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Inductively coupled plasma grown semiconductor films for low cost solar cells with improved light-soaking stability

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We investigate the performance of a single-junction amorphous Si (a-Si) solar cell fabricated with inductively coupled plasma (ICP) deposition technique. The high-density plasma resulting from high dissociation capacity of ICP enables good-quality hydrogenated Si films to be synthesized at low temperatures. High-density ICP also promotes the diffusion of reactive radicals on substrates and forms a-Si:H films with low defect density ($\sim 3 \times 10^{15} \text{ cm}^{-3}$). We demonstrate single-junction a-Si solar cells with a conversion efficiency of 9.6% and improved light-soaking stability. This low thermal-budget thin-film technique could open up the feasibility of efficient thin film solar cells on flexible substrates. © 2011 American Institute of Physics. [doi:10.1063/1.3615650]

Energy security has become the major concern of human being. Photovoltaic (PV) technology is attractive for its potential as the major carbon-free renewable energy source. Due to the long-term efforts in microelectronic industry, silicon-based PV technology has reached a mature status. However, currently single-crystal solar cells are still much more expensive than thin-film PV devices, which significantly limits the wide spread use of large-area single-crystal solar-cell panel. Hydrogenated amorphous silicon (a-Si:H) is well suited for PV applications.^{1,2} To further expand its applications on compliant substrates, thin-film solar cells must be fabricated at low temperature. Unfortunately, a-Si solar cells fabricated by radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD) below 150 °C revealed fairly poor PV conversion efficiencies.³ This is because low thermal energy of reactive radicals in RF-PECVD at low deposition temperature leads to a film with low mass density and poor electrical properties.^{4,5} Furthermore, the resulting solar cell is quickly degraded by the photo-generated defects.⁶⁻⁸ Although by using thinner absorber layer in an a-Si solar cell, researchers can reduce the photo-induced degradation to 15% after 1000-h exposure with one-sun irradiance at 50 °C, they need to employ a more sophisticated light trapping scheme in the device to maintain the PV efficiency.^{7,8}

Typically in an a-Si:H film, recombination of photo-generated charge carriers creates extra dangling bonds.^{8,9} It is highly desired to develop a low-thermal budget thin-film deposition technique for fabricating low cost PV panel with high light-soaking stability. Capacitor-type low-density plasma such as RF-PECVD generates abundant short-life silane-related radicals SiH_x ($0 \leq x \leq 2$), which eventually

form weak bonding configuration.^{4,8,9} Inductively coupled plasma chemical vapor deposition (ICP-CVD) system,^{10,11} because of its high fractional ionization capacity, can produce high-density plasma to improve diffusion of the reactive radicals on substrates even at fairly low deposition temperatures. The configuration of ICP system with high density plasma separated from the thin film growing region effectively reduces the possibility of ion bombardment on growing surface, resulting in a film with low density of defects. In this letter, by using ICP-CVD, we demonstrated single-junction a-Si solar cell with a conversion efficiency of 9.6% and improved light-soaking stability.

For a side-by-side comparison, we employed ICP-CVD and very high frequency PECVD (VHF-PECVD) to deposit a-Si:H thin films at 140 °C. Our ICP-CVD system is equipped with a 13.56-MHz RF electrical source operating at a power density of 135 mW/cm². During the thin film deposition, we maintained the pressure and hydrogen dilution ratio (H_2/SiH_4) at 700 mTorr and 10, respectively. This results in a deposition rate of a-Si:H film about 0.3 nm/s. VHF-PECVD system was operated at a frequency of 40 MHz with a power density of 83 mW/cm². Similar dilution ratio and working gas pressure were used.

The concentration of hydrogen inclusion $C_{\text{H}}(\%)$ and the microstructure parameter R of the resulting a-Si:H films were deduced from the integrated peak area of the 630-cm⁻¹ peak and ratio of the spectral peaks $I_{2070\text{cm}^{-1}} / (I_{2070\text{cm}^{-1}} + I_{2000\text{cm}^{-1}})$ of Fourier-transform infrared (FTIR) absorption spectra. Here $I_{2070\text{cm}^{-1}}$ and $I_{2000\text{cm}^{-1}}$ denote the integrated infrared absorption peak areas of stretching mode of Si-H bonds locating at internal interfaces and of the isolated Si-H bonds, respectively.^{8,12} We determined the defect densities of intrinsic a-Si:H layers with drive-level capacitance profiling (DLCP) technique.^{13,14}

For the fabrication of a-Si solar cell, a *p*-layer/intrinsic *i*-layer/*n*-layer (*p-i-n*) stack was deposited on Asahi

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substrates ($\text{SnO}_2/\text{F}/\text{glass}$) by ICP-CVD or VHF-PECVD. The thickness of the intrinsic layer (*i*-layer) was kept at 400 nm. Doped layers with thickness of 12 nm (*p*-layer) or 20 nm (*n*-layer) were synthesized with an admixture of either 13% B_2H_6 (*p*-layer) or 5% PH_3 (*n*-layer). A reflective contact of indium-tin-oxide (ITO)/Al was then deposited by direct current-sputtering on the back side to yield efficient light trapping. The ITO layers have high electrical conductivity ($<1 \times 10^{-3} \Omega \text{ cm}$) and optical transmittance ($>90\%$, 400–900 nm), which significantly improve the light collection and reduce the series resistance of the devices. We characterized the performance of the PV devices with an AM1.5G Global sun simulator (Oriol Sol3A). The light-soaking measurements were conducted with a white light source with an irradiance of $600 \text{ mW}/\text{cm}^2$ (6 Sun). During the light-soaking measurements, the device under test was not temperature-controlled. The device can rapidly reach a steady state temperature at 60°C . Therefore, the condition of our light soaking can be considered to be irradiated with 6 Sun at 60°C .

In Fig. 1(a), the FTIR absorption spectra of a-Si:H films prepared with ICP-CVD and VHF-PECVD were presented. From the 630-cm^{-1} peak, we estimated the hydrogen content of the a-Si:H films to be about 9.3% for the ICP a-Si:H and 11.7% for the VHF-PECVD film. Note that the hydrogen content in an a-Si:H film deposited by PECVD typically lies in the range of 11%–12%.¹⁵ The growth mechanism with combined effect from the formation of dense film by higher surface mobility of reactive species and the lower deposition rate due to hydrogen out-gassing predicts the hydrogen content in a film to be decreased as the deposition temperature is increased.^{16–18} However, we synthesized our ICP a-Si:H at a low deposition temperature (140°C) with a fairly high deposition rate ($0.3 \text{ nm}/\text{s}$) by using a high power density ($135 \text{ mW}/\text{cm}^2$). The resulting film still reveals lower hydrogen content than that prepared by PECVD and VHF-PECVD. The estimated microstructure parameter *R* in our ICP a-Si:H from $I_{2070\text{cm}^{-1}}/(I_{2070\text{cm}^{-1}} + I_{2000\text{cm}^{-1}})$ is nearly zero, implying a dense lattice network with a very low level of voids.^{8,12} The cross-sectional transmission electron microscopy (TEM) image of a-Si solar cell and the spatially

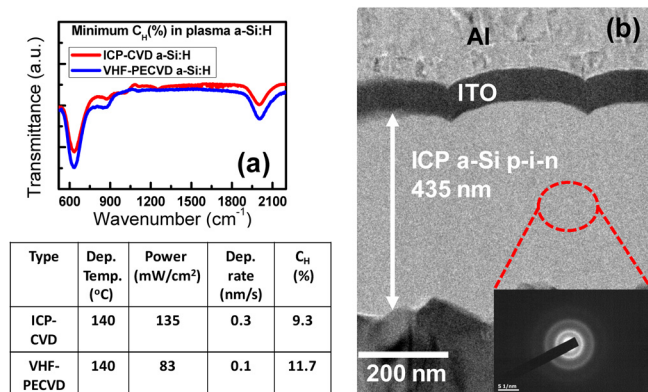


FIG. 1. (Color online) (a) FTIR absorption spectra of a-Si:H films deposited by ICP-CVD and VHF-PECVD. (b) The cross-sectional TEM image showing the Si pin stack in a solar cell fabricated by high-density ICP-CVD on Asahi U substrate. The thickness of the *i*-layer was 400 nm. Spatially resolved diffraction pattern of the a-Si:H p-i-n stack showing to verify the amorphous phase of the stack.

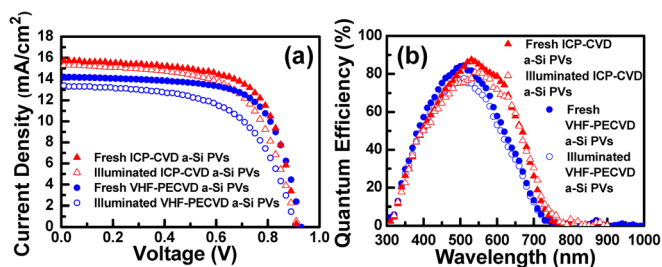


FIG. 2. (Color online) (a) I-V characteristics and (b): QE spectra of p-i-n solar cells fabricated by ICP-CVD (red-colored triangles) and VHF-PECVD (blue-colored circles) at 140°C . For comparison, the device characteristics (open symbols) after 10^4 -s exposure with 6-Sun irradiance at 60°C are also presented.

resolved diffraction pattern at the p-i-n stack presented in Fig. 1(b) clearly indicates the p-i-n stack to be an amorphous phase.

The current-voltage (I-V) curves of the solar cells prepared by ICP-CVD and VHF-PECVD are shown in Fig. 2(a). The sizes and *i*-layer thickness of the devices are 1 cm^2 and 400 nm, respectively. For the ICP a-Si solar cell, the PV conversion efficiency (η) was measured to be 9.6% under AM1.5 illumination. The device also has a fairly broad quantum-efficiency (QE) spectral profile (300–750 nm) (Fig. 2(b)), which can be attributed to a low density of defects in both the *i*-layer and at the interfaces. The broad QE spectrum also improves the absorption of broadband solar radiation by the *i*-layer, resulting in a high short-circuit current density (J_{sc}) of $15.7 \text{ mA}/\text{cm}^2$. We had succeeded in the preparation of good-quality heavily doped *p*- and *n*-layers, ensuring an open-circuit voltage V_{oc} as high as 0.91 V to be achieved. The low dark saturation current of $1.3 \times 10^{-9} \text{ A}/\text{cm}^2$, extracted from the dark I-V characteristics of the device, leads to an observed fill factor (FF) of 67.2%. For comparison, the VHF-PECVD a-Si solar cell reveals a conversion efficiency of 8.8% (Fig. 2(a)) with similar V_{oc} (0.92 V) and FF (67.6%). The short-circuit current density ($14.2 \text{ mA}/\text{cm}^2$) is lower than that of the ICP device due to a lower quantum efficiency in the long wavelength (550 nm–750 nm), suggesting a higher defect density in the absorber layer. We measured the quantum efficiency loss QE_{loss} , which is defined as the ratio of integration values of QE spectra measured at -1 V and 0 V , $QE(-1 \text{ V})/QE(0 \text{ V})$, and found QE_{loss} of ICP-CVD and VHF-PECVD a-Si solar cells to be 1.015 and 1.027, respectively (the inset table of Fig. 3). The slightly higher QE_{loss} of the VHF PECVD a-Si solar cell supports the notion that its *i*-layer has a higher defect density than the one grown with ICP-CVD.¹⁹

The major obstacle of amorphous Si PV technology is the low stability to light exposure. This Staebler-Wronski effect (SWE) originates from generation of extra defects in a-Si:H after recombination of charge carriers.^{8,9} In Fig. 2(a), the current-voltage (I-V) curves of the ICP a-Si solar cell shows a reduced conversion efficiency from 9.6% to 8.5% after 10^4 -s exposure with 6 Sun irradiance at 60°C . The PV efficiency drops by 11% (Fig. 3). While for the VHF PECVD a-Si solar cell, the I-V curves indicate a decrease in PV efficiency from 8.8% to 7.2%. The PV efficiency was degraded by 18% after 10^4 -s exposure under the same light-soaking condition (Fig. 3). The light-induced changes in I-V curves

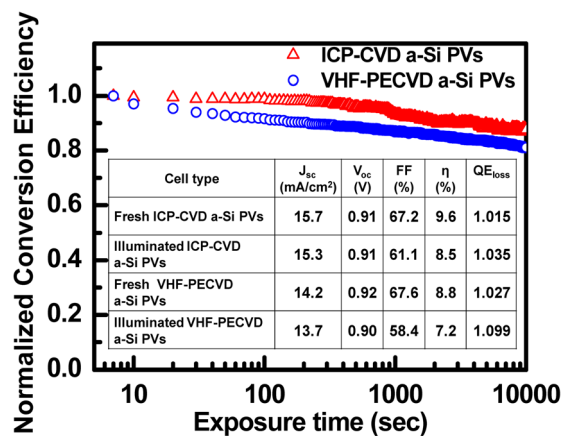


FIG. 3. (Color online) Conversion efficiency of a-Si:H p-i-n solar cells grown by ICP-CVD (open triangles) and VHF-PECVD (open circles) as a function of exposure time with a light irradiance of 6 Sun at 60 °C. The inset table shows the key parameters of above solar cells, including J_{sc} , V_{oc} , FF, η , and QE_{loss} .

mainly occur at a decrease in the fill factor and short-circuit current.

For thin-film solar cells, the major limitation on the PV efficiency originates from the trap-controlled transport. The defects in a-Si:H can act as recombination centers of carriers, which reduce the carrier lifetime and form charged defects that can further screen the electric field in the absorber layer of a solar cell. To more clearly reveal the underlying light-induced degradation process, we measured the defect density of intrinsic a-Si:H films as a function of exposure time with the DLCP method^{13,14} (Fig. 4). For the measurement, a-Si:H film with thickness of 400 nm was deposited on heavily doped *p*-type crystalline Si substrate at a temperature of 140 °C. A defect density of $3 \times 10^{15} \text{ cm}^{-3}$ in the ICP a-Si:H film was found, comparing to $6 \times 10^{15} \text{ cm}^{-3}$ in the VHF-PECVD a-Si:H. The lower defect density in the ICP a-Si:H may be due to more effective hydrogen passivation of dangling bond during layer deposition.⁸ The defect density of ICP a-Si:H film increases to $1.5 \times 10^{16} \text{ cm}^{-3}$ after 10^4 -s light-soaking with 6 Sun irradiance, comparing to $3.5 \times 10^{16} \text{ cm}^{-3}$ in the VHF-PECVD a-Si:H film under the same condition. Note that due to slower surface diffusion of SiH₃ on substrate at lower temperature, a defect density of 10^{15} cm^{-3} in a PECVD grown a-Si:H can only be achieved at a substrate temperature >250 °C. ICP system can maintain the mobility of the reactive radicals on substrate even at fairly low temperatures, combining with low ion bombardment on growing surface, leads to the deposition of a-Si:H layer at 140 °C with low defect density.

Light-induced degradation in a-Si:H was found to strongly depend on the amount of nano-sized voids and hydrogen content.¹² Recent experiments have shown that the SWE is accompanied by metastable structural changes of the underlying amorphous network.²⁰ The results of lower defect density in our ICP a-Si:H layers from the DLCP measurements and fewer defects being created by light soaking from our light soaking test support that the Si network in ICP deposited films is fairly stable and is therefore more resistant

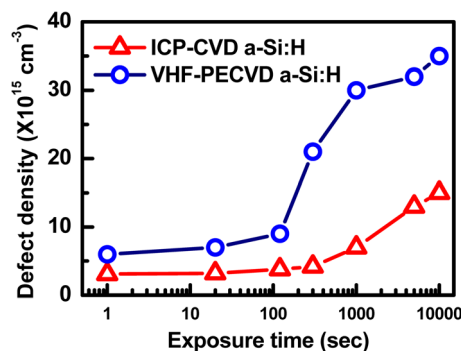


FIG. 4. (Color online) The defect densities retrieved from DLCP measurements of a-Si:H films deposited with ICP-CVD (open triangles) and VHF-PECVD (open circles) as a function of exposure time with a light irradiance of 6 Sun. The a-Si:H films with thickness of 400 nm were deposited on heavily doped *p*-type crystalline Si substrate at substrate temperature 140 °C.

to prolonged light exposure. The stability of ICP a-Si solar cell with low hydrogen content and nano-sized voids is attributed to the unique feature of high fractional ionization capacity of ICP-CVD.¹²

In summary, we developed high-density ICP-CVD system for solar cell applications. High quality a-Si:H films were deposited at a fairly low deposition temperature of 140 °C. Single-junction pin solar cells with 400-nm thick *i*-layer achieved a conversion efficiency of 9.6% with an improved light-soaking stability.

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