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To cite this article: W M Nakamura et al 2008 J. Phys.: Conf. Ser. 100 082018

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Cluster incorporation control for a-Si:H film deposition

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Abstract. To study the effects of clusters on the light induced degradation and control their deposition into films, we have developed a multi-hollow plasma CVD method by which the incorporation of clusters is reduced in the upstream region using the gas flow that drives clusters formed in discharges toward the downstream region of the reactor. Thus, we can simultaneously deposit films in which the volume fraction of clusters incorporated into films varies by changing the position of the substrate in the reactor. A-Si:H films with a lower volume fraction of clusters tend to show better stability against light exposure.

1. Introduction
Light induced degradation of hydrogenated amorphous silicon (a-Si:H) films has been an important issue to enhance the efficiency of a-Si:H solar cells [1]. Since a-Si:H films with low incorporation of amorphous Si nano-particles, hereafter referred to as clusters, show less light induced [2,3], it is important to understand how SiH$_3$ radicals (the main film precursor), higher order silane (HOS) related radicals, and clusters transport and deposit to obtain highly stable films.

We have employed a multi-hollow discharge plasma CVD method to control the deposition of the species generated in the discharges by gas flow and substrate placement. We deposited films in the upstream and downstream regions placing quartz substrates parallel to the gas flow. This configuration allows us to obtain films in which the volume fraction of each species generated in the discharges varies along the distance from the discharge region, since their transport depends on their diffusivity and may be highly influenced by gas flow depending on their size.

In this paper, we report the dissociation degree, contribution of HOS radicals to films, volume fraction of clusters in films obtained in a multi-hollow discharge plasma CVD reactor; and show that incorporation of clusters degrades the stability of a-Si:H films against light exposure.

2. Experimental
Films were deposited using a multi-hollow discharge plasma CVD reactor as shown in Fig. 1. Three electrodes separated by 2 mm were placed in a stainless steel tube of 75 mm in diameter. Each electrode had 24 holes of 5 mm in diameter, where the discharges were sustained. Pure SiH$_4$ or SiH$_4$ diluted with H$_2$ was supplied from the bottom of the reactor, pumped throughout the electrodes with a molecular drag pump. Quartz substrates were placed parallel to the gas flow in the upstream and downstream regions of the reactor. The total pressure was 66.5 or 133 Pa, and the reactor was kept isothermal at 250°C. The discharge frequency was 60 MHz, and the discharge power was 45 W.
Spatial thickness profile of the films was evaluated with an optical transmission spectroscope (JASCO V-570), or with an image scanner (Epson GT-9700F). The densities of SiH₄, Si₂H₆ and Si₃H₈ in the residual gas were measured by a quadrupole mass spectrometer (ANELVA M-QA100TS). For film stability evaluation, the defect density was measured by electron spin resonance (ESR) spectroscopy after film deposition and after light soaking. The light soaking was performed at intensity of 240 mW/cm² (2.4 SUN) of AM 1.5 spectrum for an exposure time of 7.5 h at 50°C.

3. Results and discussion

3.1. Dissociation degree

The influence of the gas flow velocity on the dissociation degree of SiH₄, as well as on the generation rate of HOS radicals, was investigated by QMS measurements. Figure 2 shows dependence of the dissociation degree D of SiH₄ on the discharge power for the gas velocity flow of 13 and 56 cm/s in the upstream and downstream regions. The dissociation degree of SiH₄ is the ratio of dissociated SiH₄ density with discharge to SiH₄ density without discharge. The dissociation degree increases with the discharge power, and the results for upstream and downstream regions are nearly the same. The dissociation degree for 56 cm/s is about 1/2 times as low as that for 13 cm/s. Since the deposition rate is proportional to 1-D, a high gas flow velocity is needed to increase the deposition rate in a high discharge power regime.

Densities of Si₂H₆ and Si₃H₈ were measured to evaluate the contribution of HOS radicals to the film growth. In the steady state, the density of a HOS radical (SiₘH₂ₙ₊₁) is given by

\[
\left[Si_m H_{2m+1}\right] = \tau k_d n_e \left[Si_m H_{2m+2}\right]
\]

(1)

where \( \tau \) is characteristic lifetime of SiₘH₂ₙ₊₁, and \( k_d \) is the rate coefficient of SiₘH₂ₙ₊₁ generation due to electron impact dissociation of SiₘH₂ₙ₊₂, and \( n_e \) is the electron density. Hence, the contribution ratio of HOS radicals to the films growth to that of SiH₃ can be evaluated as follows, when SiH₃ is the main film precursor in SiH₄ discharges.
Figure 2. Dependence of dissociation degree of SiH4 on discharge power for SiH4 2.5sccm, H2 10sccm (blue), and SiH4 2.5sccm, H2 10sccm (red) upstream and downstream regions. Total pressure was 133 Pa, and discharge power frequency was 60 MHz.

Figure 3. Dependence of \( \frac{[Si_m H_{2m+2}]/[SiH_4]}{[Si_2H_6]/[SiH_4]} \) for \( m=2 \) and \( 3 \) on discharge power \( P \) in (a) downstream and (b) upstream region. Total pressure 133 Pa, SiH4 2.5sccm, H2 10sccm, SiH4 2.5sccm, H2 10sccm.

\[
\frac{[Si_m H_{2m+2}]/[SiH_4]}{[Si_2H_6]/[SiH_4]} \propto \frac{[Si_m H_{2m+2}]/[SiH_4]}{[Si_2H_6]/[SiH_4]}
\] (2)

Figure 3 shows the dependence of \( [Si_m H_{2m+2}]/[SiH_4] \) on the discharge power as a parameter of the gas flow velocity. The gas flow velocity has little influence on \( [Si_m H_{2m+2}]/[SiH_4] \), \( m=2 \) and \( 3 \), for both upstream and downstream regions. This indicates that the characteristic diffusion time of these species is much shorter than the gas residence time in the discharges. In other words, the contribution of these HOS radicals to the film growth cannot be controlled by the gas flow velocity.

3.2. Volume fraction of clusters and stability of films

Figure 4 shows dependence of the deposition rate on the distance from the discharges. The deposition rates obtained with the two equipments agree fairly well with each other. The image scanner has two advantages of a continuous spatial profile of the deposition rate, and fast data acquisition over the optical transmission spectroscope. The deposition rate decreases exponentially with increasing the distance from the discharge region in both upstream and downstream region. Far from the discharges, the deposition rate in the downstream region is higher than that in the upstream region. This indicates that clusters are driven toward the downstream region by gas flow, which leads to an increase in the deposition rate, while in the upstream region the deposition is mainly of SiH3. Hence, the difference between the deposition rate in the upstream and downstream regions expresses the deposition rate of clusters, from which the volume fraction of clusters in the films deposited in the downstream region is deduced. The volume fraction of clusters in the downstream region increases with the distance, as shown in Fig. 4. Hence, the continuous control of the volume fraction of clusters into the film is realized by the multi-hollow discharge plasma CVD method.

Figure 5 shows dependence of film stability on distance from discharge region. The films in the upstream region tend to be more stable than those deposited in the downstream region. Moreover, the films deposited far from the discharges in the upstream region are highly stable. These results indicate that incorporation of clusters degrades the stability of a-Si:H films against light exposure.
4. Conclusions
To study the effects of clusters on the light induced degradation and control their deposition into films, we have developed a multi-hollow plasma CVD method by which the incorporation of clusters is reduced in the upstream region using the gas flow that drives clusters formed in discharges toward the downstream region of the reactor. The following conclusions are obtained in this study:

1. A high gas flow velocity is needed to increase the deposition rate in a high discharge power regime.

2. Gas flow has little influence on the transport of HOS radicals towards substrates both in the upstream and downstream regions, while it drives clusters towards the downstream region.

3. Continuous control of the volume fraction of clusters into the film is realized by the multi-hollow discharge plasma CVD method.

4. Films deposited in the upstream region tend to be more stable than those deposited in the downstream region; and the films deposited far from the discharges in the upstream region shows high stability, which indicates that the incorporation of clusters degrades the stability of a-Si:H films against light exposure.

Acknowledgement
This work was partly supported by the Industrial Technology Development Organization (NEDO).

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