# Contribution of Clusters to $SiH_2$ Bonds in a-Si:H Films

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Light induced degradation is the most important issue for hydrogenated amorphous silicon solar cells. A-Si:H films with the lower density of Si-$H_2$ bonds show higher stability, and a-Si:H particles in a size range below 10nm (clusters) have many Si-$H_2$ bonds. We studied relation of Si-$H_2$ bond density $C_{SiH2}$ in films and incorporation amount of clusters. Si-$H_2$ bond density in films is reduced to 0.4 % by eliminating the contribution of the clusters to the deposition of films.

## 1. Introduction

Light induced degradation is the most important issue for hydrogenated amorphous silicon (a-Si:H) solar cells. Matsuda et al. have pointed out that a-Si:H films with the lower density of Si-$H_2$ bonds show higher stability [1]. As shown in Fig. 1, in $SiH_4$ discharges employed for a-Si:H deposition, there are three size groups of deposition species: $SiH_x$ ($x \leq 3$) radicals, higher order silane (HOS) radicals $Si_mH_n$ ($m \leq 4$), and a-Si:H particles in a size range below 10 nm (clusters) [2]. $SiH_3$ radicals are main deposition precursors, which dominate the film deposition rate. HOS radicals are generated due to polymerization between $SiH_2$ radical and $SiH_4$ molecule. Clusters are nucleated from HOS radicals of $Si_nH_x$ (n~4) and grow due to coagulation and deposition of $SiH_x$ radicals to the surface of clusters. We have previously reported that clusters have many $SiH_2$ bonds, and cluster incorporation into films is mainly responsible for $SiH_2$ bond formation [3]. Therefore, suppression of clusters incorporated into films is the key to realizing highly stable a-Si:H films. Based on the results, we have developed a multi-hollow discharge plasma CVD method to reduce clusters incorporated into films, resulting in depositing highly stable a-Si:H films [3, 4].

We also have developed a real-time monitor of the cluster volume fraction in films $V_f$ by employing three quartz crystal microbalances (QCMs) [5]. The method provides information on amount of clusters incorporated into films as well as deposition rate due to $SiH_3$ radicals [6, 7].

In this study, we obtained the relation between Si-$H_2$ bond density $C_{SiH2}$ (atomic %) in films and $V_f$, and deduced $C_{SiH2}$ due to cluster incorporation.

## 2. Experimental

Experiments were carried out using a multi-hollow discharge plasma CVD reactor equipped with the QCMs. The discharge frequency was 60 MHz. The gas was introduced from a gas inlet ring set below the multi-hollow electrodes and evacuated by the vacuum system located at the upper side of the electrodes. The pressure was kept at 0.5 Torr.

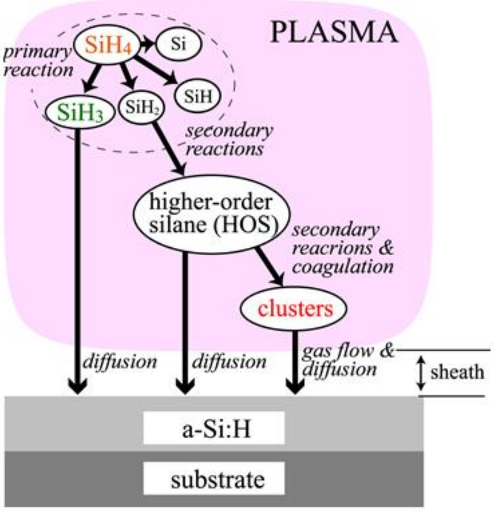

Fig.1. Deposition model in silane plasma.

The system composed of three QCMs was set in the upstream region. The QCM of channel A was used for measuring the total deposition rate $DR_{total}$ due to $SiH_3$ radicals and clusters. The QCM of channel B was applied to measure the deposition rate $DR_{radical}$ due to $SiH_3$ radicals by using the cluster eliminating filter. The filter eliminates the contribution of the clusters to the deposition of films, because the sticking probability of the clusters and the surface reaction probability of the radicals are 100% and 30%, respectively. The QCM of channel C was used as a reference sensor, because the resonance frequency of quartz crystal also depends on experimental conditions such as temperature and pressure. We employed the ratio $R=DR_{total}/DR_{radical}$ as an indicator of the amount of clusters incorporated into films. Cluster volume fraction in films $V_f$ is given by

$$V_f = 1 - \frac{1}{T_r \times R} \qquad (1)$$

where $T_r$ is a radical transmittance of the filter.

To obtain information of $C_{SiH2}$ in a-Si:H films, films were prepared on crystalline Si (111) wafers of a high resistivity (1000- 5000 Ωcm) at a substrate temperature of 250°C, and $C_{SiH2}$ in films was measured with a FTIR spectroscope.

## 3. Results and discussion

Figure 2 shows the dependence of $C_{SiH2}$ in films on 1/R. $C_{SiH2}$ decreases with increasing 1/R. For $1/R < 0.06$, 1/R has a strong correlation with $C_{SiH2}$. The results show that the main origin of $SiH_2$ bond formation in films is cluster incorporation into films. For $1/R > 0.06$, $1/R$ has a weak correlation with $C_{SiH2}$. In this region, the main origins of $SiH_2$ bond formation in films are surface reactions of $SiH_3$ radicals and/or incorporation of HOS radicals.

Here, we consider the case for $1/R < 0.06$. Under such condition, the data are well fitted by a linear function,

$$C_{SiH2}(films) = 2.28 - 30.1 \times \frac{1}{R} \qquad (2)$$

Here, $C_{SiH2}$ in films is proportional to $V_f$ because incorporation clusters in films is mainly responsible for $SiH_2$ bond formation in films,

$$C_{SiH2}(clusters) \times V_f = 2.28 - 30.1 \times \frac{1}{R} \qquad (3)$$

By comparing eq. (1) and (3), we obtain $T_r$ = 13.2, and $C_{SiH2}(clusters)$ = 2.28 %. Though $C_{SiH2}$ in clusters may depend on the discharge conditions and substrate temperature, $C_{SiH2}$ in clusters is 2.28 % in our experimental conditions. Hence, we obtained the equation as follows

$$V_f = 1 - 13.2 \times \frac{1}{R} \qquad (4)$$

We also obtain the relation between $C_{SiH2}$ in films and $V_f$ as shown in Fig. 3. $C_{SiH2}$ in films is reduced to 0.4 % by suppressing cluster incorporation. We need further experiments for identifing the origins of this remaining $SiH_2$ bond formation.

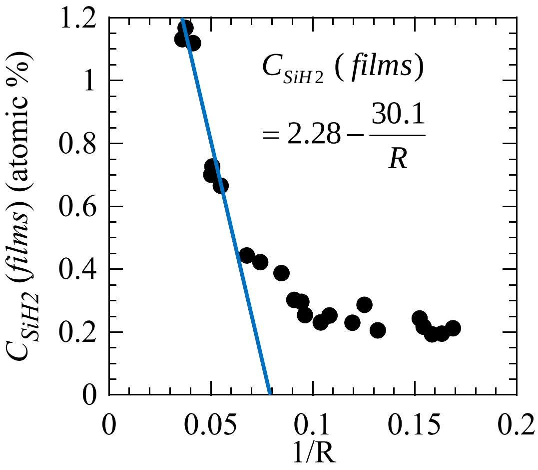

Fig. 2. Dependence of $C_{SiH2}$ in films on 1/R.

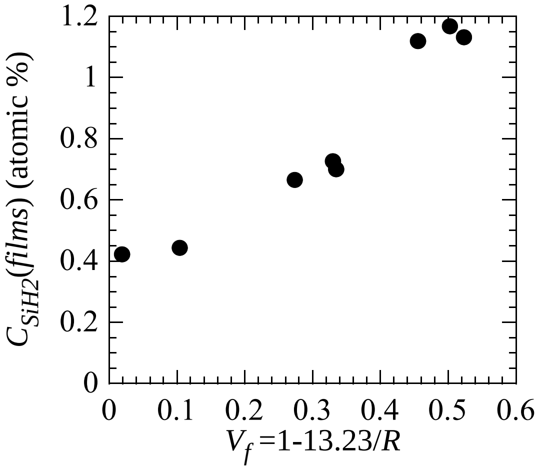

Fig. 3. Relation between $C_{SiH2}$ in films and $V_f$.

## 4. Conclusions

We studied the dependence of Si-$H_2$ bond density $C_{SiH2}$ in films on the amount of incorporation clusters. We found $C_{SiH2}$ in clusters is 2.28 % and $C_{SiH2}$ in films is reduced to 0.4 % by eliminating the contribution of the clusters to the deposition of films.

**Acknowledgements**

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