Effects of cluster deposition on spatial profile of Si-H$_x$ bond density in a-Si:H films

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Abstract

We have studied gas flow rate dependence on spatial distribution of Si-H$_x$ bond density of a-Si:H films deposited by a multi-hollow discharge plasma CVD method. For a low gas flow rate of 84 sccm, films have areas of a high density ratio I_{SiH2}/I_{SiH} of Si-H$_2$ bonds and Si-H bonds. The high I_{SiH2}/I_{SiH} films are formed due to incorporation of clusters. The films contain low I_{SiH2}/I_{SiH} areas. The low I_{SiH2}/I_{SiH} area for 84 sccm is much smaller than that for 147 sccm. Optical emission spectra for two gas flow rates are almost identical. These results indicate that cluster transport toward the substrate can be suppressed by high velocity gas flow.

1. Introduction

With the rapid development of Internet of Things (IoT) technology, energy supply for the IoT devices is an important issue. To overcome the issue, hydrogenated amorphous silicon (a-Si:H) thin film solar cells have been attracted attention due to their thin and flexible features and a relatively low cost of production compared with other solar cells. One of the key issues for a-Si:H solar cells is suppression of light-induced degradation. The lower density of Si-H$_2$ bonds in a-Si:H films shows the higher stability [1,2]. The a-Si:H films are deposited with SiH$_4$ plasmas in which a-Si:H nanoparticles in the size range below 10 nm (clusters) are generated. Clusters have a high density of Si-H$_2$ bonds and their incorporation into films leads to Si-H$_2$ bonds in films [3]. We have significantly reduced such cluster incorporation by a multi-hollow discharge plasma CVD (MHDPCVD) method together with a cluster-eliminating filter [4,5]. For the MHDPCVD method, clusters are transported to the vacuum pump by fast gas flow in discharge region. By using these methods, we have succeeded in depositing highly stable a-Si:H films. We have also succeeded in evaluating a density ratio I_{SiH2}/I_{SiH} of Si-H$_2$ bonds and Si-H bonds in film in each layer and interfaces of PIN a-Si:H solar cells using Raman spectroscopy [6]. For further reduction of the cluster incorporation, we have studied effects of gas flow rate on spatial distribution of the ratio I_{SiH2}/I_{SiH}.

2. Experimental

Figure 1 shows the MHDPCVD reactor with the cluster-eliminating filter [4,5]. We deposited undoped a-Si:H films (I-layer) on 5 cm x 5 cm substrate on which B-doped Si film (P-layer) was deposited in advance. Pure SiH$_4$ gas was fed at
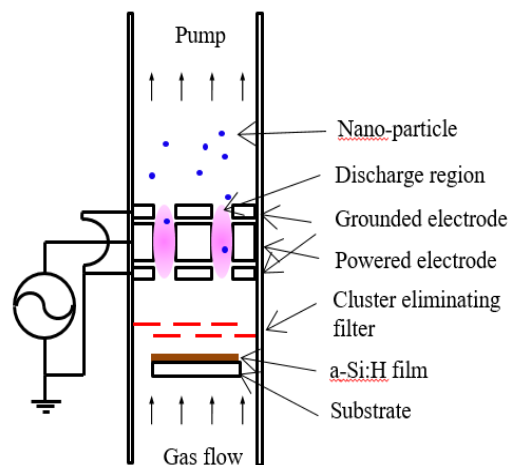

Fig. 1 Multi-hollow discharge plasma CVD method.

84–147 sccm. The total pressure was 0.08 Torr. 110 MHz discharge voltage of 300 V_{pp} was applied to the powered electrode. The substrate temperature was kept at 170 °C. The thickness of I-layer was 20 nm. Measurements of the I_{SiH2}/I_{SiH} ratio were carried out with a Raman spectroscope (JASCO, NRS-3100) equipped with HeNe laser light ($\lambda = 632.8$ nm). The scan time was 100 s and the cumulative number of measurement was 3 times. The diameter of the probe laser was 1 μm. We measured the I_{SiH2}/I_{SiH} ratio at 8 x 8 positions for each substrate. We deconvoluted Raman spectra around 2000–2090 cm^{-1} of a-Si:H films into two peaks corresponding to Si-H bonds (2000 cm^{-1}) and Si-H$_2$ bonds (2090 cm^{-1}) and eventually obtained I_{SiH2}/I_{SiH} [6].

3. Results and discussion

Figure 2 shows spatial distribution of I_{SiH2}/I_{SiH} for 84 and 147 sccm. For 84 sccm, the lowest and highest I_{SiH2}/I_{SiH} value are 0.041 and 0.169, respectively. The averaged value is 0.100. The lowest I_{SiH2}/I_{SiH} value for 147 sccm is 0.022. It is close to that for 84 sccm, while the highest value is 0.061, being much lower than that for 84 sccm. The averaged value for 147 sccm is 0.036. These spatial distributions show the high density areas of SiH$_2$ bonds are localized. This localization strongly suggests that low mobility species of clusters primarily contribute to SiH$_2$ bond formation in the areas. We succeeded in obtaining an extremely low I_{SiH2}/I_{SiH} at some positions for 147 sccm and their positions are randomly located. The density of Si-H$_2$ bonds is also formed due to surface reactions of SiH$_3$
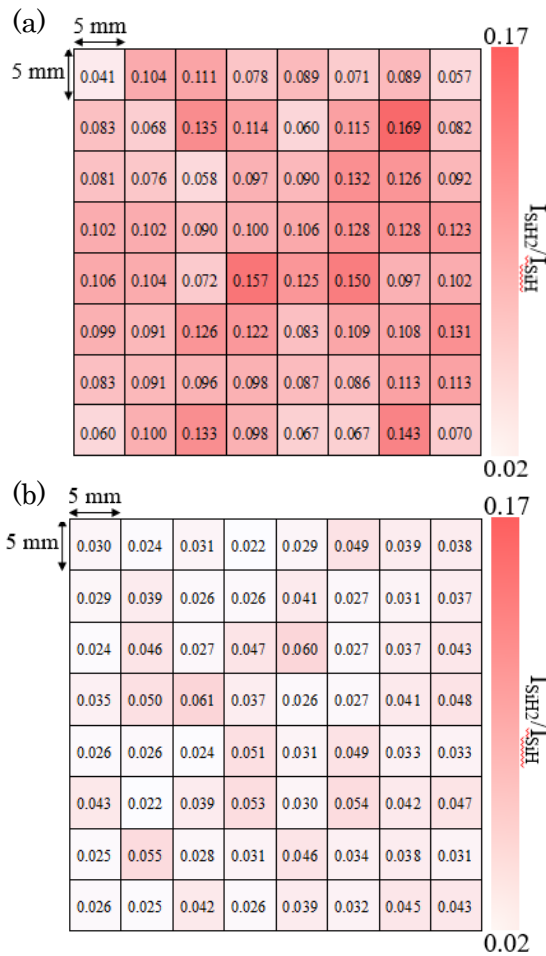
Fig. 2. Spatial distribution of I_{SiH2}/I_{SiH} for (a) 84 sccm and (b) 147 sccm.
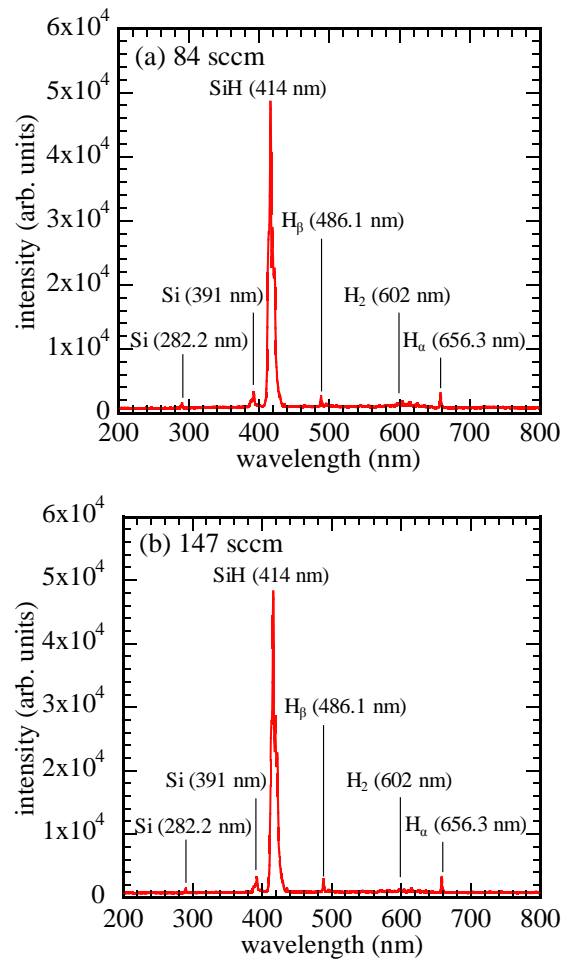

Fig. 3. Emission spectra for (a) 84 sccm and (b) 147 sccm.

radicals. This can be secondary origin of the nonuniformity, when it combined with (1) variations of thickness of I-layer because more SiH_2 bonds tend to exit at film interfaces and surfaces, and (2) variations of film quality of P-layer having strong influence on I-layer deposited on it.

Figure 3 shows optical emission spectra of the plasmas for 84 and 147 sccm. Emission lines from Si, SiH, H_α, H_2 and H_β are detected [7]. The difference between the spectra for 84 sccm and 147 sccm is little, indicating the generation of radicals and clusters in plasmas is irrelevant to the gas flow rate. Thus, transportation of clusters depends on the gas flow rate and control of the transportation is the key to suppressing Si-H_2 bond formation in the films.

4. Conclusions

We have deposited 20 nm I-layer on P-layer using the MHDPCVD method with the cluster-eliminating filter and have measured the ratio I_{SiH2}/I_{SiH}. By changing the gas flow rate from 84 sccm to 147 sccm, we have succeeded in suppressing cluster incorporation and have obtained an extremely low Si-H_2 bond density film.

References

[1] T. Nishimoto, et al., J. Non-Cryst. Solids **299-302** (2002) 1116.
[2] T. Matsui, et al., Appl. Phys. Lett. **106** (2015) 053901.
[3] S. Toko, et al., Thin Solid Films. **587** (2015) 126
[4] W. M. Nakamura, et al., Surf. Coat. Technol. **205** (2010) S241.
[5] S. Toko, et al., Suf. Coat. Technol. **326** (2017) 388.
[6] K. Keya, et al., Jpn. J. Appl. Phys. **55** (2016) 07LE03.
[7] K. Koga, et al., Phys. Status Solidi C**8** (2011) 3013-3016