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Very thin and stable thin-film silicon alloy triple junction solar cells by hot wire chemical vapor deposition

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We present a silicon-based triple junction solar cell that requires a deposition time of less than 15 min for all photoactive layers. As a low-bandgap material, we used thin layers of hydrogenated amorphous silicon germanium with lower band gap than commonly used, which is possible due to the application of hot wire chemical vapor deposition. The triple junction cell shows an initial energy conversion efficiency exceeding 10%, and with a relative performance stability within 6%, the cell shows a high tolerance to light-induced degradation. With these results, we help to demonstrate that hot wire chemical vapor deposition is a viable deposition method for the fabrication of low-cost solar cells. 

A key asset of thin-film silicon solar cells (TFSSCs) is their potential for low fabrication costs. For many applications, however, these relatively low costs currently do not outweigh the lower energy conversion efficiencies of TFSSCs compared to many other photovoltaic technologies. The production costs of TFSSCs are to a significant extent determined by the investment in vacuum deposition equipment that is needed for a given fabrication throughput. The fabrication of high-quality thin-film silicon intrinsic absorber layers often requires long deposition times, which limits the throughput and increases the production costs. This is particularly the case for hydrogenated microcrystalline silicon (µc-Si:H), which is regularly used as a low-band gap material in multijunction solar cells, requiring deposition times that range between 30 min and several hours.\(^{1,2}\) In the past, United Solar Ovonic has managed to fabricate and commercialize triple junction solar cells with µc-Si:H sub-cells instead of µc-Si:H sub-cells, but even for those structures the combined deposition time of the intrinsic layers is around 1 h.\(^{3,4}\)

In this work, we demonstrate a triple junction solar cell architecture in which the deposition time for the three absorber layers is within 15 min. To achieve this, we have utilized intrinsic layers of hydrogenated amorphous silicon (a-Si:H) and silicon germanium (a-SiGe:H) for the top, middle, and bottom cells, and hot wire chemical vapor deposition (HWCVD) as the fabrication technique. HWCVD allows for the fabrication of high quality low-band gap a-SiGe:H\(^{5,6}\) and for conformal deposition at high rates.\(^{7,8}\) HWCVD can contribute to an additional reduction of costs/ Wp compared to plasma enhanced chemical vapor deposition (PECVD), due to lower system and operating expenses as well as its excellent compatibility with roll to roll fabrication.\(^{9}\)

The three a-Si(Ge):H layers were deposited in an HWCVD reactor of a multi-chamber vacuum system at a deposition rate of 0.4–0.5 nm/s. Detailed descriptions of the vacuum system and the HWCVD deposition process are given elsewhere.\(^{6,10}\) Figure 1 shows the refractive indices and the absorption coefficients of three types of absorber materials with different Ge fraction (\(x = \text{Ge}/(\text{Si} + \text{Ge})\)). The optical constants were obtained from reflection and transmission measurements of individual layers on Corning EAGLE XG\(^{5}\) glass that were fitted using the density-of-states model of O’Leary, Johnson, and Lim.\(^{11}\) Both the real and the imaginary parts of the refractive index \(n \& k\) as well as the absorption coefficient \(a\) increase and shift to longer wavelengths with increasing germanium fraction \(x\). As the Ge fraction increases, the optical band gap \(E_g\) decreases from 1.86 eV for unalloyed a-Si:H \((x = 0)\) to 1.54 eV and 1.37 eV for \(x = 0.45\) and \(x = 0.63\), respectively.\(^{6}\) The low band gap and high refractive index of the a-SiGe:H materials allow for a thin absorber layer thickness in solar cells, which furthermore preserves the effect of light trapping textures.

![FIG. 1. Optical properties of a-Si(Ge):H films with three different germanium fractions \((x)\) that were incorporated in the triple junction solar cell. The real and imaginary parts of the refractive index \((n \& k)\) and the absorption coefficient \(a\) were determined from reflection and the transmission measurements.](image-url)
throughout the device as compared to the devices with the thicker $\mu$-Si:H layers.  

Figure 2(a) shows a schematic cross section of the triple junction n-i-p solar cell. The solar cells were fabricated on a textured substrate consisting of a 1-$\mu$m ZnO layer deposited on Corning glass by magnetron sputtering and then texture-etched with a 0.5 wt. % HCl solution for 10 s.  

The textured ZnO layer was overcoated with a 200-nm thick evaporated Ag layer and an 80-nm thick sputtered Al-doped ZnO (2 wt. % Al$_2$O$_3$) layer as electrode and back reflector. We used this type of substrate as a model textured substrate but in practice it can be replaced by flexible stainless steel or other foils with a textured back reflector. On the front part of the solar cell, sputtered 80-nm thick Sn-doped In$_2$O$_3$ (ITO) pads function as a conductive anti-reflection coating and evaporated Ag contact grids facilitate the current collection. Multiple solar cells with active areas of 13 mm$^2$ were defined in this way. The n-type and p-type layers, with thicknesses varying between 30 nm in the bottom part and 20 nm in the upper part of the structure, were deposited using 13.56 MHz PECVD in two separate reactors of the same multi-chamber system. Although these layers can also be made by HWCDV, for this work we have first concentrated our research on the rate-limiting layers in production. The layers that are part of a tunnel recombination junction (TRJ) consist of B-doped and P-doped $\mu$-Si:H for their high conductivity. The n-layer in the bottom solar cell consists of the less conductive P-doped a-Si:H, which effectively serves to limit current collection from outside the perimeter of the solar cell and the p-layer of the top cell contains B-doped $\mu$-SiO$_x$:H in order to provide high transmission. The solar cell absorber layers consist of a 90-nm and 163-nm thick intrinsic a-SiGe:H layer in the bottom and middle cells, and a 90-nm thick a-Si:H layer in the top cell, all of which are deposited in only 13 min in total. Thin (3–6 nm) intrinsic a-Si:H buffer layers made by PECVD were incorporated at the rear and front of the absorber layers to ensure a good interface between the intrinsic and doped layers. By varying the Ge fraction throughout the film in a continuous manner, U-shaped band gap profiles were incorporated in the a-SiGe:H layers to facilitate the extraction of charge carriers.  

The Ge fraction in the bottom cell absorber varied from $x = 0$ ($E_g = 1.86$ eV) to $x = 0.62$ ($E_g = 1.37$ eV) and back to $x = 0$. The material with the lowest band gap was 30 nm thick and positioned 15 nm from the i/p buffer layer. The material with the lowest band gap was situated near the front side of the absorber as most charge carriers are generated at shallower depths. At the rear side of the film, a 45-nm thick graded-band gap layer was used. The middle cell consisted of a 98-nm thick central part with $x = 0.45$ ($E_g = 1.54$ eV) and graded parts of 16 and 49 nm at the front and rear sides, respectively. The top cell had a homogeneous band gap of $E_g = 1.86$ eV. A schematic energy band diagram of the silicon-based part of the solar cell structure, including the bandgap grading, is shown in Figure 2(b).

Figure 3(a) shows the current density–voltage curve and characteristics of a typical solar cell as measured at 25 °C under a WACOM dual source solar simulator (class AAA) calibrated to the AM1.5G spectrum. The external quantum efficiency (EQE) of the top, middle, and bottom sub-cells of the triple junction solar cells are shown in Figure 3(b) and were measured under short circuit conditions using chopped monochromatic light and colored DC bias light beams. Cell area and spectrum discrepancies are small: a < 2% deviation between the short circuit current density ($J_{sc}$) and the current density derived from the EQE of the current limiting middle cell was observed. The $J$–$V$ curve in Figure 3(a) was corrected by this amount. The yield of working devices is high.

![FIG. 2. (a) Schematic cross section of the triple junction solar cell. The schematic energy band diagram: (b) displays the position of the valence band edge $E_v$, conduction band edge $E_c$, and Fermi level $E_F$ in the solar cell under short circuit conditions. The intrinsic a-SiGe:H layers have a band gap profile. The tunnel recombination junctions (TRJ) between the sub-cells allow the electrons ($e^-$) and holes ($h^+$) to recombine efficiently. All layer thicknesses in this figure are to scale, except for the ZnO on glass.](image)

![FIG. 3. (a) Current density–voltage characteristics before and after 1000 h of light soaking (LS) treatment and (b) external quantum efficiency EQE of a typical triple junction solar cell. The derived current densities in mA/cm$^2$ are shown together with the EQE responses of the individual sub-cells and their envelope.](image)
with just one shunted device (located at the edge of the substrate) of a total of 22 solar cells. Having a 10-cell average conversion efficiency ($\eta$) > 10%, the performance of these devices exceeds that of earlier efforts to fabricate triple junction a-Si: H/a-Si:H/a-Si:H solar cell with HWCVD as the method for all absorbers.\textsuperscript{19} The performance is lower than the optimized PECVD-made triple junction solar cells developed by United Solar, mainly due to the difference in the open circuit voltage ($V_{oc}$). This is expected, because we use lower band gap materials. Yet, we believe that the $V_{oc}$ of our devices can be optimized by adjusting the band gap profile and the i/n and i/p interfaces in the a-Si: Ge: H sub-cells.

The performance of TFSSCs is known to reduce during extended exposure to light. The creation of light-induced metastable defects in the intrinsic layers is thought to be driven by the recombination energy of photocarriers.\textsuperscript{20} The performance degradation often exceeds 15% for a-Si: H single junction solar cells\textsuperscript{21,22} and 10% for a-Si: Ge: H triple junction solar cells.\textsuperscript{23,24} The stability of our triple junction solar cells was investigated by light soaking (LS) under simulated AM1.5 illumination for a duration of 1000 h at a constant temperature of 50 °C and under open circuit conditions. The best performing solar cell after degradation showed a relative reduction of conversion efficiency ($\Delta \eta/\eta$) of only 6%, mainly caused by a 4% relative reduction of the fill factor (FF/FF). No reduction of $J_{sc}$ was observed. Figure 2(a) includes the characteristics of the solar cell after light soaking. We believe that the low amount of degradation is caused by the small thicknesses of the intrinsic layers, allowing for a strong internal electric field and a low recombination rate.\textsuperscript{25} Other factors that may contribute to the stability are the lower recombination energy in the low-band gap a-Si:Ge: H cells\textsuperscript{26} and the improved amorphous network structure, due to the high concentration of atomic hydrogen during the HWCVD process.\textsuperscript{27}

In conclusion, we have demonstrated a triple junction a-Si:Ge:H(1.37 eV)/a-Si:Ge:H(1.54 eV)/a-Si:H(1.86 eV) solar cell architecture that used HWCVD as the deposition method for all intrinsic absorber layers. The devices have an initial conversion efficiency of only 15 min of total deposition time, considerably increasing the feasibility for industrial production.

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