Control of electron temperature in SiH₄/H₂ plasma for obtaining high photovoltaic performance in microcrystalline silicon solar cells

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Abstract. We have proposed two novel processes for the formation of fine n/i interface to improve the photovoltaic performance in substrate-type (n-i-p type) hydrogenated microcrystalline-silicon (μc-Si:H) solar cells whose i layer is deposited at high growth rate of > 2.0 nm/sec; (1) gradual monosilane-(SiH₄)-molecule-introduction method and (2) amorphous silicon (a-Si:H) thin-layer-insertion method. When applying these two methods to the formation process of n/i interface in the solar cells, drastic improvement of the production reproducibility has been achieved in the fabrication process of high efficiency (> 9%) substrate-type μc-Si:H solar cells.

1. Introduction

Plasma-enhanced chemical-vapor-deposition (PECVD) method is popularly used to prepare high quality (low dangling-bond-defect density) hydrogenated microcrystalline silicon (μc-Si:H) films as the same process as hydrogenated amorphous silicon (a-Si:H) films. Since μc-Si:H shows high stability upon light soaking in contrast to a-Si:H, μc-Si:H is recognized as promising materials for application to solar cells [1][2]. However, photoactive-intrinsic-layer (i-layer) thickness in μc-Si:H solar cells is around 2 μm to absorb sufficient sun light. Therefore, high rate growth (> 2.0 nm/sec) of i layer is necessary condition to reduce the production cost of relevant solar cells. To increase the growth rate, being determined by the generation rate of film precursor (silyl radical; SiH₃) in the plasma, high SiH₄-gas-flow rate (high SiH₄ density) and high electron density in the plasma are required [3]. For these purposes, very high frequency (VHF) is used as the power-source frequency to obtain high electron-density plasma with low electron temperature [4][5]. Assuming that the electron-energy-distribution function (EEDF) obeys Maxwell-Boltzmann distribution, the generation-rate ratio of short lifetime species (Si, SiH, and SiH₂ whose generation-threshold energy is more than 9 eV) to film-growth precursors (SiH₃ whose threshold is almost 8 eV) is kept low under low electron-temperature conditions [6][7], resulting in a possible growth of high quality (showing low dangling-bond-defect density) μc-Si:H films. On the other hand, high quality μc-Si:H films are obtained under high working-pressure conditions by making a good use of chemical reactions of short lifetime species (Si, SiH, and SiH₂) with H₂ molecule in the plasma [8] despite that these reaction-rate constants are almost two orders of magnitude lower than the reactions of short lifetime species with SiH₄ molecule. Although high working-pressure condition is effective to decrease the defect density in the resulting film, higher-order-silane molecules (powder-like species) tend to be formed under the coexisting...
condition of high density-SiH₄ molecules and high density electrons in the plasma. Coexisting condition appears especially at the initial stage of film growth, since SiH₄ molecules are not depleted as yet. Once the powder formation occurs, electron-attachment event to powder gives rise to an elevation of electron temperature in the plasma due to an increase in the electron-loss rate, which leads to an increase of the defect density in the resulting film through an increase of generation-rate ratio of short lifetime species to SiH³ in the plasma. Therefore, the control of powder-formation process at the initial stage of film growth is a key issue to obtain high quality µc-Si:H-i layer not only at the n/i interface part but also in the bulk-i region in the n-i-p type solar-cell structure.

In this paper, we describe a method to control the production of higher-order-silane molecules (initiation step of powder-formation process) at the initial stage of film growth by applying gradual SiH₄-introduction method to the growth of intrinsic µc-Si:H films in order to realize high-SiH₄-depletion condition from the start. We also propose a novel method to avoid so-called “auto doping” phenomenon of phosphorus (P) atoms into i layer from underlying n layer to form well-controlled fine n/i-interface in the n-i-p-type µc-Si:H solar cells whose i layer is prepared at a high growth rate more than 2 nm/sec.

2. Experimental methods

2.1. Control of starting procedure for film growth and plasma diagnosis

To control the powder-formation process and obtain high quality µc-Si:H, we have adopted a gradual SiH₄-introduction method to adjust the SiH₄-partial pressure from the start of film growth. The intrinsic µc-Si:H film was prepared using the capacitively-coupled VHF(100 MHz)-PECVD system with a conventional shower-head cathode at the deposition rate of 2.2 nm/sec. H₂-flow rate, power density, electrode distance, and substrate temperature were fixed at 168 sccm, 0.17 W/cm², 6.0 mm, and 213 °C, respectively. The SiH₄-gas-introduction scheme is shown in Fig. 1. After turning on the H₂ plasma with working pressure of 9.0 Torr, SiH₄ was fed into the plasma with two different introduction times (15 sec and 120 sec from 0 to 3 sccm) as shown in the figure. The waiting times of 5 sec and 30 sec were set before starting the SiH₄ introduction in order to stabilize the H₂ plasma and to know the effect of the waiting time on the properties of n/i interface in the solar cell structure.

Optical emission spectroscopy (OES) is used as the monitoring system of plasma parameters. To know the change of electron temperature in the plasma, Hα-emission (λ = 656.3 nm) intensity is utilized in this study.

In the steady state plasma, density of Hα in the plasma is given by

$$ \frac{d [H_α]}{dt} = N_{eh}σ_h v_e [H_2] - \frac{[H_α]}{τ_{H_α}} = 0, \quad \frac{[H_α]}{τ_{H_α}} = I_{Hα} $$

where $N_{eh}$, $σ_h$, and $v_e$ are electron density for Hα formation, dissociative excitation-cross section of H₂ to Hα, and electron thermal velocity, respectively. The Hα-emission intensity ($I_{Hα}$) is then given by

$$ I_{Hα} = N_{eh}σ_h v_e [H_2] x f(T_e). $$

Under the high H₂-dilution-ratio (sufficient H₂ density [H₂]) condition, Hα-emission intensity is sensitive only to the high energy electron density for Hα formation, being the function of electron temperature in the plasma. Therefore, when monitoring the Hα-emission intensity, we know the change of electron temperature in the highly H₂-diluted SiH₄/H₂ plasmas.

2.2. Fabrication of n-i-p type µc-Si:H solar cells

Structure of µc-Si:H solar cell is Asahi type-U glass/ Ag/ ZnO:Al/ n-i-p µc-Si:H/ top-TCO/ Ag-grid. Intrinsic µc-Si:H layer was adjusted at 2 µm in thickness. Asahi type-U glass was used as the substrate to unify the surface roughness of solar cells, in which the textured surface structure scatters the incident sun light for effective light absorption by the extension of light pathway [9]. The root-mean-square (RMS) roughness of Asahi type-U glass is approximately 40 nm. The Ag layer was prepared by
radio frequency (RF: 13.56 MHz) magnetron-sputtering method as the back electrode. Top transparent conductive oxide (TCO) was composed of titanium-doped indium oxide (InTiO) and aluminum-doped zinc oxide (ZnO:Al) stacked layers for reducing the incident-light reflection with refractive-index engineering [10]. Each TCO was prepared by RF-magnetron-sputtering method. Phosphorus-doped n-type μc-Si:H and boron-doped p-type μc-Si:H was prepared by RF-PECVD.

To control the powder-formation process especially at the initial stage of i-μc-Si:H growth, gradual SiH₄-introduction method was adopted with the same time-evolution scheme as shown in Fig. 1. Thinking of the process reproducibility, another time-evolution scheme for SiH₄-gas introduction was adopted as shown in Fig. 2, where the waiting time was varied to stabilize H₂ plasma before the introduction of SiH₄. To understand the effect of waiting time, i.e., the exposure time of n layer in the n-i-p type solar-cell structure to high flux density of atomic hydrogen from the plasma, two different waiting times of 5 sec and 30 sec were tested.

3. Results and discussion

3.1. Control of electron temperature in the plasma

Figure 3 shows the time evolution of Hα-emission intensity (electron temperature in this case) for two different SiH₄-introduction times. Both for (a) and (b), the electron temperature is once decreased after introduction of SiH₄ molecules into H₂ plasma, being explained as follows. H₂ ions (H₂⁺ and H₃⁺) are the predominant positive ions in the H₂ plasma. When increasing the ratio of heavier positive ions such as SiH₄⁺ by the SiH₄ introduction into the H₂ plasma, the electron temperature is decreased owing to the reduction of ambipolar diffusion-loss rate of electrons. The electron temperature then starts to increase by the further increase of SiH₄-flow rate, which is due to an increase of electron-loss rate owing to the electron-attachment events to the powder-like higher-order-silane molecules (SiₙH₂ₙ₊₂, n > 5) produced in the plasma. In addition, at the turning point of electron-temperature after showing the minimum point, i.e., from (A) to (B) and (A’) to (B’) in Fig. 3, the structure of plasma is changed from

![Figure 3](image3.png)

**Figure 3.** Time evolution of Hα-emission intensity for two different SiH₄-introduction times.

![Figure 4](image4.png)

**Figure 4.** Picture of the plasma at the time (A), (B), (A’), and (B’) in Fig.3 showing the structure transition from double (A and A’) to single emission (B and B’).
double (two lines are seen near the sheath regions between plasma and electrodes) to single (only one bright region is seen between both electrodes) structure as shown in Fig. 4. Drastic change in the structure of plasma as shown in Fig. 4 indicates also a possible evidence of the increase of electron temperature. At the steady-state plasma (during the growth of bulk µc-Si:H-i layer), the electron temperature shows an obvious difference by the difference of the SiH₄-introduction time. Namely, when the SiH₄-introduction time is short (t = 15 sec in this case), powder formation severely occurs at the initial stage of film growth, causing higher electron temperature in the steady state plasma in contrast to the case of long SiH₄-introduction time (t = 120 sec).

It is emphasized here that the change in the dangling-bond-defect density in the bulk region of µc-Si:H deposited under the steady state plasma could be predicted when monitoring the optical emission intensity of specific line (Hα in the case of µc-Si:H growth at high rate).

3.2. External quantum efficiency spectra for µc-Si:H solar cells

External quantum-efficiency spectrum (QE) was measured to evaluate the difference of photovoltaic (PV) performance in the n-i-p type µc-Si:H solar cells whose i layer was prepared under two different SiH₄-introduction-time conditions. Results are shown in Fig. 5. QE of the solar cell, whose i layer was fabricated with short SiH₄-introduction time (t = 15 sec), shows a slight deterioration in the wavelength range longer than 550 nm as shown in Fig. 5(a) in contrast to the case shown in Fig. 5(b). This suggests that the bulk-defect density of i-layer in this solar cell fabricated with shorter SiH₄-introduction time exhibits higher value due to higher electron temperature in the plasma during i-layer-film growth as is predicted in Fig. 3. When i layer exhibits higher defect density, photo-generated electrons and holes in i layer are recombined in the entire part of i layer, showing wide range deterioration in the QE spectrum as is seen in Fig. 5(a).

Next, we have studied the effect of H₂-plasma-exposure time before introducing SiH₄ on the resulting n-i-p solar-cell performance. Two H₂-plasma-exposure times were tested for the initial stage of i-layer growth, e.g., H₂-plasma-exposure times were set at 6 sec and 30 sec before introducing SiH₄ with an identical SiH₄-introduction time of 120 sec. Figure 6 shows the QE spectra for two µc-Si:H solar cells whose i layer was fabricated with different H₂-exposure times before introducing SiH₄. As is clearly seen in the figure, QE spectrum for the solar cell (c) shows a remarkable deterioration in the wavelength range at around 700 nm in contrast to that for the solar cell (b) in Fig. 6. We have proposed a model to explain the severe deterioration of QE spectrum for the solar cell (c) in Fig. 6, in which the auto doping of phosphorus occurs from underlying n layer into i layer by the influence of high atomic hydrogen-flux density especially at the starting stage of i-layer growth in the case of solar cell (c) in the figure. This model is plausible and supported by two experimental facts described below.

Figure 5. QE spectra for two solar cells whose i-layer growth was performed with different SiH₄-introduction times (t) of 15 sec (a) and 120 sec (b).

Figure 6. QE spectra for two solar cells whose i layer was prepared with different H₂-plasma-exposure times of 5 sec (b) and 30 sec (c).
when the phosphorus-doped n-type μc-Si:H films are exposed to H₂ plasma produced under the same condition as the initial stage of i-layer growth, films are etched out with quite high rate of 0.3 nm/sec. (2) when the intrinsic a-Si:H film is placed just adjacent to n-type μc-Si:H film and they are exposed to H₂-plasma together for 30 sec, the electric conductivity of intrinsic a-Si:H film near the n-type μc-Si:H film is strictly increased from $1.6 \times 10^{-10}$ S/cm to $3.5 \times 10^{-10}$ S/cm, indicating that silicon and phosphorus atoms etched out by the H₂ plasma are deposited on the surface of adjacent a-Si:H film through a chemical transport process (auto doping). Therefore, under the condition of i-layer growth for the solar cell (c), silicon and phosphorus are etched out from the surface of underlying n layer and incorporated into i layer grown simultaneously. Incorporation of phosphorus in i-layer region near n/i interface causes the formation of “flat band” in the solar cell band diagram, resulting in the severe deterioration in QE of the solar cell in the wavelength region at around 700 nm due to the weakened electric field near n/i interface.

To prevent the phosphorus auto doping from underlying n layer into i layer in the n-i-p type solar-cell-fabrication process under the condition for obtaining high PV performance with very high reproducibility, we propose a novel method, in which thin intrinsic a-Si:H layer is deposited (called as “victim” layer) on n layer with proper thickness to be vanished by the H₂-plasma exposure. When 10 nm-thick a-Si:H layer is deposited on n layer as a victim layer, for instance, this layer is vanished by 30-sec H₂-plasma exposure completely before introducing SiH₄. It should be noted here that any auto doping is not observed during the victim-layer growth when using high quality a-Si:H-growth condition with pure SiH₄. Figure 7 shows QE spectra with and without using victim a-Si:H layer under the conditions of 30-sec H₂-plasma-exposure time and 120-sec SiH₄-introduction time. As is seen in the figure, QE spectrum (d) shows a remarkable improvement in the wavelength region at around 700 nm, meaning that the phosphorus auto doping from underlying n layer into growing i layer is successfully suppressed and flat-band formation near the n/i interface is avoided.

4. Conclusion
We have proposed two novel processes to form fine n/i interface in n-i-p type μc-Si:H solar cells, e.g., (1) gradual SiH₄-introduction method to avoid the powder formation at the starting process of i layer growth and (2) victim a-Si:H-layer-insertion method to prevent phosphorus auto doping from underlying n layer into i layer by the influence of H₂-plasma exposure also at the starting stage of i-layer growth.

High SiH₄ depletion is achieved by the gradual SiH₄-introdcution method from the start of film growth, by which the formation of higher order SiH₄ molecules (powder-like species) is well controlled. By the control of powder-formation process, electron temperature in the steady-state plasma during i-layer growth is decreased through the reduction of electron-attachment events to
powders in the plasma, giving rise to the growth of high quality intrinsic \( \mu c \)-Si:H layers with low dangling-bond-defect density.

However, high atomic hydrogen-flux density from the plasma at the initial stage of gradual SiH\(_4\)-introduction process gives rise to the auto doping of phosphorus into growing \( i \) layer from underlying \( n \) layer in the fabrication process of \( n-i-p \) type \( \mu c \)-Si:H solar cells. To avoid phosphorus auto doping, we have proposed a novel method, in which thin a-Si:H layer is deposited on \( n \) layer surface as a victim layer with proper thickness to be vanished by H\(_2\)-plasma exposure. Utilization of this victim layer, phosphorus auto doping from underlying \( n \) layer is successfully suppressed. When applying these two methods to the fabrication process of \( n-i-p \) type \( \mu c \)-Si:H solar cells whose \( i \) layer is grown at high rate more than 2 nm/sec, high solar cell performance (> 9% in efficiency) is achieved with fairly good reproducibility.

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### References

[1] Yamamoto K Yoshimi M Suzuki T Tawada Y Okamoto Y and Nakajima A 1998 *Proc. Mater. Res. Soc. Symp.* **507** p 131

[2] Meier J Dubail S Fluckinger R Fischer D Keppner H and Shah A 1994 *Proc. Ist World Conf. Photovolta. Energy Conf. (Hawai)* vol 1 (IEEE) p 409

[3] Kondo M, Fukawa M, Guo L and Matsuda A 2000 *J. Non-Cryst. Solids* **266-269** 84

[4] Fukawa M Suzuki S Guo L Kondo M and Matsuda A 2001 *Sol. Energy Mater. Sol. Cells* **66** 217

[5] Chantana J Tsutsui Y Sobajima Y Sada C Matsuda A and Okamoto H 2011 *Jpn. J. Appl. Phys.* **50** 045806

[6] Matsuda A, Takai M, Nishimoto T and Kondo M 2003 *Sol. Energy Mater. Sol. Cell.* **78** 3

[7] Matsuda A 2004 *J. Non-Cryst. Solids* **338–340** 1

[8] Sobajima Y, Matsuda A and Okamoto H 2011 *Proc. Mater. Res. Soc. Symp.* **1321** p375

[9] Müller J, Rech B, Springer J, and Vanecek M 2004 *Solar Energy* **77** 917

[10] Sobajima Y Muto H Shinohara Y Sada C Matsuda A and Okamoto H 2011 *Tech. Digest 21st Int. Photovoltaic Science and Engineering Conf.* (Fukuoka) 4A-2O-06