Control of Nanostructure of Plasma CVD Films for Third Generation Photovoltaics

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Abstract
One of the requirements for successful application of hydrogenated amorphous silicon (a-Si:H) to promising tandem cells, that aim at high efficiency and low production cost, is to overcome its light induced degradation, which reduces significantly the initial conversion efficiency with light exposure. Our previous studies indicate a relation between light induced degradation and the incorporation of amorphous silicon nanoparticles (clusters) into a-Si:H films. Here we report control of nanostructure of a-Si:H films using a multi-hollow plasma CVD reactor. Deposition with low or non-incorporation of clusters is realized in the upstream region far from discharges in the reactor, whereas in the downstream region the volume fraction of clusters in films increases with the distance from discharge region. Films with a lower volume fraction tend to show better stability against light exposure.

1. Introduction
The photovoltaics are classified into three generations: the “first generation” silicon wafer-based solar cells of high production costs and moderate efficiency, the “second generation” thin film ones of low production costs and rather low efficiency, and the “third generation” thin film ones of low production costs and high efficiency. The most promising third generation cells may be achieved with the concept of the tandem cells, which increases photovoltaic conversion efficiency by adding different bandgap cells, each of them converting a narrow range of photon energies [1]. Hydrogenated amorphous silicon (a-Si:H) film is most widely employed as a top cell in thin film Si tandem cells. However, due to a significant efficiency reduction over light exposure, the light induced degradation of a-Si:H represents the key issue for its application to Si tandem solar cells [2].

Previous studies indicated that a-Si:H films having a less Si-H$_2$ bond concentration show less light induced degradation [3]. Therefore, the mechanisms and species that lead to the formation of Si-H$_2$ bonds should be identified to reduce the light induced degradation. In SiH$_4$ discharges employed for a-Si:H deposition, there coexist three deposition precursors: SiH$_3$ radicals, high order silane related (HOS) radicals in a size range below 0.5 nm, and amorphous nanoparticles (clusters) in a size range between 0.5 nm and 10 nm [4, 5]. SiH$_3$ radicals are the main deposition precursor for high quality films. Incorporation of clusters into a-Si:H films has been pointed out to increase the Si-H$_2$ bond concentration and cause the light induced degradation, whereas that of Si$_3$H$_8$ and Si$_3$H$_4$ radicals has not [6]. However, the mechanisms of such degradation, as well as the minimum size and amount of clusters which lead to the light induced degradation, still remain unclear.
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 cluster incorporation varies by changing the position of the substrate in the reactor, since the transport of species varies with their size. Here we report the distance dependence of stability of films against light exposure, their deposition rate and their microstructure parameter R which is a ratio of hydrogen concentration associated with Si-H₂ bonds to that with Si-H bonds. We expect that these results will help us to find the minimum size and amount of clusters which causes the light induced degradation of a-Si:H, and to control their deposition into films.

2. Experimental

A-Si:H films were deposited using a multi-hollow plasma CVD reactor, in which quartz glass substrates were placed in both downstream and upstream regions in a way that their surfaces were parallel to the gas flow, as shown in Fig. 1 [7]. The reactor has three electrodes, each with 24 holes of 5mm in diameter, and placed 2 mm apart in a stainless steel tube of 60 mm in inner diameter.

Gas of pure SiH₄ or SiH₄ diluted with H₂ was supplied from the bottom of the reactor at a total flow rate of 10-50 sccm, and was pumped out through the electrodes with a molecular drag pump. The total pressure was 66.5-200 Pa. Discharges were sustained in the holes, where SiH₃, HOS radicals and clusters were generated, by supplying a 60 MHz voltage to the powered electrode. The discharge power was 10-60 W. The reactor was kept isothermal at 250°C to avoid thermophoretic force on clusters due to thermal gradient.

Microstructure parameter R was deduced from an intensity ratio of absorption at 2090 cm⁻¹ to 2000 cm⁻¹, measured by the Fourier-transform infrared (FTIR) ATR spectroscopy. The deposition rate was evaluated by measuring the film thickness with an optical transmission spectroscopy. The defect density was measured by electron spin resonance (ESR) spectroscopy.

3. Results and discussion

By placing the substrates as shown in Fig.1, we obtained films with different contribution of SiH₃, HOS radicals and clusters to films for a given deposition condition, since the spatial density distribution of these species depends on their transport in the reactor. We evaluated the stability of the
films against light exposure, their thickness and their microstructure parameter $R$; to then, by comparing the films, find the dependence of these parameters on the distance from the discharge region during deposition, and how these parameters are related to the light induced degradation.

![Figure 2. Dependence of defect density on light exposure time $t$. Circles and squares denote results for $z = -31$ mm and $z = 72$ mm, respectively. Light exposure condition: 240mW/cm$^2$ (2.4 SUN) of AM1.5 spectrum, 50°C. Discharge conditions: SiH$_4$ 10sccm, H$_2$ 40sccm, 66.5 Pa, 60MHz, 29 W, 250°C.](image1)

![Figure 3. Dependence of deposition rate and volume fraction of clusters in films on distance from electrode. Discharge conditions: SiH$_4$ 40sccm, 66.5 Pa, 60MHz, 45 W, 250°C.](image2)

3.1 Stability of films
To evaluate stability against light exposure of films deposited using the reactor, we have measured the dependence of their defect density on light exposure time $t$ using an intense light intensity of 240mW/cm$^2$ (2.4 SUN). The results are shown in Fig. 2.

We deposited a film with 2 µm in thickness in the upstream region at 31 mm from the surface of the powered electrode at the downstream region ($z=-31$ mm), at a deposition rate of 0.12 nm/s. This film had its defect density stable at a low value of $5 \times 10^{15}$ cm$^{-3}$ for $t=0$-$240$ h. Under the same deposition conditions, a film of 0.65 µm in thickness prepared in the downstream region at 72 mm from the powered electrode surface ($z=72$ mm), at a deposition rate of 0.04 nm/s, had its defect density increased from an initial value of $5 \times 10^{15}$ cm$^{-3}$ to $2 \times 10^{16}$ cm$^{-3}$ for $t=240$ h. Such increase in the defect density, due to light exposure, is common for the conventional a-Si:H films.

These results motivated us to study in detail the properties of films deposited in different positions from the electrode along the axial axis. We then evaluated the dependence of volume fraction of clusters and the stability of films on distance from electrode for films deposited under other deposition condition as follows.

3.2 Volume fraction of clusters in films
Figure 3 shows the dependence of deposition rate and volume fraction of clusters in films on the distance from the electrode. The deposition rate tends to decrease exponentially with increasing the distance from the discharge region along axial axis. Moreover, in the downstream region far from the discharges the deposition rate 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 was mainly of SiH₃. Hence, the difference between the deposition rate in the upstream and downstream 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 increases with the distance from the discharges in the downstream region.

### 3.3 Microstructure parameter R and defect density of films

Figure 4 shows the dependence of the microstructure parameter R on the distance from discharge region. In the downstream region the ratio R increases from 0.2 up to 0.8 with the distance, while R decreases from 0.1 to 0 with increasing the distance in the upstream region.

Figure 5 shows the dependence of the defect density stability on distance from the discharge region. The downstream films were less stable than the upstream ones, and the films deposited in the upstream region far from the discharge were highly stable.

These results indicate that films without containing clusters have few SiH₂ bonds and are highly stable against light exposure, whereas those containing clusters deposited in the downstream region have Si-H₂ bonds and show metastability.

**Figure 4.** Dependence of microstructure parameter R on distance from electrode. Discharge conditions: SiH₄ 40sccm, 66.5 Pa, 60MHz, 45 W, 250°C.

**Figure 5.** Dependence of film stability on distance from electrode. Light exposure condition: 240mW/cm² (2.4 SUN) of AM1.5 spectrum, 50°, exposure time: 7.5h. Discharge conditions: SiH₄ 40sccm, 66.5 Pa, 60MHz, 45 W, 250°C.

### 4. Conclusions

Here we reported that multi-hollow discharge plasma CVD method allows the deposition of a-Si:H films which are highly stable against light exposure. The deposition rate decreases exponentially for both downstream and upstream regions. Films deposited in the downstream region of the reactor had a higher deposition rate far from the discharges compared to the upstream films, which indicates that clusters driven from the discharge region by gas flow deposit there; while the deposition in the upstream region is mainly of SiH₃. The concentration of SiH₂ bonds was also higher in the downstream films, which indicates the close relation between SiH₂ bonds formation and incorporation of clusters. Moreover, the downstream films were less stable against light exposure, which indicates the influence of clusters incorporation on light induced degradation of films. Hence, find the minimum size and amount of clusters which causes the light induced degradation, and then control their
deposition into the films is the matter of the utmost importance to overcome the light induced degradation and successful apply a-Si:H in the third generation of photovoltaics.

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**References**
[1] Green M A 2003 *Third generation photovoltaics* (Berlin: Springer) pp 1-4
[2] Schropp R E I and Zeman M 1998 *Amorphous and Microcrystalline Silicon Solar Cells* (Boston: Kluwer Academic Publishers) pp 99
[3] Nishimoto T, Miyahara H, Shimosawa M, Kondo M, and Matsuda A 2002 *J. Non-Cryst. Solids* **299** 1116
[4] Koga K, Matsuoka Y, Tanaka K, Shiratani M and Watanabe Y 2000 *Appl. Phys. Lett.* **77** 196-8
[5] Koga K, Kaguchi N, Shiratani M and Watanabe Y 2004 *J. Vac. Sci. & Technol. A* **22** 1536-9
[6] Watanabe Y, Harikai A, Koga K, and Shiratani M 2002 *Pure Appl. Chem.* **74** 483
[7] Koga K, Inoue T, Bando K, Iwashita S, Shiratani M and Watanabe Y 2005 *Jpn. J. Appl. Phys.* **48** L1430-2