Dependence of volume fraction of clusters on deposition rate of a-Si:H films deposited using a multi-hollow discharge plasma CVD method

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(Received: 12 September 2008 / Accepted: 20 February 2009)

We have studied dependence of volume fraction of clusters in a-Si:H films on deposition rate of the films using a multi-hollow discharge plasma CVD method The maximum deposition rate realized for each pressure exponentially increases from 0.014 nm/s to 0.96 nm/s with decreasing pressure from 1.0 Torr to 0.1 Torr, whereas the volume fraction of clusters slightly increases with increasing the deposition rate, suggesting that highly stable a-Si:H films can be deposited at a high rate by using the multi-hollow discharge plasma CVD method.

Keywords: multi-hollow discharge plasma CVD, a-Si:H, light-induced degradation, clusters, volume fraction of clusters, deposition rate, gas pressure, gas residence time

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is most widely employed as a top cell material of thin film Si tandem solar cells. Because light exposure creates light induced defects in a-Si:H films, their light induced degradation represents a key issue for their applications such as the tandem solar cells [1,2]. Figure 1 shows a model of main reactions in conventional silane (SiH_4) discharges employed for depositing a-Si:H films [3], which is obtained based on our experimental results [4-6]. In SiH_4 discharges, there coexist three deposition precursors: SiH_3, higher-order silane (HOS) related radicals in a size range below 0.5 nm, and amorphous nanoparticles (clusters) in a size range between 0.5nm and 10 nm [5]. SiH_3 radicals are the main deposition precursor for high quality films. HOS related radicals and clusters are incorporated into the films during the deposition and may degrade film qualities. In our recent studies, a-Si:H films with a less volume fraction of clusters in the films have been found to show less light induced degradation [5,7]. We have succeeded in depositing highly stable a-Si:H films using a multi-hollow discharge plasma CVD method by which the volume fraction of clusters in films deposited in upstream region is significantly reduced by driving clusters towards the downstream region. There is a remaining issue that the deposition rate is a rather low rate of 0.12 nm/s compared to a goal value of 2.0 nm/s [8]. To deposit stable a-Si:H films at a high rate above 2.0 nm/s, we have measured dependence of deposition rate and the volume fraction on gas residence time as a parameter of gas pressure using the multi-hollow discharge plasma CVD method. Here, we report the results.

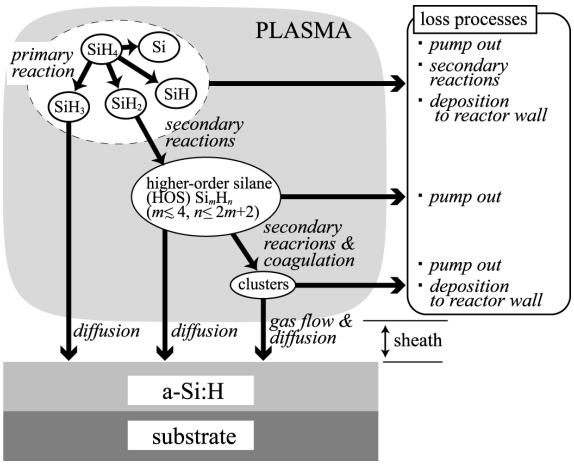

Fig. 1. A model of main reactions in silane plasma.

2. Experimental

Experiments were carried out using a multi-hollow discharge plasma CVD reactor as shown in Fig. 2. Three electrodes, each of which had 24 holes of 5 mm in diameter, were placed 2 mm apart in a stainless steel tube of 60 mm in inner diameter. Gas of SiH_4 was fed from a gas inlet at a flow rate of 4-40 sccm and was pumped out through the electrodes with a molecular drag pump (ALCATEL MDP5030). The gas pressure was 0.1-1.0 Torr. The discharge frequency and peak-to-peak voltage were 60MHz and 150 V, respectively.

SiH_3 radicals and clusters are generated in the discharges. Clusters are transported to the downstream

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region by gas flow when their diffusion velocity v_d is less than the gas velocity v_g [8]. The diffusion velocity is obtained from an equation of characteristic diffusion time τ

$$\frac{1}{\tau}=\frac{D_c}{\Lambda^2}, \quad (1)$$

where D_c is the diffusion coefficient of clusters, Λ their characteristic diffusion length. The v_d is expressed as

$$v_d=\frac{\Lambda}{\tau}=\frac{D_c}{\Lambda}. \quad (2)$$

The solid line in Fig. 3 shows the lower limit size of clusters transported toward the downstream region for pressure p=0.2 Torr, gas temperature T=100°C, and Λ=0.55cm (a half of the hole length). SiH_3 radicals are transported towards the upstream and downstream region due to their fast diffusion of 3.66x10^{3}cm/s p=0.2 Torr, T=100°C. Therefore, incorporation of clusters into the films deposited in the upstream region can be significantly suppressed using the multi-hollow discharge plasma CVD method [9, 10].

A substrate was set at 20mm upstream from the lower grounded electrode. The volume fraction of clusters in films was deduced from the ratio of a deposition rate of clusters to the total one.

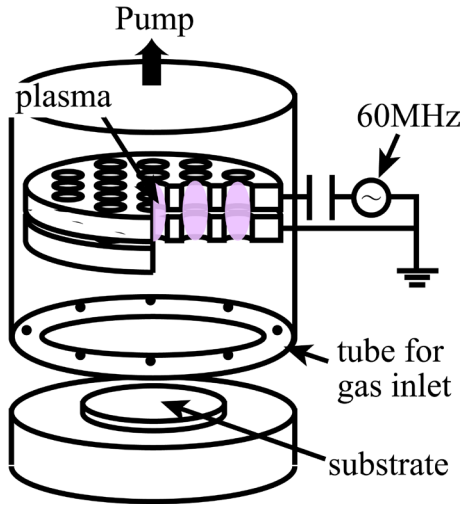

Fig. 2. Multi-hollow discharge plasma CVD reactor.

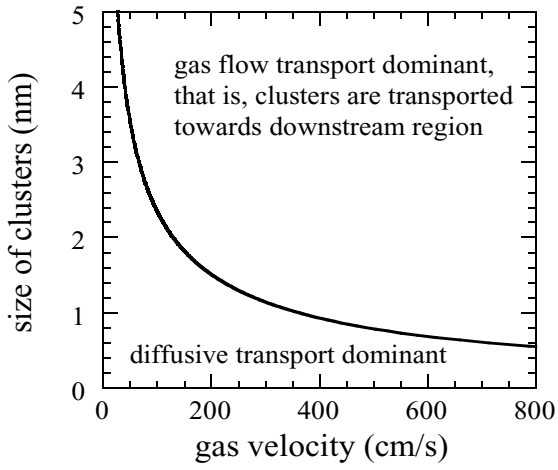

Fig. 3. Dependence of lower limit size of gas flow transport dominant region on gas velocity for p=0.2Torr, T=100°C.

3. Results and Discussion

We have studied dependence of the deposition rate and the volume fraction on the gas residence time τ_g in a hollow as a parameter of gas pressure. The τ_g is obtained from the gas flow rate FR(sccm) and the pressure P(Torr). From the equation of state for a perfect gas and the pressure P, the number of gas molecules in hollows n_h=5.63x10^{15}xP (molecules). Since the gas flow rate is volume flow rate (cm^3/min) at standard conditions of 0°C and 1.013x10^5 Pa, the number of the molecules supplied to the hollow per second n_f=1.88x10^{16}xFR (molecules/s) is deduced from the equation of state for a perfect gas. τ_g is a ratio of n_h to n_f.

$$\tau_g=\frac{n_h}{n_f}=0.299\times\frac{P}{FR}(s). \quad (3)$$

As shown in Fig. 4, for 0.1 Torr, the deposition rate increases from 0.73 nm/s to 0.96 nm/s with increasing τ_g from 0.0019 s to 0.0027 s, and then it decreases from 0.96 nm/s to 0.6973 nm/s with further increasing τ_g from 0.0027 s to 0.0037 s. For 0.2 and 0.5 Torr, the τ_g dependence of the deposition rate is similar to that for 0.1 Torr. For 1.0 Torr, the deposition rate monotonously increases with increasing τ_g for τ_g< 0.062 s. The maximum deposition rate realized for each pressure increases exponentially from 0.014 nm/s to 0.96 nm/s with decreasing the pressure from 1.0 Torr to 0.1 Torr. The gas residence time at a maximum deposition rate increases with increasing the pressure.

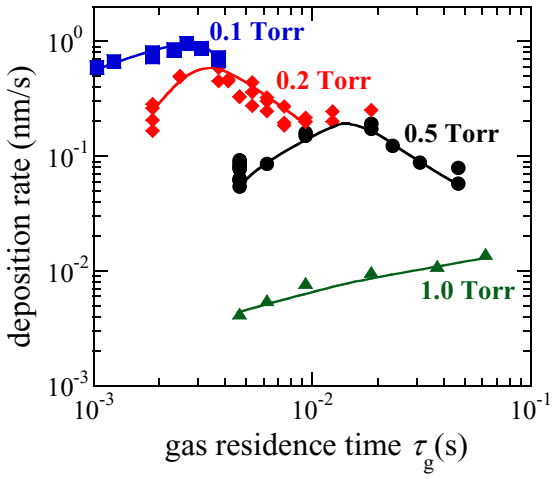

Fig. 4. Dependence of deposition rate on gas velocity as a parameter of pressure. Conditions: SiH_4 100%, 60MHz, 150Vpp, substrate temperature 100°C.

To discuss the dependence of deposition rate on the gas residence time, we consider simple rate equations. In silane discharges, SiH_3 radical is the main precursor of the films deposition [11, 12]. Rate equations of the SiH_3 and SiH_4 density are given by

$$\frac{d[SiH_3]}{dt} = k_{dis} n_e [SiH_4] - \frac{D}{L^2}[SiH_3] - \frac{[SiH_3]}{\tau_g}, \quad (3)$$

$$\frac{d[SiH_4]}{dt} = \frac{[SiH_4]_0}{\tau_g} - \frac{[SiH_4]}{\tau_g} - k_{dis} n_e [SiH_4], \quad (4)$$

where $[SiH_3]$ is the SiH_3 density, k_{dis} the rate coefficient of SiH_3 due to electron impact dissociation of silane, n_e electron density, $[SiH_4]$ density of silane molecules in the discharges, D diffusion coefficient of SiH_3, τ_g gas residence time, and $[SiH_4]_0$ initial density of silane. L is the characteristic length of SiH_3 diffusion. The L is given by

$$L = \sqrt{L_0^2 + l_0 \lambda}, \quad (5)$$

where L_0=r/2.405 [13], r the hole radius. For a semi-infinite axial length:

$$l_0 = \frac{\text{volume of diffusion region}}{\text{surfacearea of diffusion region}} \rightarrow \lim_{\text{length}\to\infty} l_0 = \frac{r}{2}. \quad (6)$$

The linear extrapolation length λ is a distance between the wall and a position at which the density of SiH_3 radicals extrapolates to zero beyond the wall when SiH_3 radicals deposit at a surface reaction probability β [13,14]. The λ is expressed as

$$\lambda = \frac{4D(1-\beta/2)}{\overline{v_{th}}\beta}, \quad (7)$$

where $\overline{v_{th}}$ is the thermal speed of SiH_3 radicals. From eqs. (3) and (4), the SiH_3 density $[SiH_3]$ in the discharges in the steady state is

$$[SiH_3] = \frac{k_{dis} n_e [SiH_4]_0}{1 + \tau_g k_{dis} n_e} \frac{L^2 \tau_g}{\tau_g D + L^2}. \quad (8)$$

From eq.(9), the $[SiH_3]$ has a maximum value at a gas residence time, which is

$$\tau_{gm} = \sqrt{\frac{L^2}{k_{dis} n_e D}}. \quad (9)$$

For $\tau_g < \tau_{gm}$, the density of SiH_3 radicals decreases with decreasing τ_g due to fast gas flow. For $\tau_g > \tau_{gm}$, the density decreases with increasing τ_g due to gas depletion.

We deduce relation between τ_{gm} and the pressure from eq. (9) as shown in Fig.5. The solid lines in Fig. 5 are obtained for k_{dis}=1.59x10^{-10}cm^3/s [15], β=0.28 [16], and T=100°C as a parameter of electron density, n_e. The experimental results exist between theoretical lines of n_e=1x10^{9}cm^{-3} and 1x10^{11}cm^{-3}, which are typical values. To obtain more accurate theoretical results, information about electron density and electron temperature is needed. Such experiments are underway.

Figure 6 shows dependence of the maximum

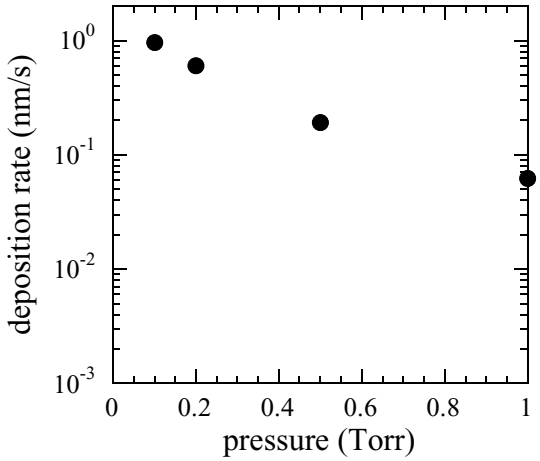

Fig. 6. Dependence of the maximum deposition rate for each pressure on pressure.

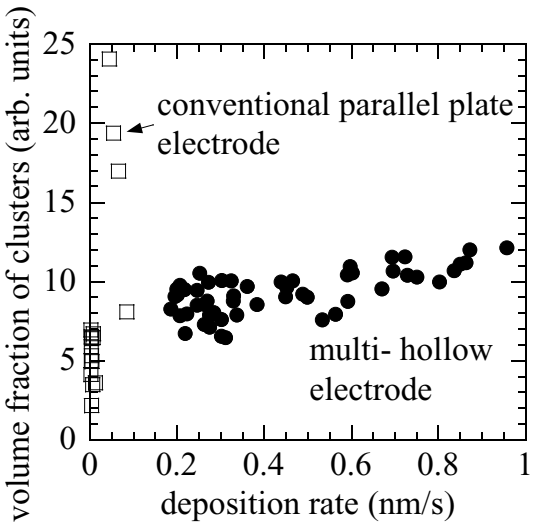

Fig. 7. Dependence of volume fraction of clusters on deposition rate for the multi-hollow electrode (solid circles) and the conventional parallel plate electrode (open squares). Experimental conditions are the same as those of Fig. 4.

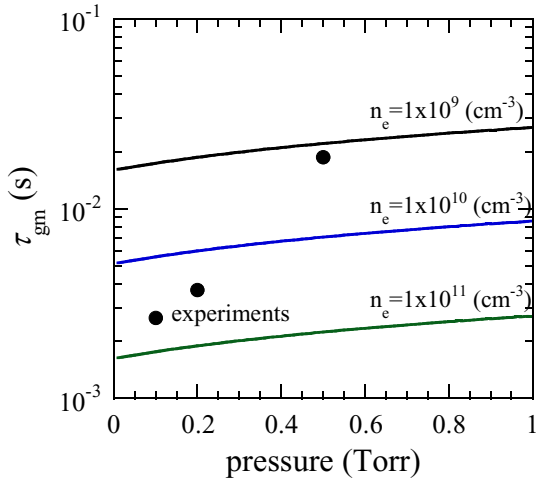

Fig. 5. Dependence of τ_{gm} on pressure. Solid circles indicate experimental results. Line shows the theoretical curve.

deposition rate on the pressure. The deposition rate exponentially increases with decreasing the pressure because of the faster diffusion of SiH_3 at the lower pressure.

Figure 7 shows dependence of the volume fraction on the deposition rate from the dependence of the deposition rate and the volume fraction on gas residence time. The volume fraction slightly increases with increasing the deposition rate for the multi-hollow discharge plasma CVD method, whereas it significantly increases up to 25 at a deposition rate of 0.05 nm/s with the deposition rate for the conventional method. Thus, the dependence of the volume fraction on the deposition rate depends strongly on deposition method. Further information about plasma parameters such as electron density and electron temperature is needed to discuss the dependence. Such experiments are underway.

4. Conclusions

We have studied dependence of deposition rate and volume fraction on gas residence time as a parameter of pressure. The maximum deposition rate realized for a each pressure increases exponentially from 0.014 nm/s to 0.96 nm/s with decreasing the pressure from 1.0 Torr to 0.1 Torr, while the volume fraction increases slightly with the deposition rate. These results suggest that highly stable a-Si:H films can be deposited at a high rate by using the multi- hollow discharge plasma CVD method.

Acknowledgments

This work was partly supported by Japan Society for the Promotion of Science (JSPS) and New Energy and Industrial Technology Development Organization (NEDO).

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