Open-circuit voltage analysis of p–i–n type amorphous silicon solar cells deposited at low temperature*

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This paper identifies the contributions of p–a–SiC:H layers and i–a–Si:H layers to the open circuit voltage of p–i–n type a–Si:H solar cells deposited at a low temperature of 125 °C. We find that poor quality p–a–SiC:H films under regular conditions lead to a restriction of open circuit voltage although the band gap of the i-layer varies widely. A significant improvement in open circuit voltage has been obtained by using high quality p–a–SiC:H films optimized at the "low-power regime" under low silane flow rates and high hydrogen dilution conditions.

Keywords: amorphous silicon, solar cell, low temperature, open-circuit voltage

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1. Introduction

A reduction in the fabrication costs of thin-film silicon solar cells[1] can be achieved by using cheap plastic substrates, with the added benefits of flexibility and reduced weight.[2] The deposition of thin film silicon layers at a very low substrate temperature (around 120 °C) opens the way for a variety of temperature-sensitive polymer substrates, such as PET and PEN.[3,4] Due to its high optical quality, PET can be used in the same manner as glass substrate for fabricating p–i–n type amorphous silicon (a–Si:H) solar cells, augmenting industrialized production.

It is well known that a–Si:H contains more hydrogen and its bandgap increases when the deposition temperature is lower.[5] The open circuit voltage (V_{oc}) of a–Si:H solar cell depends on the built-in potential and therefore wide bandgap materials may be expected to show a higher V_{oc}.[6] Great effort has been made in the past decade to optimize the performance of a–Si:H solar cells deposited at low temperatures. However, most V_{oc} values are between 0.90 V to 0.92 V,[7−9] which are relatively low in comparison with what is expected for an i-layer with a band gap of 2.0 eV, and it is expected to be higher in comparison with the high temperature cell, which has a much lower band gap (∼1.8 eV).

In this paper, we report our studies of the V_{oc} of p–i–n type a–Si:H solar cells prepared by a radio-frequency plasma-enhanced chemical vapour deposition (RF-PECVD) technique at a low temperature of 125 °C. We attempted to establish a relationship between the changes in V_{oc} with the changes in the properties of p–a–SiC:H and i–a–Si:H layers. The effect of the electrical properties of p layers and the band gap of p and i layers on V_{oc} has been investigated in detail. We observe that the p–a–SiC:H layer properties play a more important role than the band gap of i layers in improving the properties of a–Si:H solar cells at low temperatures. High quality p–a–SiC:H films were optimized at the "low-power regime" under low silane flow rates and high H_2 dilution conditions. Based on this technique, a significant improvement in the V_{oc} of a–Si:H solar cell has been achieved.

2. Experimental details

All films and solar cells were deposited in an in-line seven-chamber RF-PECVD system at a low temperature of 125 °C. The plasma-excitation frequency of the system was 13.56 MHz. For i–a–Si:H films, the silane concentrations ($SC = SiH_4/SiH_4+H_2$) were var-

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ied from 20% to 4%, whereas the total pressure and RF power were kept at 85 Pa and 10 W, respectively. The p–a–SiC:H films were deposited from appropriated gaseous mixtures of SiH_4, CH_4, H_2, and B_2H_6.

We deposited p–a–SiC:H and i–a–Si:H films on both Corning 7059 glass substrates and crystalline silicon wafers. The films deposited on glass substrates were used for Raman spectroscopy, conductivity, reflectance-transmittance, and thickness measurements. The films fabricated on silicon wafers were used for Fourier-transform infrared (FTIR) absorption spectroscopy measurements. Raman spectroscopy was performed by using an Ar^+ laser with a wavelength of 488 nm. The FTIR spectra were taken by using a Magna 560E.S.P. in the wave number range of 400 cm^{-1}–4000 cm^{-1}. Reflectance and transmittance measurements were performed at normal incidence in the spectral range between 200 nm and 1800 nm with a double beam Cary 5000 spectrophotometer. The band gap E_{04} is normally given for the absorption coefficient $\alpha = 10^4$ cm^{-1}.

The a–Si:H solar cells were deposited in a p–i–n sequence on SnO_2:F coated glass (Asahi U-Type glass) substrates at a low temperature of 125 °C. The structure of the solar cells was glass/SnO_2:F/p–a–SiC:H (15 nm)/buffer (5 nm)/i–a–Si:H/n–a–Si:H (30 nm)/Al. The photo J–V characteristics for the fabricated solar cells were measured at 25 °C under 1-sun (AM1.5, 100 mW/cm^2) solar simulator radiation. A quantum efficiency (QE) measurement was also performed to evaluate the spectral response of the fabricated cells.

3. Results and discussion

With the objective of increasing the optical band gap and obtaining a higher V_{oc} for a p–i–n solar cell, intrinsic a–Si:H films were deposited under different SCs at a substrate temperature (T_s) of 125 °C. Figure 1 shows the variation in the optical band gap (E_g) of i–a–Si:H films as a function of SC. Compared with the reference film made at a high temperature of 200 °C, the E_g of i–a–Si:H at 125 °C increased from 1.78 eV to 1.87 eV at SC = 20%. The previous studies[10] of FTIR spectra show that lowering the T_s results in a significant increase in the amount of the SiH_2 bond, which leads to a high E_g but a remarkable deterioration of electronic properties. With the decrease in SC from 12% to 6%, E_g increases monotonically from 1.82 eV to 1.88 eV. The E_g widening is principally due to a high hydrogen content, mostly in the form of monohydride of silicon. On the other hand, at lower SCs, the enhanced concentration of atomic hydrogen facilitates the diffusion of radicals and also the structural relaxation of the Si–Si network of a–Si:H films, which play some role in increasing the E_g of the i-layer. With a further decrease in SC to 5.2%, the E_g begins to decrease due to the structural change from the amorphous phase to a mixed amorphous + microcrystalline phase, as shown in the inset of Fig. 1.

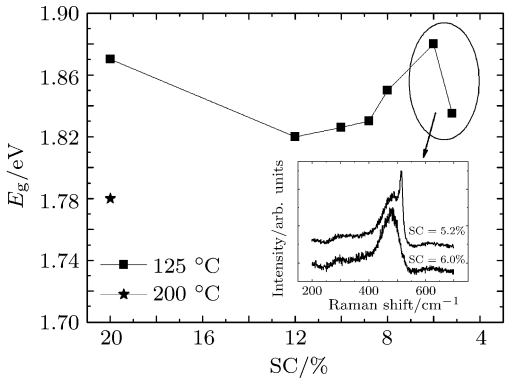


Fig. 1. The E_g of i–a–Si:H deposited at different silane concentrations (SCs). Inset: Raman spectra of i–a–Si:H with SC= 6% and SC = 5.2%.

As the window layers of thin film silicon solar cells, a high optical band gap together with low activation energy will result in a high built-in potential (V_{bi}) and a high V_{oc}. Table 1 presents the dark conductivity (σ_d), photo conductivity (σ_{ph}), photosensitivity (σ_{ph}/σ_d), activation energy (E_a), and optical band gap (E_{04}) of p–a–SiC:H films deposited at a relatively high temperature 215 °C and a low temperature of 125 °C. It is clear that P_0 at 215 °C exhibits high σ_d (1.4×10^{-7} S/cm) in conjunction with high E_{04} (2.00 eV), which is suitable for the window layer of a–Si:H solar cell. However, there is a trade-off between the wide band gap and high conductivity in optimizing p–a–SiC:H films, especially at low temperatures below 150 °C.[7,11] As listed in Table 1, P_1 has similar deposition parameters to P_0, except for a decrease of T_s to 125 °C. The σ_d and E_{04} drop dramatically due to the low temperature deposition process. Then, as a result of increasing doping concentration (DC = $B_2H_6/(SiH_4 + CH_4)$) from 1% to 2%, the σ_d of P_2 increases to 2.5×10^{-7} S/cm, while the E_{04} decreases to 1.71 eV.

Two series of p–i–n type a–Si:H solar cells were deposited with different p layers and the SCs of i layers, while other process parameters were kept constant. The variations in V_{oc} values of a–Si:H solar cells with P_1 and P_2 window layers as a function of the SC of the i-layer are shown in Fig. 2. The V_{oc} values remain nearly constant at each kind of p-layer while the

Table 1. Dark conductivity (σ_d), photo conductivity (σ_{ph}), photosensitivity (σ_{ph}/σ_d), activation energy (E_a), and optical band gap (E_{04}) of p–a–SiC:H films at 125 °C and 215 °C.

Sample	T_s/°C	σ_d/S·cm^{-1}	σ_{ph}/S·cm^{-1}	σ_{ph}/σ_d	E_a/eV	E_{04} /eV
P_0	215	1.4×10^{-7}	3.0×10^{-7}	2.2	0.54	2.00
P_1	125	5.2×10^{-8}	2.1×10^{-7}	4.0	0.60	1.80
P_2	125	2.5×10^{-7}	8.5×10^{-7}	3.4	0.46	1.71

E_g of the i-layer varies from 1.82 eV to 1.88 eV. The a–Si:H solar cells with higher σ_d p-layers but lower E_{04} (sample P_2) obtain higher V_{oc} values at around 0.93 eV to 0.94 V.

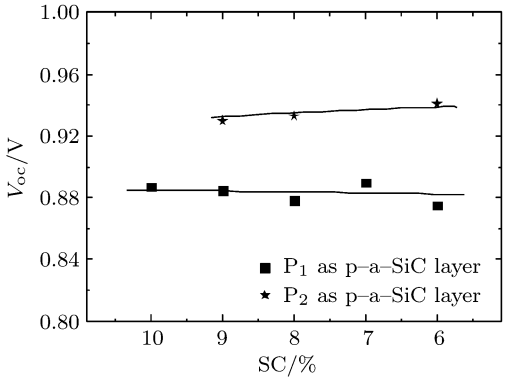


Fig. 2. The V_{oc} values of a–Si:H solar cells with different p–a–SiC:H layers as a function of the SC of the i-layer.

It is well known that the V_{oc} of a p–i–n a–Si:H solar cell depends on built-in potential (V_{bi}), which is set up by the doped layers. In such a model, the V_{bi} is given by[6,12,13]

$$V_{bi} = E_g(\text{p layer}) - E_a(\text{p layer}) - E_a(\text{n layer}). \quad (1)$$

Thus, the V_{bi} values of a–Si:H solar cells with P_1 and P_2 calculated by Eq. (1) are 0.96 V and 1.01 V, respectively. On the other hand, the E_g of either P_1 or P_2 is lower than the lowest E_g of the i-layer (1.82 eV), which may lead to a restriction of V_{oc} values by the properties of the p-layer.

In order to obtain both high σ_d and wide E_g at a low temperature of 125 °C, p–a–SiC:H films were optimized at the "low-power regime" under low SiH_4 flow rate conditions, which has been proven to be an effective method for obtaining high quality wide band gap a–SiC:H films at high temperatures.[14,15] In this case, the RF power is sufficient to break the SiH_4 molecules, but insufficient for the more stable CH_4 bonds. Therefore, all the carbon atoms in the p–a–SiC:H films are incorporated through chemical reactions between SiH_4 radicals and methane molecules. In this mode, the growth mechanism of a–SiC:H films are much simplified and easier to control.

At a low temperature of 125 °C, p–a–SiC:H films from standard PECVD suffer from inferior structural quality due to a decrease in diffusion length of the precursors on the growing surface, which causes a remarkable deterioration of their electronic properties. It seems reasonable that "low-power regime" conditions will reduce the structural disorder and improve both the optical and electronic properties of p–a–SiC:H films.

Several series of p–a–SiC:H films at 125 °C were studied by varying the CH_4 concentrations ([CH_4] = $CH_4/(CH_4+SiH_4)$ %) with different B_2H_6 concentrations (DC). The DC varies from 0.5% to 2%. Figure 3 shows the variation in the σ_d and E_{04} of the p–a–SiC:H films with DC for [CH_4] = 60% and 50%. The results indicate that the σ_d increases with DC for the entire series, which can be attributed to an increase in the doping level. On the other hand, the E_{04} of both series drops dramatically from ∼2.0 eV to 1.84 eV with increasing DC, which is often attributed to the removal of hydrogen bonds[16] or the increase in disorder in the network and the broadening of the band tails produced by doping.[17]

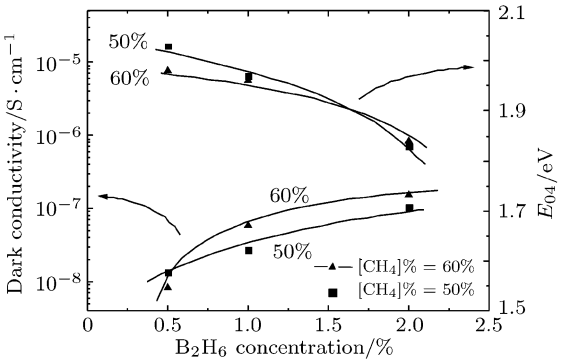


Fig. 3. The σ_d and E_{04} of p–a–SiC:H films with different CH_4 concentrations ([CH_4] = 60%, 50%) as a function of the B_2H_6 concentration (DC). The lines are intended as visual guides.

In this case, sample P_3 is chosen with the deposition conditions of [CH_4] = 60% and DC = 1%. Then, a relatively high σ_d of 1.5×10^{-7} S/cm together with wide E_g of 1.84 eV is achieved. Figure 4 shows the variation in V_{oc} and FF of a–Si:H solar cells with different SCs of the i-layer by utilizing a P_3 window layer. The V_{oc} increases continuously and then decreases when the SC of the i-layer decreases from 8% to 4%. A high V_{oc} of 0.96 V is obtained before the onset of the transition region from amorphous to microcrystalline phase. On the other hand, the FF decreases continuously over the whole SC range. We

speculate that the band edge discontinuities between the p-layer (1.84 eV) and wide E_g i-layers (> 1.85 eV) significantly influence the interface resistance and also built-in potential of a–Si:H solar cells.

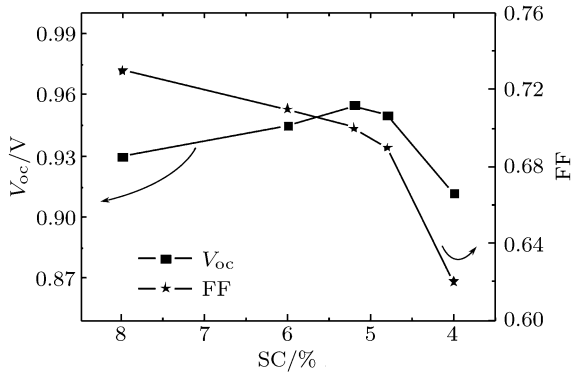


Fig. 4. The V_{oc} and FF of a–Si:H solar cells with different SCs of the i-layer.

The spectral response of the quantum efficiency (QE) of a–Si:H solar cells contains valuable information about the contributions to the photovoltaic performance. Figure 5 shows the QE curves of a–Si:H solar cells with different SCs of the i-layer. The cell deposited at 200 °C with the same i-layer thickness is shown as a reference. As shown in the inset of Fig. 5, it is clear that the "cutoff wavelengths" at QE = 0.2 decrease continuously as the i-layer band gap increases, demonstrating a good match with the increase in V_{oc} values.

In order to achieve further improvement of the properties of p–a–SiC:H window layers, high hydrogen dilution series were developed on the basis of the "low-power regime" series. The hydrogen dilution ratio (R_H) is defined as $R_H = H_2/(CH_4+SiH_4)$. Two series of lower R_H(=60) and higher R_H(=76) were prepared by changing CH_4 concentrations ([CH_4]) of 0, 22%, 44%, 66%, 88%, 100%, and 33%, 44%, 55%, respectively. The deposition rate of direct decomposition of pure CH_4 (sample at [CH_4] = 100%) is vanishingly slow, which can be used as a practical definition of the "low-power regime".[14] As shown in Fig. 6(a), there is a tendency for both σ_d and σ_{ph} to decrease as [CH_4] increases, while the σ_d of the two series are almost all higher than 1.0×10^{-7} S/cm (except for the high carbon condition of [CH_4] = 88%). We can also see in Fig. 6(b) that the photo sensitivities of p–a–SiC:H films deposited at high hydrogen dilution conditions show relatively high values of over 20 when the [CH_4] is lower than 50%. It is highly possible that the structural disorder in the films and also the gap state density around the Fermi level decrease[18,19] with increasing R_H for p–a–SiC:H films, which leads to a high σ_{ph} and photo sensitivity.

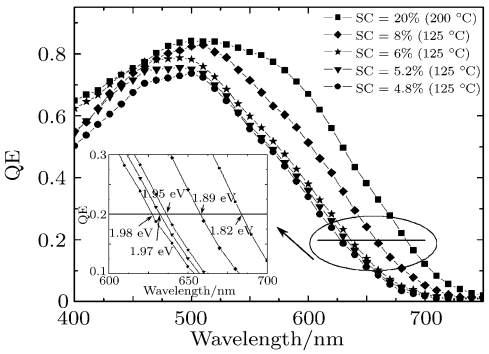


Fig. 5. The QE curves of a–Si:H solar cells with different SCs of the i-layer. Inset: close-up on long wave areas of QE curves. The "cutoff wavelengths" at QE = 0.2 correspond to 1.82, 1.89, 1.95, 1.97, 1.98 eV, respectively.

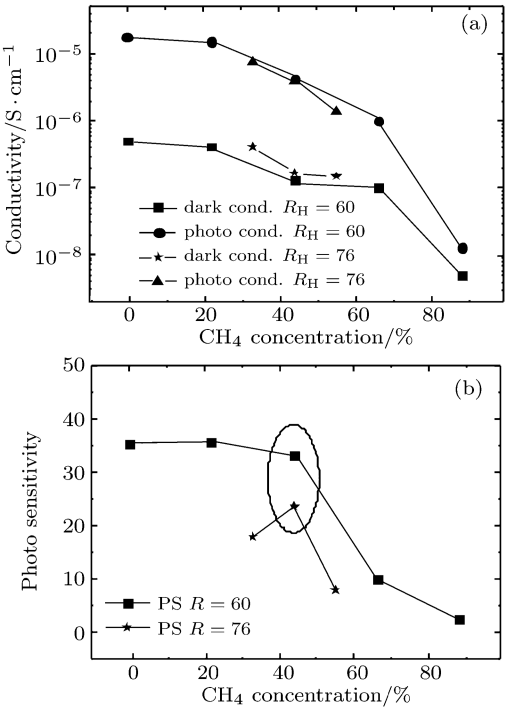


Fig. 6. The dark conductivity (σ_d), photo conductivity (σ_{ph}) (a) and photo sensitivity (σ_{ph}/σ_d) (b) of p–a–SiC:H films with different R_H (R_H = 60, 76) as a function of [CH_4].

Furthermore, the relationship between E_g of p–a–SiC:H layers and V_{oc} of a–Si:H solar cells for the two R_H series was investigated. Figure 7 shows the ΔE_g of p–a–SiC:H films with different R_H (R_H = 60, 76) as a function of [CH_4]. The E_g of p–a–Si:H film deposited at [CH_4] = 0% was used as a reference. It is clear that the E_g of both R_H series increases as [CH_4] increases. The R_H = 76 series shows higher band gaps than R_H = 60 at similar [CH_4], which is

beneficial to improve the structural order and doping efficiency of wide gap p–a–Si:H films. Thus, the highest V_{oc} of 1.01 V for a p–i–n type a–Si:H solar cell was achieved with high property p–a–SiC:H films of $\sigma_d = 1.7 \times 10^{-7}$ S/cm, $\sigma_{ph}/\sigma_d = 24$ and $E_{04} = 2.02$ eV.

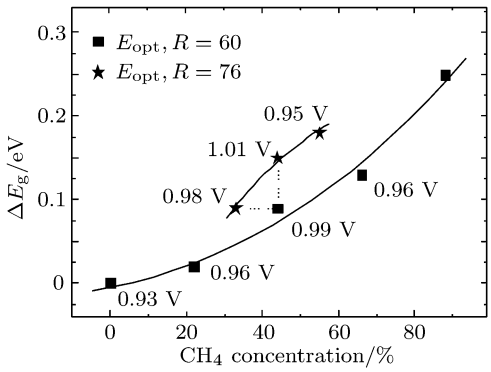


Fig. 7. The ΔE_g of p–a–SiC:H films with different R_H ($R_H = 60, 76$) as a function of [CH_4]. The E_g of p–a–Si:H film deposited at [CH_4]=0% was used as a reference. The V_{oc} values shown in the figure indicate the maximum V_{oc} of a–Si:H solar cells achieved by using the relative p–a–Si:H films.

Figure 8 shows the initial photo J–V characteristics for the fabricated p–i–n type a–Si:H solar cells. At a low temperature of 125 °C, a single junction a–Si:H solar cell with an efficiency of 7.5% ($V_{oc} = 0.97$ V) was obtained by using the best p–a–SiC:H layer and an SC = 8% i-layer. High V_{oc} of a 1.01-V a–Si:H solar cell was achieved by changing the SC of the i-layer to 5.2%, which is promising for use as the a–Si:H top cell of a–Si/μc–Si tandem solar cells.

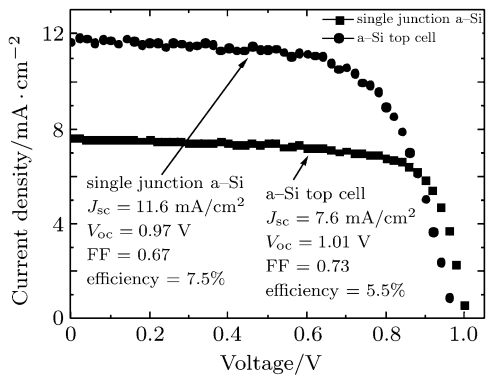


Fig. 8. The initial photo J–V characteristics for the fabricated p–i–n type a–Si:H solar cells.

4. Conclusion

In summary, high quality p–a–SiC:H window layers and a–Si:H solar cells have been fabricated at a low temperature of 125 °C by a RF-PECVD technique. The p–a–SiC:H films deposited under regular conditions at low temperatures show low band gap values, which lead to a restriction of V_{oc} though the E_g of the i-layer varies widely. High-ordered p–a–SiC:H films with high electrical properties and wide band gaps were optimized at the "low-power regime" under low SiH_4 flow rates and high hydrogen dilution conditions. With the combination of a wide band gap p–a–SiC:H window layer and the i-layer, a high V_{oc} of 1.01 V was obtained for a single junction a–Si:H p–i–n solar cell, which is promising for use as the top cell in an a–Si/μc-Si tandem structure.

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