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Guiding Principles for Preparing High Quality Microcrystalline Silicon at High Growth Rates

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We present guiding principles for preparing high-quality microcrystalline silicon (μc-Si:H) films with regard to film-precursors and to their reactions on the film-growing surface, in which the contribution of short lifetime reactive species to film-growth plays a role in determining the defect density of the resulting films except for temperature dependence. The importance of annihilation reactions of the short lifetime species with SiH_4 as well as that of their low generation rate is emphasized. The consideration of co-existing annihilation reaction of atomic hydrogen, important species for μc-Si:H formation, is also included. Based on the guiding principles, we propose a high rate deposition technique using high density very high frequency plasma produced with a newly designed interconnected multi-hollow cathode. Spatially-resolved optical emission spectroscopy indicated a radical separation effect introduced by the cathode. Device-grade μc-Si:H films with low defect densities (~ 5 x 10^{15} cm^{-3}) have been successfully prepared at growth rates approaching 8 nm/s by means of this technique.
Key words: Microcrystalline silicon, Plasma enhanced chemical vapor deposition, Silane, Film-growth, Defect

1. INTRODUCTION

Hydrogenated microcrystalline silicon (μc-Si:H), commonly prepared by plasma-enhanced chemical vapor deposition (PECVD), attracts a lot of attention as a promising material for thin film solar cells owing to its spectral response at long wavelength and high stability against light exposure. A μc-Si:H solar cell requires, however, a rather thick intrinsic layer > 2.0 μm to sufficiently absorb the sunlight because of its indirect optical transition, though an active layer thickness of only 300 nm is sufficient for hydrogenated amorphous silicon (a-Si:H) solar cells. Therefore, high rate growth of μc-Si:H is a crucial issue for low-cost industrialization of solar cells. However, high rate growth of the μc-Si:H is usually accompanied by a large number of dangling-bond (DB) defects in the resulting film, which act as recombination centers for photo-excited carriers, leading to a deterioration in the device performance. Although there have been many approaches of the high rate growth of high quality μc-Si:H films,[1-3] the quality of the films grown at high rates is still not satisfactory for photovoltaic application, and further improvement is required.

In this paper, we present guiding principles for preparing high-quality μc-Si:H films at high growth rates (GRs) with regard to film-precursors and to their reactions on the film-growing surface, in which the contribution of short lifetime reactive species, such as SiH_2, SiH, and Si, to film-growth, in addition to the contribution of main film-precursor, SiH_3 radicals, determines the defect density, N_{DB}, of the resulting films, except for dependence on substrate temperature, T_s. Based on the guiding principles, we propose a high rate deposition technique using a very high frequency (VHF) PECVD reactor with a newly designed interconnected multi-hollow (ICMH) cathode.[4, 5] This technique has been adopted for deposition, and a drastic reduction in N_{DB} of μc-Si:H films prepared at high GRs was successfully demonstrated.

2. GUIDING PRINCIPLES FOR PREPARING HIGH-QUALITY μc-Si:H FILMS

2.1 μc-Si:H film-growth process by PECVD

In a-Si:H or μc-Si:H film-growth process by PECVD, monosilane (SiH_4) and hydrogen (H_2) molecules, usually used as source gas materials, are dissociated into various neutral, emissive or ionic species through a dissociative excitation by an inelastic collision with energetic electrons in plasma. SiH_3 radicals are known to be favorable as film-precursor, possessing long lifetime in SiH_4/H_2 plasma, which are, indeed, the main film-precursor. The necessary electron energy for production of SiH_3 through one-electron impact dissociation of SiH_4 is 8.75 eV.[6] That for one-electron impact dissociation of H_2 is also rather low (8.8 eV). On the other hand, $SiH_{x \leq 2}$ species, though as harmful species showing high reactivity surface reactions with or without defect creation (details are undermentioned), are produced through one-electron impact dissociation of SiH_4 by electrons with higher energies > 9.47-10.53 eV.[6] Since necessary electron energy is lower for production of SiH_3 than for those of $SiH_{x \leq 2}$, the N_{ex}/N_{e3} is associated with a slope of a high energy tail of the electron energy distribution function of the plasma, being related to the electron temperature, T_e, where N_{ex} and N_{e3} are the densities of electrons with energies

sufficient for production of $SiH_{x\leq 2}$ and for that of SiH_3, respectively, through one-electron impact dissociation of SiH_4. The $SiH_{x\leq 2}$ / SiH_3 generation ratio which is proportional to the N_{ex}/N_{e3} is thus related to the T_e of the plasma. The species produced in the plasma diffuse and are transported to substrate. For a high rate film-growth, a high flux density, ϕ_{SiH3}, of film-precursors (SiH_3) to substrate is required. For μc-Si:H formation at a low T_s, in addition, high flux density, ϕ_H, of atomic hydrogen to substrate or high ϕ_H/ϕ_{SiH3} is necessary.[7-9]

In a-Si:H or μc-Si:H film-growth process at a T_s < 300 °C usually used for deposition, film-growing surface is completely passivated by hydrogen atoms, and arriving SiH_3 radicals firstly diffuse on the surface. Assuming only contribution of SiH_3 as film-precursor for simplification, film-growth consists of 1) creation of Si DBs on the surface through abstraction of the surface-bonded hydrogen by SiH_3, and 2) bonding of the surface-diffusing SiH_3 radicals to the surface DBs.[10] The SiH_3 radicals can find stable low potential sites through surface-diffusion, and the sticking of one SiH_3 radical to one surface DB contributes to saturation of the DB. On the contrary, the $SiH_{x\leq 2}$ species can not diffuse on the surface because of the strong reactivity of their insertion reactions into surface Si-H bonds. Furthermore, the sticking of $SiH_{x\leq 1}$ species to the surface creates DBs. Contribution of the $SiH_{x\leq 2}$ to film-growth, therefore, leads to an enhanced creation of surface DBs, and hence, results in high N_{DB} in the resulting film, on the assumption that the surface DB defects become statistically incorporated in the film.[10, 11]

Then, we suppose that the contribution ratio of $SiH_{x\leq 2}$ to SiH_3 toward film-growth determines the density of DBs on the surface, $N_{DB\ s}$, and thus the N_{DB} in the resulting films, except for T_s-dependence of the N_{DB},[11, 12] particularly at a low T_s (< 300°C) where the creation of surface DBs through hydrogen thermal desorption can be neglected. We assume also that ion bombardment which can cause defect creation when highly energetic ions are accelerated is not an origin of defect creation under normal deposition conditions. The $N_{DB\ s}$ is supposed to be the sum of the N_{DBs} for growth only with SiH_3, and the additional increase in $N_{DB\ s}$ due to the contribution of $SiH_{x\leq 2}$ to film-growth. The latter is proportional to the $SiH_{x\leq 2}/SiH_3$ contribution ratio to film-growth, which is related to their density ratio in plasma, through the transport of the species to the film surface, as follows:

$$\text{Additional increase in } N_{DB\ s} \propto \frac{\phi_{SiH_x}}{\phi_{SiH_3}} \propto \frac{[SiH_x]}{[SiH_3]} \quad (1)$$

where ϕ_{SiHx} is the flux density of $SiH_{x\leq 2}$ to the film surface, $[SiH_x]$ and $[SiH_3]$ are the densities of $SiH_{x\leq 2}$ and of SiH_3 in plasma, respectively. It indicates that, minimizing the $[SiH_x]/[SiH_3]$ is required in order to minimize the additional increase in $N_{DB\ s}$ due to the contribution of $SiH_{x\leq 2}$ to film-growth.

2.2 SiH_x/SiH_3 contribution ratio to film-growth

Let us now consider how to minimize the $[SiH_x]/[SiH_3]$ density ratio in plasma. The $[SiH_3]$ is deduced from the following rate equation as the counterbalance of the generation rate of the SiH_3 radicals by their annihilation rate:

$$\frac{d[SiH_3]}{dt} = N_{e3}\,\sigma_3\,v_e\,[SiH_4] - \frac{[SiH_3]}{\tau_3} = 0$$
$$\therefore [SiH_3] = N_{e3}\,\sigma_3\,v_e\,\tau_3\,[SiH_4] \quad (2)$$

where σ_3, v_e, $[SiH_4]$, and τ_3 are the cross-section for one-electron impact dissociation of SiH_4 producing SiH_3, the thermal velocity of electrons, the steady state density of SiH_4 in plasma, and the characteristic lifetime of SiH_3 in plasma, respectively. Similarly, the $[SiH_4]$ is deduced from the following rate equation:

$$\frac{d[SiH_4]}{dt} = FR(SiH_4) - N_{et}\,\sigma_t\,v_e\,[SiH_4] - \frac{[SiH_4]}{\tau_4} = 0$$
$$\therefore [SiH_4] = \frac{FR(SiH_4)}{N_{et}\,\sigma_t\,v_e + \frac{1}{\tau_4}} \quad (3)$$

where $FR(SiH_4)$, N_{et}, σ_t, and τ_4 are the SiH_4 flow rate, the total density of electrons effective for dissociation of SiH_4, the total dissociation cross-section of SiH_4, and the characteristic residence time of SiH_4 in plasma, respectively. Under conditions with high N_{et} and low $FR(SiH_4)$ where SiH_4-depletion results in μc-Si:H growth, the $[SiH_4]$ can be simplified as follows:

$$[SiH_4] = \frac{FR(SiH_4)}{N_{et}\,\sigma_t\,v_e}. \quad (4)$$

By substituting equation (4) into (2), $[SiH_3]$ is given as:

$$[SiH_3] = \frac{N_{e3}\,\sigma_3\,v_e\,\tau_3\,FR(SiH_4)}{N_{et}\,\sigma_t\,v_e} \propto FR(SiH_4). \quad (5)$$

Since the GR is proportional to the $[SiH_3]$,[13] equation (5) indicates that the GR is $FR(SiH_4)$-limited under SiH_4-depletion conditions for μc-Si:H growth, whereas it is N_{et}-limited under a-Si:H growth conditions with sufficiently high $FR(SiH_4)$.[14] In the transition region between a-Si:H and μc-Si:H growth, the GR is controlled by both N_{et} and $FR(SiH_4)$. On the other hand, the $[SiH_x]$ is given by the following rate equation:

$$\frac{d[SiH_x]}{dt} = N_{ex}\,\sigma_x\,v_e\,[SiH_4] - k_1[SiH_x][H_2] - k_2[SiH_x][SiH_4] = 0$$
$$\therefore [SiH_x] = \frac{N_{ex}\,\sigma_x\,v_e\,[SiH_4]}{k_1[H_2] + k_2[SiH_4]} \quad (6)$$

where σ_x and $[H_2]$ are the cross-section for one-electron impact dissociation of SiH_4 producing $SiH_{x\leq 2}$, and the steady state density of H_2 in plasma, respectively, k_1 and k_2 are the reaction-rate constants for annihilation reactions of $SiH_{x\leq 2}$ with H_2 and with SiH_4, respectively. Since k_2 (~ 10^{-10} cm^3/s) is sufficiently larger than k_1 (~ 10^{-14} cm^3/s for reactions of Si or SiH, ~ 10^{-12} cm^3/s for that of SiH_2 with H_2),[15] the $[SiH_x]$ can be simplified as:

$$\therefore [SiH_x] = \frac{N_{ex}\,\sigma_x\,v_e\,[SiH_4]}{k_2[SiH_4]} \propto N_{ex} \propto N_{et}. \quad (7)$$

It indicates that N_{et} controls the $[SiH_x]$ determining the generation rates of the $SiH_{x\leq 2}$, and the $[SiH_4]$ is not a limiting factor, because SiH_4 molecules play both for the generation and the annihilation of the $SiH_{x\leq 2}$. From equations (5) and (7), the $[SiH_x]/[SiH_3]$ is given as:

$$\frac{SiH_{x\leq 2}}{SiH_3}\text{-contribution ratio to film-growth}$$

$$\propto \frac{[SiH_x]}{[SiH_3]} \propto \frac{N_{ex}}{N_{e3}\,\tau_3[SiH_4]}$$

$$\propto \frac{N_{ex}N_{et}}{N_{e3}\,\tau_3 FR(SiH_4)} \propto \frac{N_{et}}{FR(SiH_4)} f(T_e) \qquad (8)$$

where N_{ex}/N_{e3}, correlated with the T_e in plasma as aforementioned, is rewritten as a function of T_e, $f(T_e)$. Thus, under SiH_4-depletion conditions which favor μc-Si:H growth, both $N_{et}/FR(SiH_4)$ being related to the degree of SiH_4-depletion and T_e being related to the $SiH_{x\leq 2}$ / SiH_3 generation ratio determine the $[SiH_x]$ / $[SiH_3]$. The degree of SiH_4-depletion is associated to the annihilation rate of $SiH_{x\leq 2}$.

In consequence, equations (5) and (8) suggest that low SiH_4-depletion with high $FR(SiH_4)$ and low T_e are required for high rate growth of μc-Si:H films with low N_{DB}. However, an increase in $F(SiH_4)$ leads to deterioration in crystallinity due to the annihilation of hydrogen atoms through the reaction with SiH_4 ($H + SiH_4 \rightarrow H_2 + SiH_3$). Then, in order to keep high crystallinity, an increase in N_{et} is required, which increases, however, the $[SiH_x]$ and the $[SiH_x]/[SiH_3]$. Thus, μc-Si:H film-growth obliges one to optimize the balance between the annihilation reactions of $SiH_{x\leq 2}$ with SiH_4 and those of hydrogen atoms with SiH_4. Beneficially, the rate-constants for the former reactions, k_2, are higher than that for the latter reaction, k_3 (10^{-12} cm^3/s).[15] Otherwise, one can adjust H_2 dilution of SiH_4 by increasing the H_2 flow rate in order to keep high crystallinity, which tends, however, to deteriorate the GR owing to a decrease in $[SiH_4]$.

The discussion above is focused on minimizing the additional increase in $N_{DB\ s}$ in equation (1) through minimizing the $[SiH_x]/[SiH_3]$. However, there is another controllable parameter. In equation (1), the ϕ_{SiHx}/ϕ_{SiH3} is related to the $[SiH_x]/[SiH_3]$ through the transport of the species to substrate. Let us now consider the space through which the species are transported, as a controllable parameter. Providing space between plasma and substrate is considered to be effective for selective transport of long lifetime SiH_3 to substrate because short lifetime $SiH_{x\leq 2}$ species have many opportunities to collide with SiH_4 and annihilate during the transport through the space. This concept of radical separation has been previously applied to film-growth process, in a triode configuration[16] where the plasma is produced apart from the substrate placed on the anode, with a negatively biased mesh electrode inserted between cathode and anode. This method is, however, not suitable for high rate growth because of the insertion of the semitransparent mesh electrode.

3. EXPERIMENTAL RESULTS

3.1 Interconnected multi-hollow (ICMH) cathode

In previous studies,[1, 2] the N_{DB} of μc-Si:H films prepared at high GRs has been reduced from the very high values obtained under conventional radio-frequency (RF) PECVD low pressure conditions to the lower values obtained by the use of VHF and high pressure conditions with optimization of SiH_4-depletion, as shown in Fig. 1, which is attributed to a reduction in T_e of the plasma and the optimized SiH_4-depletion. However, the quality of the μc-Si:H films deposited at

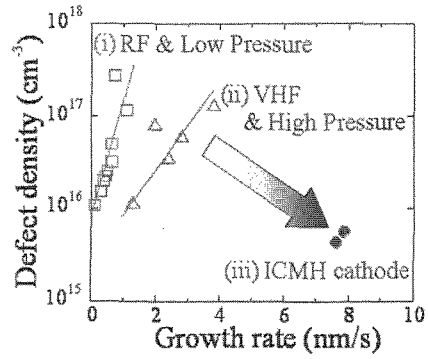
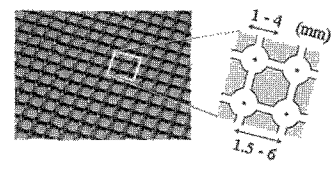


Fig.1. Defect density (N_{DB}) vs. growth rate (GR), for the μc-Si:H films prepared under (i) RF low pressure conditions,[2] (ii) VHF high pressure conditions,[2] and (iii) VHF high pressure conditions with the ICMH cathode.

rates required for industrialization was not sufficiently high. Then, aiming to introduce the radical separation effect into μc-Si:H deposition at high GRs, we designed a novel reactor with a cathode having specific surface structure which enables the production of uniformly distributed and stable high density plasma spots near the cathode surface.[4, 5] The structure of the cathode is schematically shown in Fig. 2 with the picture of the surface structure. Numerous hollows are arranged on the cathode surface, with interconnecting slots to induce a coupling among plasma spots produced in each hollow site, from which a source gas is injected.

Spatially-resolved optical emission spectroscopy (OES) analysis has been performed in Ar plasma produced with the newly designed interconnected multi-hollow (ICMH) cathode. The ratio of the optical emission intensity at a wavelength of 750.4 nm, $I_{(Ar\,750.4)}$, to that at 800.6 nm, $I_{(Ar\,800.6)}$, was taken as measure of the ratio of high energy electron density to low energy electron density in plasma.[17] Axial distribution of the $I_{(Ar\,750.4)}/I_{(Ar\,800.6)}$ around the hollow, observed from the direction parallel to the cathode-surface, is shown in Fig. 3.[18] It is revealed that when bright spots are produced at/inside the hollows, high density plasma with high fraction of high energy electrons is realized in the bright spots. It is effective for gas dissociation. The generation of the high density and high energy electrons is due to stochastic heating of electrons in the oscillating sheath between the plasma spot and the hollow wall with an electron confinement effect of the hollow,[18] in addition to gamma effect. On the other hand, the space between



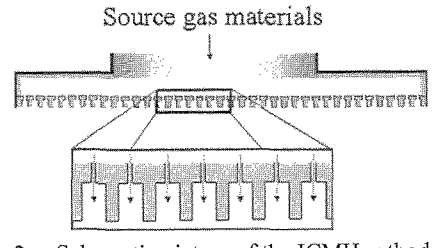


Fig.2. Schematic picture of the ICMH cathode.

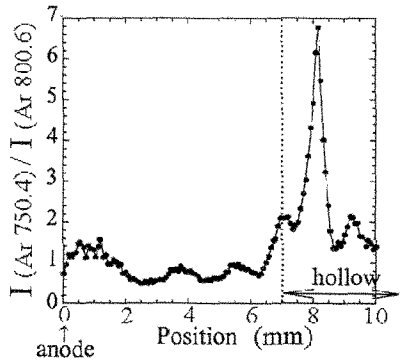


Fig.3. Axial distribution of the $I_{(Ar\ 750.4)}$ / $I_{(Ar\ 800.6)}$ optical-emission-intensity ratio around the hollow on the ICMH cathode surface.[18]

the plasma spots in the hollows and the substrate (anode) shows very low $I_{(Ar\ 750.4)}/I_{(Ar\ 800.6)}$. The production of the plasma where gas dissociation occurs apart from the substrate brings about the radical separation effect in μc-Si:H growth process, like in the triode method[16] even without any insertion between cathode and anode.

3.2 Reduction in defect density of the μc-Si:H films prepared at high rates

The ICMH cathode has been adopted for μc-Si:H film-growth. A capacitively coupled VHF PECVD reactor with the ICMH cathode (with a hollow diameter of 2 mm) was employed for deposition. The typical deposition conditions were as follows: plasma excitation frequency of 60 MHz, total pressure of 9.3 Torr, spacing between cathode and anode of 7 mm, VHF power density of 4 W/cm^2, FR(SiH_4) varying from 20 to 70 sccm, H_2 gas flow rate of 300 or 700 sccm. Substrate holder temperature was initially set at 200°C. Corning glass was used as substrates.

Following our guiding principles, we increased the FR(SiH_4) in order to decrease the $[SiH_x]/[SiH_3]$ in equation (8) for reduction in N_{DB} of μc-Si:H films prepared at high GRs. An increase in GR and a reduction in N_{DB} are simultaneously achieved with increasing FR(SiH_4),[14] according to equations (1), (5), and (8). In addition, an increase in FR(SiH_4) possibly reduces T_e,[19] resulting in lower $SiH_{x\leq 2}$ / SiH_3 generation ratio. However, the crystallinity deteriorates rapidly with increasing FR(SiH_4),[14] owing to an increase in number of the annihilation reactions of hydrogen atoms. In consequence, the N_{DB} of μc-Si:H films prepared at high GRs has been drastically reduced by means of the ICMH cathode, which is attributed to the radical separation effect under VHF and high pressure conditions. Through optimization, device-grade μc-Si:H films with N_{DB} as low as 5 x 10^{15} cm^{-3} have been obtained at GRs approaching 8 nm/s, as shown in Fig. 1.[14] It is a demonstration of the effectiveness of the method using the ICMH cathode and also a confirmation of the validity of our guiding principles for obtaining high quality μc-Si:H films at high GRs.

4. CONCLUSIONS

We present guiding principles for preparing high quality μc-Si:H films in which the $SiH_{x\leq 2}$ / SiH_3 contribution ratio to film-growth determines the defect density, N_{DB}, of the resulting films except for the temperature dependence. The importance of low SiH_4-depletion with increasing SiH_4 flow rate, FR(SiH_4), and low electron temperature, T_e, of the plasma is emphasized. The necessity of optimization of the balance between the annihilation of $SiH_{x\leq 2}$ and that of atomic hydrogen is indicated. Based on the guiding principles, we propose a high rate deposition technique using a VHF PECVD reactor with a newly designed interconnected multi-hollow (ICMH) cathode. Spatially-resolved OES analysis indicated a radical separation effect introduced by the cathode. Device-grade μc-Si:H films with N_{DB} as low as 5 x 10^{15} cm^{-3} have been successfully prepared at rates approaching 8 nm/s by means of this technique.

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