Amorphous Hydrogenated Silicon Film Deposited by Reactive Electron Cyclotron Resonance Plasma†

Wei CHEN*, Shoji MIYAKE and Tomio ARIYASU*****

Abstract

Amorphous hydrogenated silicon (a-Si:H) films were prepared by an electron cyclotron resonance (ECR) plasma in silane and/or hydrogen diluted gases with the pressure of several Pa. In the film formation the local feature of ECR phenomenon was correlated with the film synthesis and the experiments reported here were carried out in a divergent magnetic filed and the microwave power input was varied up to 500 W. The effect of the local ECR phenomenon on the film synthesis was discussed with deposition electric property and composition of the films. It was found that the deposition rate and properties of the films changed drastically while their were deposited at different axial position in the plasma. The highest deposition rate was obtain near the axial resonance point with the value of 16 micrometer per hour in the silane plasma at the gas pressure of 4 Pa.

Meanwhile the optical gap of the film shown lowest value of 1.74 eV. Furthermore it was found that the photo conductivity of the films were also change remarkably while the distance L of the substrate holder and resonance region in axis was changed. The highest photo conductivity was obtained at L = 6 cm with the value of 1.5×10^{-7} S/cm, where the light intensity was 100 μW in 550 nm of the wavelength.

KEY WORDS: (a-Si:H) (ECR plasma) (plasma CVD) (photo conductivity) (optical gap) (FT-IR)

1. Introduction

Since the first successful fabrication of hydrogenated amorphous silicon (a-Si:H) solar cell by Carlson and Wronski [1], a-Si:H deposited by thermal and plasma chemical vapor deposition (CVD) have been widely studied in process of the film synthesis and the application of thin-film semiconductor devices of transistors, solar cell and so on. [2,3] In recent process study, the plasma sources usually are DC discharge, radio frequency (RF) discharge and an ECR plasma as new plasma source reveals many advantage characteristics due to a high electron temperature resulting higher ionization in a lower than 1 Pa gas pressure. Thus the ECR plasma attractively and successfully applied in CVD, sputtering and etching processes in comparison to the conventional sources.

The application of ECR plasma in sputtering by using the flux of the plasma from ECR source at down stream of the plasma was first reported by Matsuoka et al. [4] in 1982. After that many studies of the application of ECR plasma in the process had been reported and most of the studies was carried out in the down stream of the plasma where it is so-called reactive chamber. [4-6] However ECR effect is local phenomenon in the space, so that our interest is the information around the resonance zone and its application and more efficiency process carrying out near ECR zone is expected.

In our previous study, [7] the electron energy and its density in the plasma space indicated a remarkably non-uniform distribution in mirror and divergent magnetic fields, in hydrogen gas at the pressure range of several Pa to 10^{-2} Pa, inherent to the local feature of ECR phenomenon. The electron temperature and density have shown a higher value around the resonance region than those in the down stream region of the plasma. Appearance of these peak values was found to correspond well to the cyclotron damping of the input microwave near the resonance zone [8]. The propagation and damping of the microwave has shown that the plasma production is dominated by cyclotron absorption of the wave. While in our experiment of films synthesis [9] the highest deposition rate was obtained around the resonance region and also the film compositions were found to difference in space.

From these results we have demonstrated that studying the local effect of the ECR phenomenon is a key problem in the optimum and high quality film synthesis by ECR

† Received on May 6, 1992

* Graduate School Student of Osaka University

** Professor

*** Professor of Kansai University

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process plasmas.

In amorphous hydrogenated silicon films formation, the source plasmas have typically been RF discharges and the plasma properties have been studied by LIF [10], IR absorption [11], QMS [12]. Some simulation studies have also been performed for gas plasma [13] and surface reaction [14].

Study on a-Si:H film synthesis by ECR plasmas, however, has not been given so much [15-17] and we consider further extensive research is necessary, especially taking into account the local structure of the plasma.

In this paper the property of a-Si:H films prepared in a silane and/or hydrogen mixture ECR process plasma is reported in correlation with spatial structure of the plasma.

2. Experimental

A schematic drawing of the ECR plasma source is shown in **Fig. 1(a)**. The diameter of vacuum chamber is about 108 mm and mirror coils was set at the side of the vacuum chamber. The 2.45 GHz microwave was injected into vacuum chamber from the right side of the chamber in TE11 mode. As a basic configuration of this system, the length of the observation window to the microwave input window was set in 125 mm and this length was also changed in case. The gas inlet was also set at the same axial position of the observation window. In the present paper the operating gases are hydrogen and silane. The experiment was operated at a pressure range of 10^{-3} to several Pa. The plasma was measured by Langmuir probe from left side of the vacuum chamber in axis. A amorphous hydrogenated silicon films are prepared in the plasma with an axial movable water cooled substrate holder and films were also prepared with a heating substrate holder on the midplane between the two mirror coils where the gas inlet port and the observation window are settled in same axial position. The distance between the substrate and resonance zone is changed by both moving the substrate holder or by varying the coil current magnetic coil. The distribution of the mirror magnetic field on the axis is shown in the **Fig. 1(b)**.

The films were deposited on the substrate of fused quartz glass, Corning glass(# 7059) plate and silicon wafer. The substrate holder is water cooled and/or heated by a filament and the temperature of the substrate during the film synthesis was monitored by a thermocouple. The property of prepared films are evaluated with visible and ultraviolet absorption spectroscopy, infrared absorption spectroscopy, and by the photo/dark conductivity measurement. In the measurement of photo conductivity an Xe lamp was used and the wavelength was selected by a monochromator in 550 nm and the light intensity was set at 100 microwatt.

3. Results and discussion

Based on the study of the spatial property of ECR plasma, the experiments on the thin film synthesis were performed in SiH_4 (or H_2 diluted) gases, paying attention to the localized character of the process inherent to the ECR phenomenon.

Firstly a-Si:H films were prepared in a pure silane plasma at the microwave of 300 W with the gas pressure of 4 Pa. **Figure 2** shows the deposition rate variation to the distance L between the sample substrate and axial resonance point. The experiment was carried out in the divergent magnetic field by using a single coil of the right side

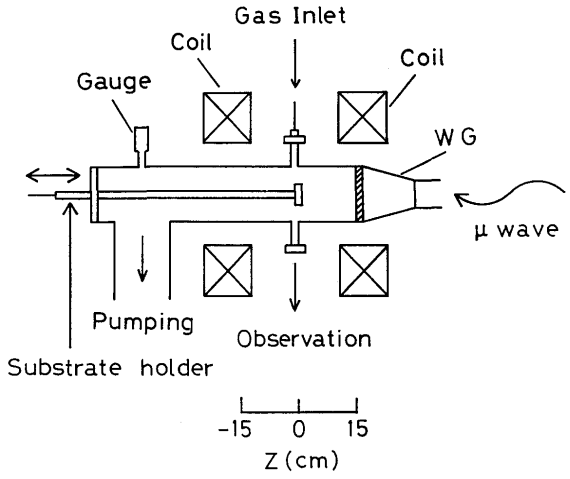

Fig. 1 (a) Schematic diagram of experimental apparatus.

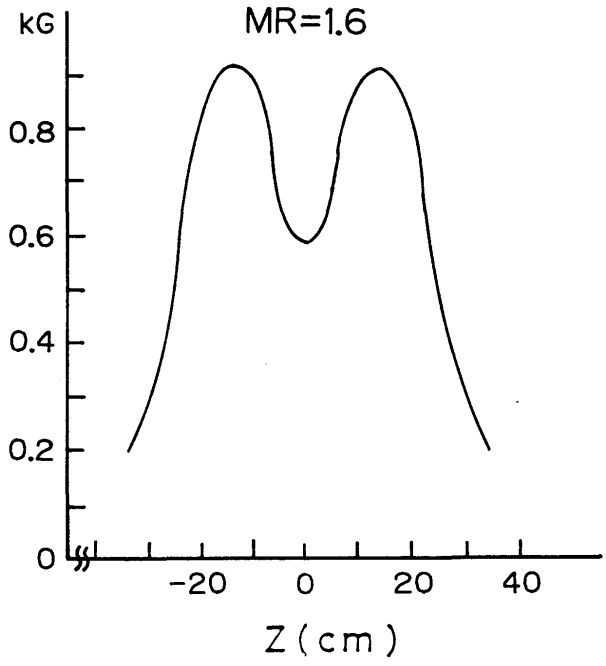

Fig. 1 (b) Axial distribution of the mirror magnetic field.

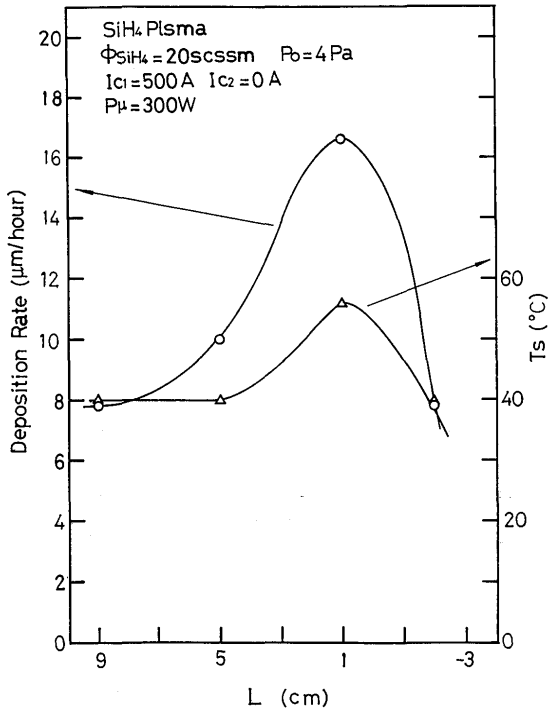

Fig. 2 Axial variation of a-Si:H film deposition rate in SiH_4 plasma.

as shown in fig. 1. It is clear that the deposition rate has a maximum near the resonance region with the value of 16 micrometer per hour. This result shows a same tendency of a-C:H film formation [9] and it demonstrated that the multi-dissociative gas was most efficiently dissociated and decomposed near the resonance region.

The non-uniform dissociation of the reactive gas in ECR plasma is not only influence on the deposition rate but also reflecting on the property and composition of the films.

The films prepared in the SiH_4 plasma were evaluated by FTIR spectroscopies. **Figure 3** shows the absorbance profiles of the films which was described in fig. 2. These profiles clearly reflect that non-uniform decomposition of the SiH_4 gas in axis, Where stretching band of SiH and SiH2 are at wave number of 2000 and 2100 cm^{-1}, respectively. [18] Comparison with the a-C:H film synthesis [9] we found the same tendency of the non-uniform decomposition of the reactive gases and the variation of the films composition which they were prepared at different axis position in the plasma. It was also found that the concentration of the hydrogen atom in the a-Si:H film is less than that in the a-C:H film.

The films of a-Si:H were also measured by visible-voilet absorption. The Tacu plot from these absorption spectra is shown in **Figure 4**. The film deposited near the resonance zone shows the lower optical gap (Eopt) of 1.74 eV. This is considered that a relative higher concentration of the

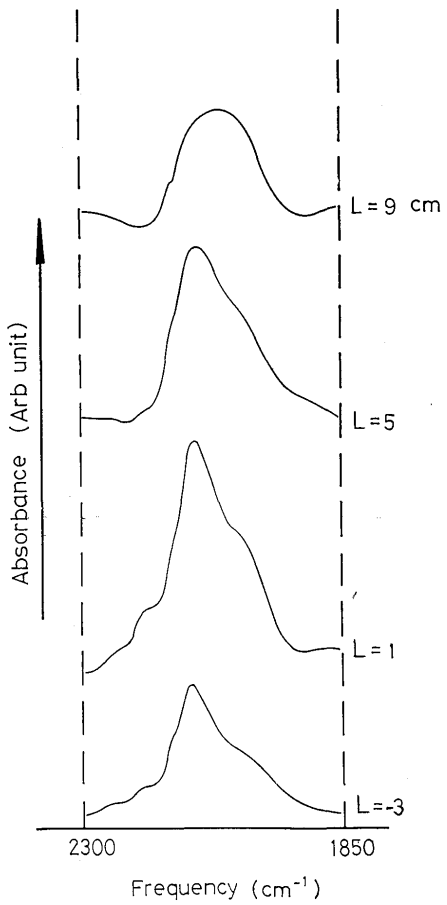

Fig. 3 Absorption profile of FTIR of a-Si:H film prepared in silane plasma.

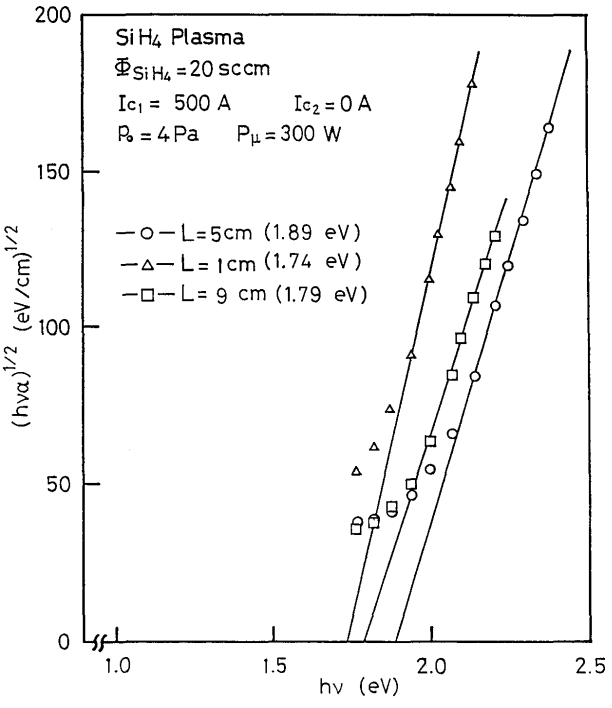

Fig. 4 Visible-violet charateristics of the a-Si:H films.

hydrogen in the film induced the change of the distribution of the density of state in the film.

The photo conductivity of these films also shows different, but the value was low at 10^{-8} Scm^{-1} order by an Xe lamp at the wavelength of 550 nm with irradiation power of 100 microwatts, where it is considered that the silane gas was over dissociated near the resonance zone at the microwave power of 300 W. So that the experiment were carried out further at much lower power of 50 W also by varying the distance L between the sample holder and axial resonance point. The deposition rate has a same tendency to compare with that deposited at the power of 300 W whose distribution in axis is shown in the **Figure 5**. The variation of photo conductivity and dark conductivity of the films are shown in **Figure 6**. The photo conductivity of the films depends strongly on the distance L and changes over one order even in such a short distance of about several cm. This result demonstrates that the property of the films exhibits strong correlation with the axial nonuniformity of the plasma. This result also indicates that the formation of the silane decomposition in the plasma strongly influences on the film deposition in comparison with the effect from ion and electron.

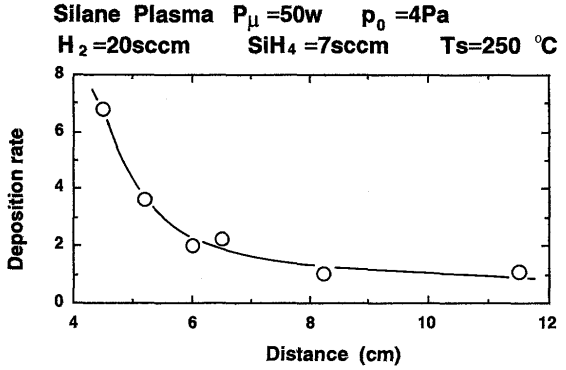

Fig. 5 Variation of the deposition rate of a-Si:H film as a function of the distance L between the sample substrate and axial resonance point.

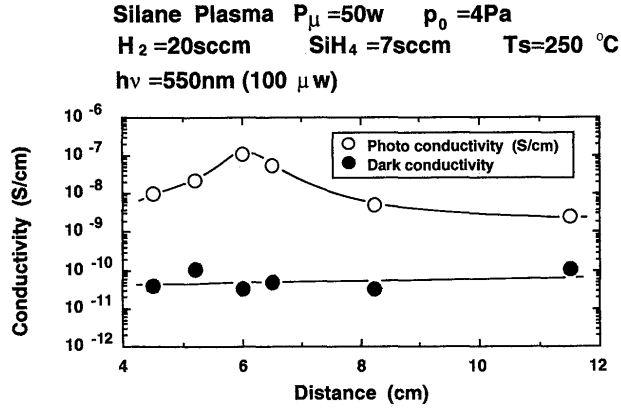

Fig. 6 Photo/dark conductivity of the films versus the distance between the sample and resonce point on the axis.

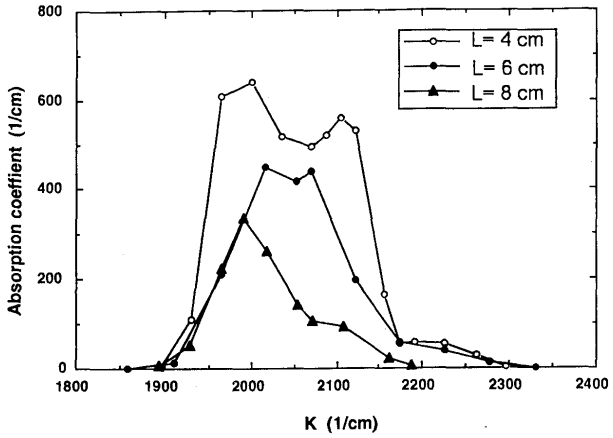

Fig. 7 FTIR absorption spectra of C-H stretching band of a-Si: H film.

Figure 7 shows the IR absorption coefficient spectra of the stretching band of SiH and SiH_2 in these films. Here certainly the spectra were normalized by the film thickness. It is clear that the composition of the films varied remarkably while the films deposited at different axial position. From this absorption spectra we calculated the concentration the hydrogen atoms containing the films by the equation [19] of

$$N_H = A\int \frac{\alpha(\omega)}{\omega} d\omega$$

$A = 1.4\times10^{20}\ cm^{-2}$ (Stretching mode)

where the N_H and $\alpha(\omega)$ are the bonding hydrogen atom density and absorption coefficient, respectively.

The calculated result is shown in **Figure 8**. The concentration of the hydrogen atoms in the film decreased when the distance L between sample substrate and axial resonance point was increased. The film with highest photo conductivity corresponds the concentration of the hydrogen atoms of about 10% in the film. This result indicates that silane and hydrogen gases are dissociated strongly near the resonance zone, so that the density of hydrogen atom were much higher than the other area.

Next we deposited films at position far from the resonance zone of L = 16 cm by varying the microwave power of 50 to 500 W. The change of photo conductivity of these films is shown in **Figure 9**. It is clear that the photo conductivity of the films increased with input microwave power. This result indicates that the silane gas dissociates and/or dissolves mainly in the resonance region and extensively recombined before reaching the sample surface positioned at L = 16 cm. It demonstrates that the controllability of decomposition of the silane gas is a key point to prepare a high quality film with higher photo conductivity.

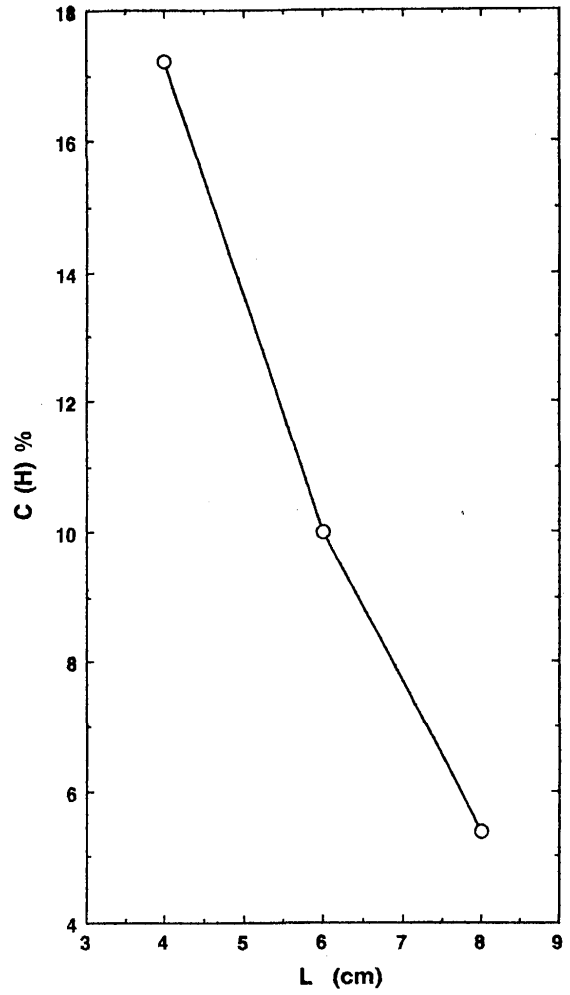

Fig. 8 The concentration of bonded hydrogen atoms in the a-Si:H films.

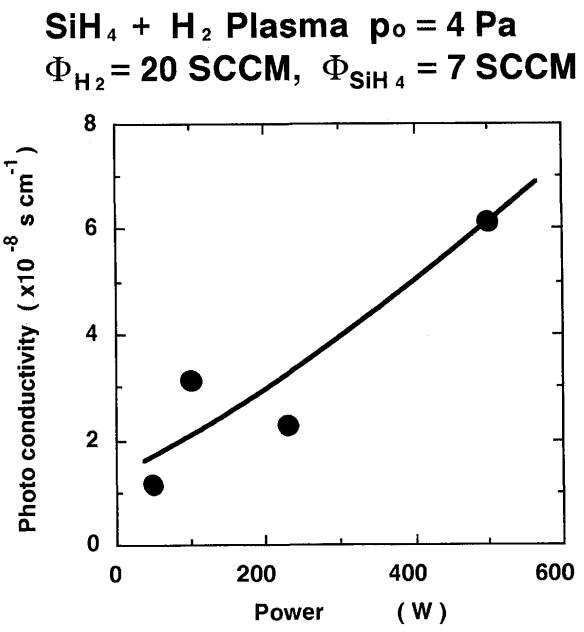

Fig. 9 The dependence of the photo conductivity of the film on the input micowave power.

4. Conclusion

In SiH_4(or diluted by H_2) at gas pressure of 4 Pa, a drastic variation of the film deposition rate and its properties such as optical gap and photo conductivity were found, when the distance between the substrate and the resonance zone point on the axis changed only about 10 cm. The variation of the film properties corresponds well to the spatial structure of the plasma inherent to the local effect of ECR phenomenon.

The result from this study also demonstrated the possibility of that the a-Si:H film can be deposited in high quality as well as high deposition rate in the ECR plasma by control the resonance zone in the plasma space.

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