diluted p-a-Si_{1-x}C_x:H buffer layer contributes to the improvement of the stabilized efficiency by enhancing V_{oc} . The FF exhibits the largest light-induced degradation effect. Furthermore, the stabilized multilayer cell displays a perfect recovery to its initial value after 1 h thermal annealing at 133 °C, whereas an a-Si:H solar cell with the same structure shows a recovery of 94 %. Thus, the pc-Si:H multilayer solar cell has faster annealing behavior than a-Si:H solar cells.

For the QE dependence against the bias voltage in Fig. 7, the cell with the H₂-diluted p-a-Si_{1-x}C_x:H buffer layer shows a less variation in the short wavelength region than its bufferless analog. From the reverse bias ratio QE (-1 V)/QE (0 V), the bufferless cell shows a considerable increase in the wide short wavelength region of 380 - 500 nm, which corresponds to the initial part of i-a-Si:H. This can be ascribed to the recombination of photogenerated carriers at or near the p/i interface. We conclude that the lightly doped H₂-diluted p-a-Si_{1-x}C_x:H buffer layer successfully reduces the recombination at the heterojunction interface by blocking diffusion of boron into i-a-Si:H and relaxing the strain⁽²⁰⁾. Judging from the less pronounced enhancement of the ratio in the wavelength region of 500 - 600 nm, the buffer generates a higher electric field. This higher electric field causes the increase in FF. The increase in FF is also due to the reduced total p-layer thickness caused by the etching and the increase in the dark conductivity of the window layer cause by the natural hydrogen treatment before the buffer layer deposition. From the forward bias ratio QE (0.4 V)/QE (0 V), we also observed the higher electric field and well-ordered interface structure by applying the double p-a-Si_{1-x}C_x:H layer structure.

Figure 8 exhibits the band diagram that explains the improvement of the built-in potential (V_{bi}) by using the highly conductive H₂-diluted p-a-Si_{1-x}C_x:H buffer layer, which

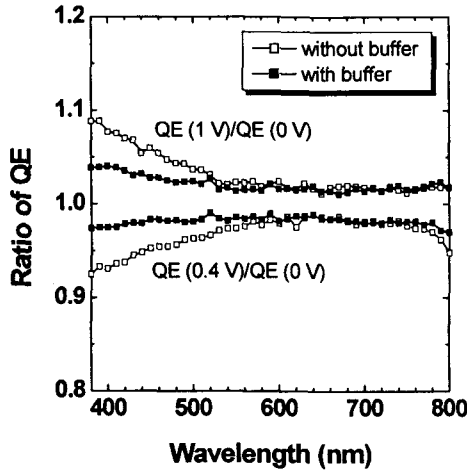


Figure 7. Ratios of reverse (-1 V) and forward biased QE (0.4 V) to QE (0 V) as a function of wavelength.

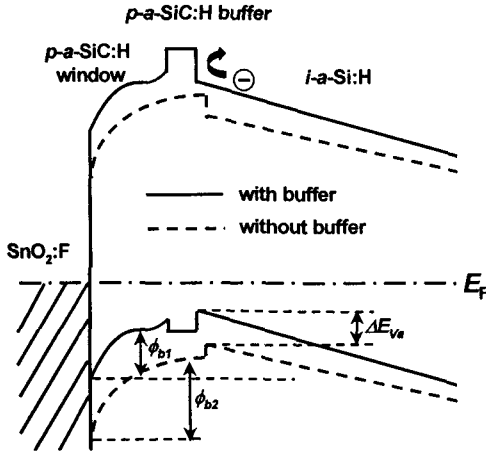


Figure 8. Band diagram variation due to the deposition of the H₂-diluted p-a-Si_{1-x}C_x:H buffer layer. The difference between ϕ_{b1} and ϕ_{b2} denotes a decrease in the barrier height for holes at the SnO₂:F/undiluted p-a-Si_{1-x}C_x:H window interface caused by the improved dark conductivity of the window during the buffer preparation. The ΔE_{va} value describes the band lift arising from the Fermi level location of the buffer closer to the valence band edge of the i-a-Si:H absorber.

can be expressed as the following equation:

$$V_{bi} = \phi_{b2} - \phi_{b1} + \Delta E_{va} \quad (1)$$

It is considered that a high conductivity of the buffer improves the built-in potential of a-Si:H solar cell: (i) by lowering a barrier potential ($\phi_{b2} - \phi_{b1}$) between the SnO₂:F transparent front electrode and the

undiluted p-a-Si_{1-x}C_x:H window layer 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 (ΔE_{va}) of the i-a-Si:H absorber due to the highly conductive H₂-diluted p-a-Si_{1-x}C_x:H buffer layer. Because of the improvement of V_{bi} , the cell with the buffer shows the higher V_{oc} than its bufferless analog (see Fig. 4). As mentioned above, this improvement of V_{bi} is also beneficial to prevent the electron back diffusion.

4. Conclusions

We have successfully achieved a highly stable conversion efficiency of 9.0 % for a (p-i-n)-type pc-Si:H multilayer solar cell fabricated by incorporating a double p-a-Si_{1-x}C_x:H structure and an i-layer with a multilayered structure obtained through alternating H₂ dilution. The pc-Si:H multilayer leads to weak light-induced degradation that is superior to conventional a-Si:H and pc-Si:H single layers due to its rapid stabilization and recovery. We found that the natural hydrogen treatment (etching the defective undiluted p-a-Si_{1-x}C_x:H window layer and improving order in the window layer) is generated just before the highly conductive, low absorption, and well-ordered H₂-diluted p-a-Si_{1-x}C_x:H buffer layer deposition onto the window layer. Due to the natural hydrogen treatment effect, we can effectively reduce the recombination at the p-window/p-buffer/i interfaces, resulting in the dramatic improvement of all solar cell parameters including V_{oc} , J_{sc} , and FF. Consequently, we have achieved the considerable initial conversion efficiency of 10.94 % without any back reflector. Therefore, we try to achieve a higher conversion efficiency via a highly stable and textured intentionally hydrogen-doped ZnO (ZnO:H)⁽²¹⁾ or ZnO:H/Ag back reflector.

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