Research Article

Simulation and Experimental Study of Photogeneration and Recombination in Amorphous-Like Silicon Thin Films Deposited by 27.12 MHz Plasma-Enhanced Chemical Vapor Deposition

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Amorphous-like silicon (a-Si:H-like) thin films are prepared by 27.12 MHz plasma-enhanced chemical vapor deposition technique. The films are applied to p-i-n single junction thin film solar cells with varying i-layer thickness to observe the effects on the short-circuit current density, as well as the open-circuit voltage, fill factor, and conversion efficiency. The most significant experimental result is that J_{sc} has two different behaviors with increasing the i-layer thickness, which can be related to carrier collection efficiency in the long wavelength region. Furthermore, technology computer-aided design simulation software is used to gain better insight into carrier generation and recombination of the solar cells, showing that for the i-layer thickness of 200 to 300 nm the generation dominates the carrier density and thus J_{sc} , whereas for the i-layer thickness of 300 to 400 nm the recombination becomes the leading factor. The simulation results of cell performances are in good agreement with experimental data, indicating that our simulation has great reliability. In addition, the a-Si:H-like solar cells have low light-induced degradation, which in turn can have a great potential to be used for stable and high-efficiency solar cells.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) thin films have been widely studied in photovoltaic technology in recent years. Because of a high-absorption coefficient of a-Si:H in the visible range of the solar spectrum, 1 μm thick a-Si:H layer is enough to absorb 90% of usable solar energy. However, large deviations in bonding angles and bonding lengths between the neighboring atoms in a-Si:H result in the weak or strained bonds, which would easily break and thus form defects in the atomic network. As a result, a-Si:H suffers from the photoinduced problem of degradation, known as Staebler-Wronski effect, which reduces the efficiency of solar cells after light illumination. One alternative is the use of hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$), in which small crystals of highly ordered material in the range of tenths of nanometers

are embedded. The amplitude of the degradation is a function of the crystallinity of the $\mu\text{c-Si:H}$ layer: the lower the crystallinity, the higher the light-induced degradation. It is demonstrated more precisely that light-induced degradation is proportional to the ratio of the amorphous volume over the crystalline volume [1, 2]. For solar cell applications the $\mu\text{c-Si:H}$ absorber is typically larger than 1 μm representing an increase in production time and thus fabrication cost [3].

Recently a-Si:H-like materials, intermediate between a-Si:H and $\mu\text{c-Si:H}$, have been deposited [4, 5]. The films consist of silicon crystallites and/or clusters (less than 3 nm) which is difficult to be observed from the morphology of the films. Further, a-Si:H-like films have the same optical absorption coefficient as a-Si:H but the improved transport properties of $\mu\text{c-Si:H}$. In particular, the quantum efficiency-mobility-lifetime ($\eta\mu\tau$) product of electrons can be a factor of

TABLE 1: Deposition conditions of the intrinsic and doped a-Si:H-like layers.

Deposition condition	p-type a-SiC:H	Buffer layer	Intrinsic layer	n-type layer
Power (W)	10	10	10	10
Pressure (Pa)	90	90	90	60
E/S (mm)	20	20	30	25
Temperature (°C)	200	200	200	200
SiH ₄ flow rate (sccm)	20	20	40	40
H ₂ flow rate (sccm)	40	40	160	80
CH ₄ flow rate (sccm)	18	18	—	—
B ₂ H ₆ flow rate (sccm)	5	—	—	—
PH ₃ flow rate (sccm)	—	—	—	5
Layer thickness (nm)	10	6	200–400	30

100 higher than that of typical a-Si:H in the as-deposited state, while $\eta\mu\tau$ product values after light soaking are comparable to typical a-Si:H before degradation [6–8]. Furthermore, the values of the deep defect density estimated from an analysis of modulated photocurrent (MPC) are about 10 times lower than those of typical a-Si:H [9]. Although the basic properties of a-Si:H-like films have been proposed, the application in solar cell research is not well investigated [6–12].

In this study, we apply the a-Si:H-like films to fabricate p-i-n single junction solar cells and vary the i-layer thickness from 200 to 400 nm. Effects of the i-layer thickness on the device performances such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and conversion efficiency (η) are investigated. We use 27.12 MHz high-frequency plasma-enhanced chemical vapor deposition (HF-PECVD) to deposit silicon thin films, and the films almost always contain small crystalline fractions even under low H₂/SiH₄ gas ratios. This kind of a-Si:H-like films could also be obtained by 13.56 MHz radio frequency PECVD but usually requiring a high H₂/SiH₄ ratio which might dramatically decrease the deposition rate. Moreover, technology computer-aided design simulation software (TCAD) is used to gain better insight into charge carrier generation and recombination of the devices.

2. Experimental

The a-Si:H-like single junction thin film solar cells were fabricated with structure of Asahi SnO₂:F-coated glass/p/buffer/i/n/ZnO:Al/Ag. All of the Si layers were prepared by HF-PECVD at a frequency of 27.12 MHz. Diborane (B₂H₆) and phosphine (PH₃) gases were used as the doping gas to fabricate the a-Si:H-like p- and n-layers. To reduce the band offset between the energy bands of a wide band-gap p-type SiC (1.9 eV) and intrinsic layers, a buffer layer was used at the p/i interface [13, 14]. The detailed deposition conditions are summarized in Table 1. Five single junction solar cells were fabricated, and the i-layer thickness was varied from 200 to 400 nm. The electrical, optical, and structural properties of the i-layer a-Si:H-like films are listed

TABLE 2: The properties of a-Si:H-like films compared to those of typical a-Si:H films.

	a-Si:H	a-Si:H-like
Crystallinity (%)	—	12
Dark conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	1×10^{-10}	2.3×10^{-10}
Photo conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	1×10^{-5}	6.1×10^{-4}
Defect density (cm^{-3})	$\sim 10^{16}$	10^{15}
Hydrogen content (at.%)	15	10
Absorptivity at 400 nm (cm^{-1})	5×10^5	1.3×10^6
Absorptivity at 600 nm (cm^{-1})	3.5×10^4	7.5×10^4
Activation energy (eV)	0.8	0.76
Band gap (eV)	1.8	1.67

in Table 2 in comparison with a-Si:H. In Table 2, the values of the left column (a-Si:H) were obtained from [15]. The values of the right column (a-Si:H-like) were measured from our experimental films. The crystallinity was evaluated by micro-Raman spectroscopy. The dark conductivity was measured at room temperature using a source-measure unit (KEITHLEY 2400). The photoconductivity measurement was carried out under AM1.5G (100 mW/cm²) of a solar simulator. The defect density was obtained by electron spin resonance (ESR). The bonded hydrogen content was determined by Fourier transform infrared (FTIR) spectroscopy. The absorptivity was obtained by means of UV-VIS spectrophotometer. The activation energy was calculated from temperature-dependent dark conductivity measurements. The band gap was estimated by a linear fit to a Tauc plot. The area of individual solar cells was defined by the $1 \times 1 \text{ cm}^2$ sputtered ZnO:Al/Ag back contact. The film thickness was determined using an alpha-step profilometer. The solar cells were characterized by current density-voltage (J - V) measurement under 1-sun (AM1.5G, 100 mW/cm²) solar simulator irradiation and spectral response measurement from which external quantum efficiency (EQE) was obtained. The 1-sun standard light soaking test was performed in a climate chamber at 50°C for 500 h (IEC 61646).

To simulate thin film solar cells the commercially available software Silvaco TCAD, from Silvaco Inc., was used. The simulation program solved the Poisson equation coupled with the continuity equations of electrons and holes for the virtual device by dividing the whole structure into finite elements. The physical models that we used were Shockley-Read-Hall recombination model, concentration-dependent lifetimes, and low field mobility model. The photogeneration model, including a ray tracing algorithm, was used to calculate the absorption and transmission of light in the semiconductor layers. The solar cells considered here operate under the global standard solar spectrum (AM1.5G) illumination with 100 mW/cm² total incident power density. Table 3 lists the minimum set of input optical, electrical, and structural parameters used in this simulation without buffer layers between each layer. The theoretical values of the band mobility for a-Si:H-based thin films were around $1\text{--}10 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. The hole mobility was assumed to be smaller than the electron mobility. The i-layer thickness varied

TABLE 3: The minimum set of input parameters used in our simulation work.

Device parameter	Value		
Device area (μm^2)	1		
Average haze (%)	18		
Exterior rear reflectance (%)	95		
Light source	One sun (AM 1.5, 100 mW/cm^2)		
Layer parameters	p-layer	i-layer	n-layer
Thickness (nm)	10	200–400	10
Doping concentration (cm^{-3})	1×10^{18}	1×10^{10}	1×10^{19}
Mobility gap (eV)	1.92	1.67	1.7
Electron mobility (cm^2/Vs)	8	4	8
Hole mobility (cm^2/Vs)	2	0.7	2
Effective DOS in CB (cm^{-3})	2.0×10^{20}	2.0×10^{20}	2.0×10^{20}
Effective DOS in VB (cm^{-3})	2.0×10^{20}	2.0×10^{20}	2.0×10^{20}
Dielectric constant	11.9	11.9	11.9
Electron affinity (eV)	3.9	4	4
Tail state (cm^{-3})	10^{20}	10^{20}	10^{20}
Gaussian-state (cm^{-3})	5×10^{16}	5×10^{16}	5×10^{16}

between 200 and 400 nm, while both p- and n-layers were fixed to 10 nm, 30 nm, respectively. The average haze was set to be 18% for the device constructed with rough textured surfaces between layers. The distribution of states in the energy gap of a-Si:H assumed in the simulation is the general standard model of density of states (DOS), having two exponential band tails and two Gaussian distribution of states in the mobility gap [15, 16].

3. Results and Discussion

For each i-layer thickness, twenty solar cells were fabricated and they had very similar performances (error less than 5%). Figure 1 is a representative result of I - V curves of solar cells with different a-Si:H-like i-layer thickness. It can be seen that the cell with a 300 nm i-layer has the highest J_{sc} value of 17 mA/cm^2 , while the other cells show J_{sc} values around 15.5 – 16 mA/cm^2 . Only little variation in V_{oc} is seen, and this may agree to that V_{oc} would rather be affected by the qualities of thin film and p/i interface [17, 18]. From this result, the best combination of V_{oc} and J_{sc} can be found for an i-layer thickness of 300 nm.

Figure 2 shows the EQE of the cells with different a-Si:H-like i-layer thickness. The result is helpful to evaluate the carrier collection efficiency at a particular wavelength. It is found that the curves remain the same in the short-wavelength region ($<500 \text{ nm}$) for each i-layer thickness due to the good performances of the p-doped layer [19]. But the curves vary in the long-wavelength region ($>500 \text{ nm}$) with their peaks red-shifting. At the wavelength of 600 nm, the EQE values for the thickness of 200–400 nm are 61%, 65%, 69%, 68%, and 63%, respectively. It is interesting to clarify that the EQE differences in the long-wavelength region might result from the thickness variation rather than the crystalline fractions in the a-Si:H-like films. This can also be evidenced

FIGURE 1: Experimental I - V characteristics of a-Si:H-like solar cells with different i-layer thickness.

FIGURE 2: Experimental quantum efficiencies of a-Si:H-like solar cells with different i-layer thickness.

by the observation that the cutoff wavelength of each cell is about 800 nm, same as that of a-Si:H.

Figure 3 shows a comparison of the i-layer thickness dependences between experimental (closed symbol) and simulation (open symbol) data. The simulation results show that FF monotonously decreases with the i-layer thickness due to the longer carrier transport length and thus increased series resistance. The V_{oc} is calculated from [20]

$$V_{oc} = \frac{kt}{q} \ln \left(\frac{J_{sc}}{J_0} \right) + \frac{qw_d^2}{2\epsilon} \left(\frac{N_i N_p}{N_i + N_p} \right), \quad (1)$$

where J_0 is the temperature-independent saturation current, w_d is the depletion width which usually equals to the i-layer

FIGURE 3: Simulated (open symbol) and experimental (closed symbol) results of external parameters of a-Si:H-like solar cells with different i-layer thickness.

thickness for a p-i-n device, and N_i and N_p are the majority carrier concentration in the i-layer and in the p-layer, respectively. The last part of the equation is the built-in voltage across the i-layer. Therefore, V_{oc} would vary depending on the values of w_d and J_{sc} . For the i-layer thickness of 300–400 nm, the loss in V_{oc} caused by the decreased J_{sc} is compensated by the increased w_d . Finally, the trend of η is similar to that of J_{sc} implying that the cell efficiency is mainly dominated by J_{sc} . Overall, the trends of the simulation results match well with that of experimental ones.

FIGURE 4: Simulated carrier generation rate and recombination rate as a function of the i-layer thickness.

Figure 4 shows the generation rate, $g(x)$, and the recombination rate, $r(x)$, of hole-electron pairs to further explain the J_{sc} behavior. In the textured i-layer, $g(x)$ with respect to a certain point, x , is based on [21]

$$g(x) = \int [1 - R^2(\lambda)] S(\lambda) \alpha(\lambda) e^{-\alpha x} d\lambda, \quad (2)$$

where $R(\lambda)$ is the reflectance, $S(\lambda)$ the incident photon flux (photon $\text{cm}^{-2}\text{s}^{-1}$) of the AM1.5G solar spectrum, and $\alpha(\lambda)$ the absorption coefficient. We assume R is squared due to the textured surface that reduces the reflection. The y-axis scale is logarithmic showing that there is an enormously greater generation of electron-hole pairs near the front side of the i-layer, while further into the solar cell the generation rate exponentially decreases and finally becomes nearly constant. On the other hand, the recombination of charge carriers is assumed to be determined by Shockley-Read-Hall recombination with a recombination rate given by [22, 23]

$$r(x) = \frac{n(x)p(x) - n_i^2}{\tau_p [n(x) + n_i] + \tau_n [p(x) + n_i]}, \quad (3)$$

where $n = n_0 + \Delta n$, $p = p_0 + \Delta p$, n_0 , p_0 are the equilibrium carrier densities, Δn , Δp are the excess carrier densities, τ_n , τ_p are the carrier lifetimes at the dangling bond state D^0 , and n_i is the intrinsic carrier density. Since most of photons are absorbed in the front part of the i-layer, the regions close to p/i interface have a high recombination rate. The total generation, G , and the total recombination, R , in the i-layer can be given by

$$G = \int_0^d g(x) dx, \quad (4)$$

$$R = \int_0^d r(x) dx.$$

FIGURE 5: The total generation and recombination of solar cells with different i-layer thickness. The inset of Figure 6 shows the calculation result of the net charge carrier density for each i-layer thickness.

Note that the integral should be extended only from $x = 0$ to the value of corresponding thickness, d . The calculation results are plotted in Figure 5. The total generation increases rapidly with the i-layer thickness, and a saturation occurs since the contribution at the deeper region of the i-layer can be neglected. Therefore, it is easy to obtain the net free carrier concentration, N_{net} , as given by

$$N_{\text{net}} = G - R. \quad (5)$$

The calculation result of N_{net} is illustrated as an inset in Figure 5. The trend is consistent with that of J_{sc} observed from the experimental I - V measurement. However, N_{net} would finally be a constant indicating that J_{sc} would still saturate after a temporary decrease. It is interesting that if the texture is not considered, the saturation of the generation will shift to the thick region. As a consequence, N_{net} simply increases and then saturates without having a decrease.

Figure 6 shows the conversion efficiencies of the cells after 500 h exposure to 100 mW/cm² AM1.5G light for different i-layer thickness. It can be seen that degradation increases from 8.39% to 16.96% as i-layer thickness increases. The i-layer thickness of 300 nm shows the best stabilized efficiency of 9% and a degradation of 11% smaller than the typical value (>15%) observed from a-Si:H solar cells. The 200 nm and 250 nm thick i-layers show lower initial efficiencies of 9.65% and 9.88%, respectively, but their stabilized efficiencies are close to that of the 300 nm thick i-layer. Degradation in the cells with the 350 and 400 nm thick i-layer are about 13.2% and 16.9%, respectively. Apparently, the thicker cells have a higher degradation, and this might be attributed to two reasons. First, a thick absorber leads to a weak electric field, which in turn decreases the carrier collection efficiency. Second, the total amount of the light-induced defects caused by the hydrogen out-diffusion from Si-H bonds is larger

FIGURE 6: Light soaking effect for solar cells with different i-layer thickness.

for thicker absorbers. These defects will further flatten the electric field and thus increase the degradation.

4. Conclusions

In conclusion, the a-Si:H-like films deposited by 27.12 MHz PECVD have been applied to p-i-n single junction solar cells to investigate the influences on photovoltaic performances. The TCAD simulation result is in good agreement with the experimental data, showing great reliability. The carrier generation and recombination profiles are shown to explain the J_{sc} behavior. The generation dominates the device current density when the thin absorber is used, while for the thicker absorber the recombination begins to offset the current gain and results in a temporary reduction in J_{sc} . The i-layer thickness of 300 nm can have the optimum balance between the generation and the recombination. The solar cell with the 300 nm i-layer also has a comparable initial efficiency and a low degradation compared to that of a-Si:H cells. As a result, the thin absorber and good stability make the a-Si:H-like material suitable for solar applications.

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