Optical Emission Spectroscopy of a Magnetically Enhanced Multi-hollow Discharge Plasma for a-Si:H Deposition

William M. NAKAMURA, Yuuki KAWASHIMA, Masatoshi TANAKA, Hiroshi SATO, Jun UMETSU, Hiroomi MIYAHARA, Hidefumi MATSUZAKI, Kazunori KOGA and Masaharu SHIRATANI

Kyushu University, Dept. Electronics, 744 Motooka, Fukuoka 819-0395, Japan

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Multi-hollow discharges enhanced with a magnetic field of 400 G have shown suitable results for a-Si:H films deposition, such as a deposition rate increase by 20-100% and a cluster volume fraction reduction by 14-80%. To understand the effects of the magnetic field on the reactions that take place in silane discharges, we have carried out optical emission spectroscopy (OES) of discharges sustained in the multi-hollow electrodes with an optical multichannel analyzer. The magnetic field reduces the density ratio of electrons in a high energy tail of the electron energy distribution function (EEDF) to that in a low energy part of EEDF, and hence it reduces the generation rate ratio of SiH_2 to SiH_3, whereas it increases significantly the radical generation rates.

Keywords: multi-hollow discharge plasma CVD, a-Si:H, metastability, optical emission spectroscopy, cluster, electron energy distribution function

1. Introduction

It is expected that hydrogenated amorphous silicon (a-Si:H) films will play an important role for the development of the third generation of photovoltaics, which are based on thin film solar cells of low production costs and high efficiency [1, 2]. However, light induced degradation of a-Si:H films has been an important issue to successfully apply a-Si:H to solar cells [1-3]. Previous studies indicated that Si-H_2 bond concentration in films is related to its stability, since a-Si:H films having a less Si-H_2 bond concentration are highly stable against light exposure [4]. Therefore, the mechanisms and species that lead to the formation of Si-H_2 bonds should be identified to obtain a-Si:H of high stability. 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 [5-7]. 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_2H_x and Si_3H_x radicals has not [8]. 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.

We have obtained a-Si:H films with high stability against light exposure by suppressing incorporation of clusters into the films. The incorporation of clusters can be controlled by using a multi-hollow discharge plasma CVD reactor, in which transport and deposition of species generated in discharges varies spatially along the distance from the discharge region and can be influenced by the gas flow [7, 9]. We have deposited a-Si:H films in the upstream and downstream regions placing quartz substrates parallel to the gas flow. In this configuration we can deposit films in which the volume fraction of each species generated in the discharges varies along the

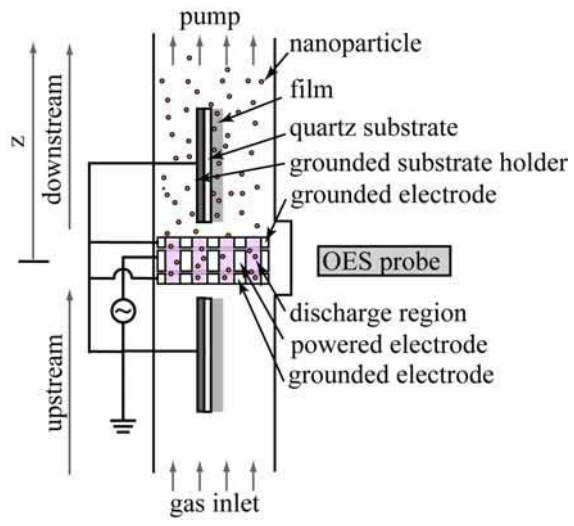

Fig.1. Multi-hollow discharge plasma CVD reactor.

w.nakamura@plasma.ed.kyushu-u.ac.jp

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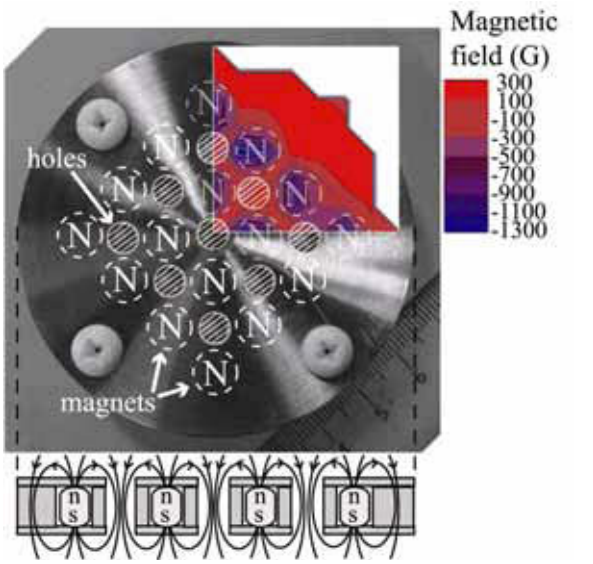

Fig.2. Multi-hollow electrode with magnets.

distance from the discharge region, since their transport depends on their diffusivity and may be highly influenced by gas flow depending on their size [10, 11]. Recently, we have succeeded in increasing by 20-100% the deposition rate and decreasing by 14-80% the volume fraction of clusters into a-Si:H films by applying a magnetic field of 400 G in the discharge regions.

To understand the effects of magnetic field on the reactions that take place during the discharges, we have carried out optical emission spectroscopy (OES) of discharges sustained in the multi-hollow electrodes with an optical multichannel analyzer. Here we report the results.

2. Experimental

Figure 1 shows the multi-hollow discharge plasma CVD reactor. Three electrodes were placed 1.5 mm apart in a stainless steel tube of 75 mm in inner diameter. Each electrode had 9 holes of 5 mm in diameter, in which the discharges were sustained. In the powered electrode 16 magnets were set.

To deposit films, we supplied pure SiH_4 gas from the bottom of the reactor at a total flow rate of 40 sccm pumped out through the electrodes with a molecular drag pump. The total pressure was 66.5 Pa. SiH_3, HOS radicals and clusters were generated in the discharges, by supplying a 60 MHz voltage to the powered electrode. The discharge power was 45 W. The reactor was kept isothermal at 250 ^{o}C to avoid thermophoretic force on clusters due to thermal gradient. Quartz substrates were placed parallel to the gas flow in both upstream and downstream regions.

We performed optical emission spectroscopy of discharges sustained in the multi-hollow electrodes with

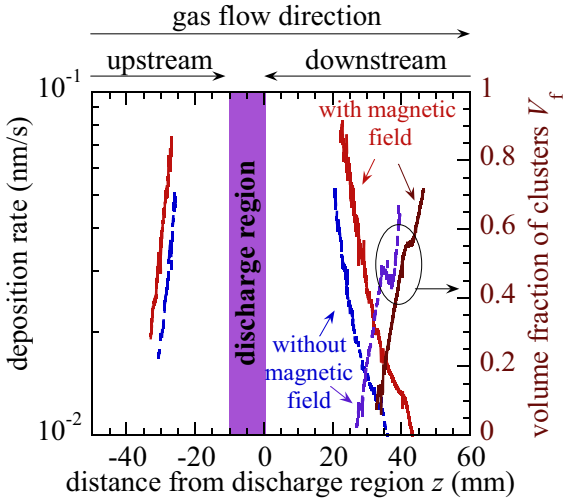

Fig.3. Deposition rate and volume fraction of clusters on distance from discharge region for discharges with and without magnetic field.

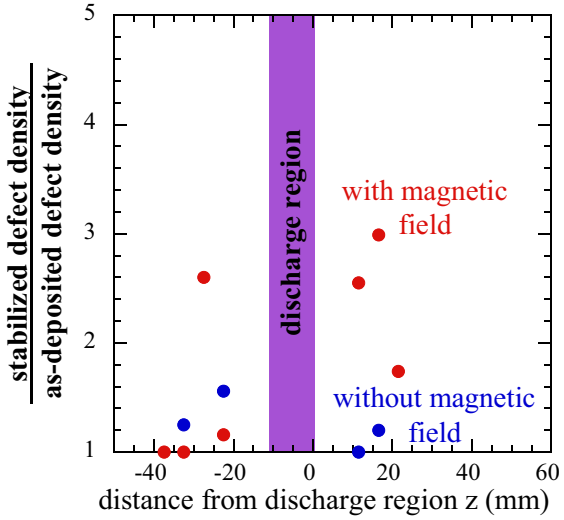

Fig.4. Stability of films on distance from discharge region for discharges with and without magnetic field.

an optical multichannel analyser (Hamamatsu Photonics, PMA-11-C7473). Optical emission from discharges in holes passes through a narrow gap (1 mm) between powered electrode and upper grounded electrode and reaches an optical fiber placed outside of chamber. To obtain information about electron energy distribution function, we add a small amount (2.4 sccm) of a mixture of trace gases Xe (30.6%), Ne (30.6%), and He (38.8%) to the SiH_4 and H_2 mixture gas (40 sccm). Moreover, the discharge power was varied from 20 to 240 W at 60 MHz.

3. Results and Discussion

We evaluated the dependence of the deposition rate on distance from discharges with and without applying

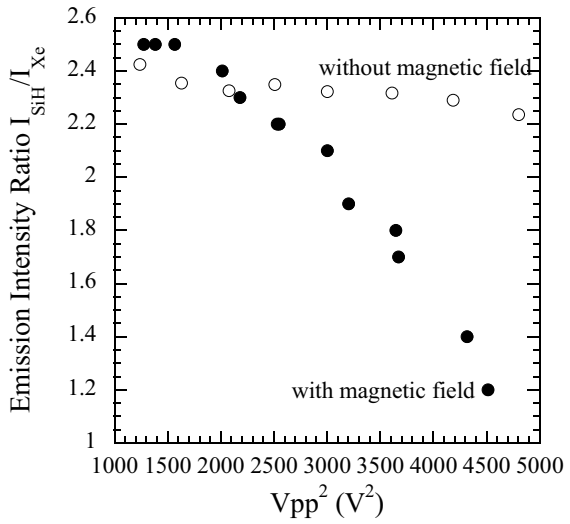

Fig.5. Dependence of emission intensity ratio of SiH to Xe on discharge power for discharges with and without magnetic field.

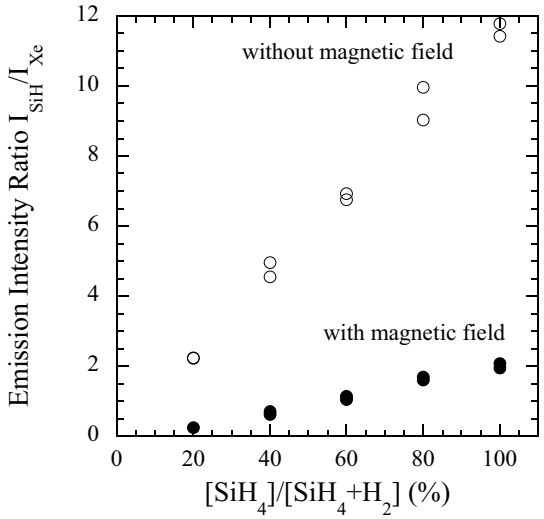

Fig.6. Dependence of emission intensity ratio of SiH to Xe on $[SiH_4]/[SiH_4+H_2]$ for discharges with and without magnetic field.

the magnetic field, as shown in Fig. 3. Without the magnetic field the deposition rate at z = 25 mm was 0.023 nm/s in the downstream region, and at z = -30 mm was 0.020 nm/s in the upstream region. Under the same deposition conditions, we obtained at z = 25 mm a deposition rate of 0.056 nm/s in the downstream region, and 0.032 nm/s at z = -30 mm in the upstream region; hence, a higher deposition rate when the magnetic field was applied. The increase of the deposition rate was of 20-100% in films deposited in both upstream and downstream regions.

The deposition rate decreases exponentially with increasing the distance in both, upstream and downstream regions, and for far regions from the discharges, the deposition rate in the downstream region is higher than that in the upstream region. The density of SiH_3, which is the main deposition precursor for high quality films [9, 12, 13], decreases exponentially with the distance from the discharges due to loss to the walls, whereas clusters, which are generated in the discharges, are driven towards the downstream region by gas flow and are incorporated into films there. The volume fraction of clusters incorporated into films is obtained as the ratio of the deposition rate of clusters to the total deposition rate. The deposition rate of clusters was deduced by fitting an exponential function of the downstream deposition rate near the discharges, where the deposition is mainly due to SiH_3, and taking the difference between the deposition rate and this extrapolation at a given z and r [14]. In the upstream region, however, the cluster volume fraction is negligible.

Comparing the films deposited with and without the magnetic field, a lower volume fraction of clusters into films when the magnetic field is applied, even though the deposition rate is higher. This result indicates that the application of magnetic field can increase the deposition rate of the main precursor of film deposition without increasing the incorporation of clusters significantly, which degrades film's qualities. Hence, this method allows us to increase the deposition rate and keep a high film quality.

Figure 4 shows the stability of films as the ratio of stabilized defect density to as-deposited defect density measured by electron spin resonance (ESR) spectroscopy. Films obtained by applying the magnetic field show stability comparable to those films deposited without magnetic field.

Figure 5 shows a comparison between dependence of emission intensity ratio of SiH (414 nm) to Xe (823 nm) on discharge power (proportional to Vpp^2) for discharges with and without magnetic field B. For discharges without B, the ratio is nearly constant while it decreases for discharges with B as the discharge power increases. Moreover, the difference between discharges with and without B is remarkable at high discharge power.

Figure 6 shows a comparison between the dependence of ratio of SiH to Xe emission intensities on SiH_4 dilution ratio for discharges with and without magnets. Since the threshold energy for SiH (414 nm) and Xe (823 nm) emissions are 10.33 eV and 9.82 eV respectively [15, 16], the results in Figs. 2 and 3 show that the magnetic field reduces the density ratio of electrons in a high energy tail of EEDF to that in a low energy part of EEDF, and hence it reduces the generation rate ratio of SiH_2 to SiH_3, while it increases significantly the radical generation rates. This is suitable for a-Si:H deposition since SiH_3 is the main film precursor while

SiH_2 leads to film metastability. Moreover, the intensities ratio is lower for lower $[SiH_4]/ [SiH_4+H_2]$.

Intensities of emissions from He and Ne are too weak to be detected for discharges without and with magnetic field, indicating that there are few high energy electrons above 19 eV in the multi-hollow discharges.

4. Conclusions

We applied a magnetic field in the discharge region of the multi-hollow discharge plasma CVD reactor to increase the deposition rate. The deposition rate with magnetic field is 20-100% higher than that without magnetic field, and the cluster volume fraction is 14-80% lower; which indicates that we can increase the deposition rate by applying the magnetic field without degrading the film quality.

The magnetic field reduces the density ratio of electrons in a high energy tail of EEDF to that in a low energy part of EEDF, and hence it reduces the generation rate ratio of SiH_2 to SiH_3, while it increases significantly the generation rate of SiH_3. These results will help us to optimize plasma parameters for deposition of highly stable a-Si:H films at a high deposition rate.

Acknowledgement

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5. References

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