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https://doi.org/10.15017/16738

出版情報：九州大学大学院総合理工学報告. 26 (3), pp.337-340, 2004-12. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

九州大学大学院総合理工学報告
第26巻 第3号 337 - 340 頁 平成16年12月

Engineering Sciences Reports, Kyushu University
(KYUSHU DAIGAKU SOGORIKOGAKU HOKOKU)
Vol. 26, No. 3 pp. 337 - 340 DEC. 2004

Investigation of 915 MHz ECR Plasma Parameters with SiH_4/H_2 Mixtures

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(Received October 29, 2004)

Plasma parameters were measured successfully in a 915 MHz ECR plasma with H_2 and SiH_4/H_2 mixtures using a heated Langmuir probe. The experimental results show that there is a correlation between electron temperature and crystallinity of microcrystalline silicon. From the data analysis, it was found that there is a possibility that the electron temperature increased by production of negative ions promotes the crystallinity via some chemical reactions.

Key words: *Microcrystalline silicon; ECR plasma; Electron temperature; Heated Langmuir probe*

1. Introduction

Microcrystalline silicon (μc-Si) thin film has been much attractive to semiconductor device such as solar cell and thin film transistor for PDP [1, 2]. Recently, the industry strongly requires higher deposition rate, more uniformity over large area and longer operation life. So far, several methods were tried for the fabrication of μc-Si thin film. For instance, mercury sensitized photo chemical vapor deposition (CVD) utilizing decomposition reaction of SiH_4 molecules with photo excited Hg, reactive sputtering of crystalline-silicon targets with $Ar+H_2$ plasma, direct photo CVD method where high energy photons from Xe-resonance lamp or low pressure Hg lamp are used for direct excitation of SiH_4 molecules, hot-wire CVD method to decompose SiH_4 and H_2 by means of catalytic reactions on heated metal surface. However, from the viewpoint of mass production with high quality, plasma enhanced CVD method (PECVD) is the most useful method [3-7].

Electron cyclotron resonance (ECR) plasma has superior characteristics such as high electron density ($n_e \sim 10^{18}$ m^{-3}) under low gas pressures ($\sim 10^{-3}$ Torr) [8,9], which meets high deposition rate and high quality film with less dust particles. In addition, the use of 915 MHz excitation for ECR plasma leads to higher controllability of electron temperature and sheath potential [10] than conventional 2.45 GHz excitation.

In this paper, we produced a 915 MHz ECR plasma with SiH_4/H_2 mixtures at low pressure and measured the plasma parameters in details under various experimental conditions. Furthermore, we prepared μc-Si thin films on glass substrates and analyzed their property in order to examine the relationship between plasma parameters and film quality. According to the recent fabrication of μc-Si thin film, the dilution ratio of H_2 to SiH_4 is extremely high and typically 0.9. Under such conditions, there are only few discussions about plasma parameters based on experimental data.

2. Experiment

A schematic diagram of the experimental apparatus is shown in Fig. 1. The cylindrical vacuum chamber was made of stainless steel with an inner diameter of 290 mm and a length of 1200 mm. The chamber wall was grounded. The substrate was located at the axial position of z = 550 mm from the quarts window, and isolated electrically and heated at a constant of 250 ℃. The 915 MHz microwaves with TM_{01} mode were injected into the chamber at the input power of 0.6 kW to 2.2 kW. As a working gas, pure H_2 and SiH_4/H_2 mixtures with different mixture ratio were used.

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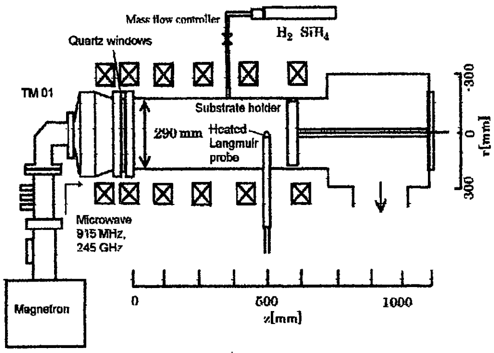

Fig. 1. Schematic diagram of the experimental apparatus

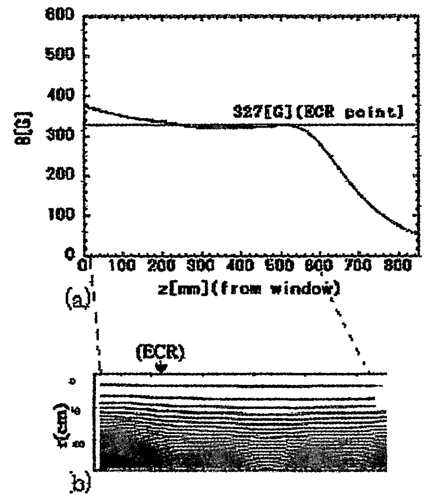

Fig. 2. Magnetic field configuration. (a) Axial distribution and (b) two-dimensional contour diagram of the magnetic field.

The gas flow rate was 10 to 200 sccm for H_2, and 60 to 200 sccm for SiH_4/H_2 mixtures. The total pressure was kept at 10 mTorr.

The magnetic field B was applied using 6 magnetic coils. In the previous research using nitrogen, the electron temperature of 915MHz ECR plasma was considerably controlled by changing the magnetic field distribution [11]. Accordingly, we used similar magnetic configuration in expectation of high controllability of electron temperature. Figure 2(a) and 2(b) show the magnetic field distribution and the contour plot corresponding to the magnetic field, respectively. The ECR position corresponding to B= 0.0327 T was set over relatively wide area (250 mm $\leq$ z $\leq$ 550 mm) in order to increase the controllability of electron temperature T_e [11].

The plasma parameters were measured carefully using Langmuir probe because the analysis of probe characteristics measured in magnetized plasma is limited. In addition, in the ECR plasma with SiH_4/H_2 mixture gas, the thin films always cover the probe surface and make the measurement error increase. The heated probe developed by ourselves can make this contamination infection decrease adequately. The probe made of the tungsten wire with 0.3 mm diameter was heated by the DC current of 2 A typically.

3. Results

First, the electron temperature and electron density of 915 MHz ECR plasma with pure hydrogen were measured as a function of microwave power.

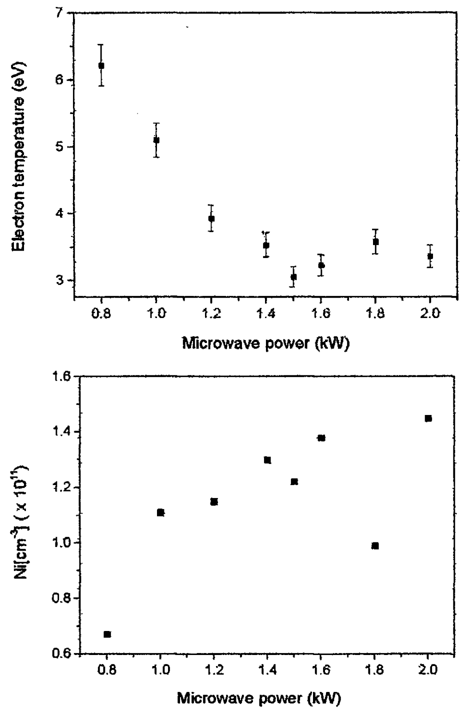

Fig. 3. The microwave power dependences of (a) T_e and (b) n_e in H_2 plasma at 10 mTorr.

As shown in Fig. 3, the electron temperature (T_e) decreased as microwave power increased from 0.8 to 1.5 kW, and slightly increased above 1.5 kW. The electron density (n_e) increased monotonically as the microwave power increased from 0.8 to 2 kW except 1.8 kW. In the previous experiment, with N_2, O_2, Ar gas, Te always increased as microwave power increased. At the present stage, we cannot explain the tendency T_e in H_2 plasma. Probably some chemical reactions have an important role and the discussion will be done in the future.

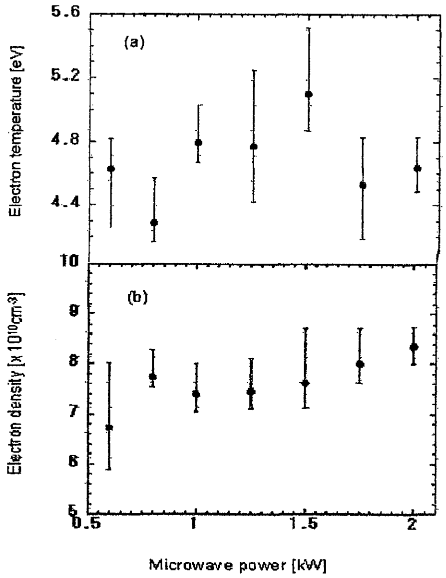

Fig. 4. The microwave power dependences of (a) T_e and (b) n_p in SiH_4/H_2 mixture plasma at 10 mTorr, D=0.1.

Next, we show the results for SiH_4/H_2 mixture plasma. Figures 4(a) and 4(b) show the electron temperature and the positive ion (n_p) dependence on the microwave power, respectively. Here we define D as H_2 flow rate/ (SiH_4 flow rate + H_2 flow rate). n_p was calculated by assuming that the positive ions are composed of both H^+ and SiH_3^+. It was observed that T_e had a local maximum value at 1.5 kW. On the other hand, n_p was observed to be slight monotone increase.

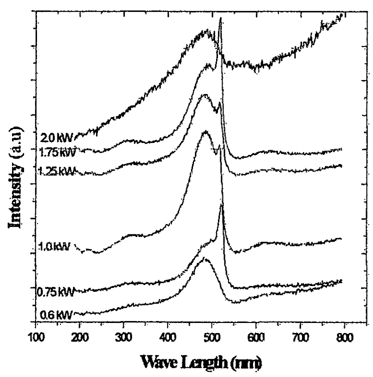

Fig. 5. Raman scattering spectrum from the thin film with changing the microwave power

Furthermore, Si thin films were actually prepared on the glass substrate (Corning 7059) at a constant temperature of 250 ℃ in accordance with the experimental conditions described above.

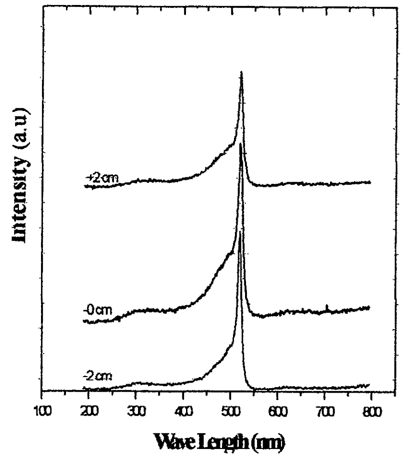

Fig. 6. Raman scattering spectrum at 1.5 kW where the best microcrystallines was obtained.

They were evaluated by Raman scattering spectroscopy as shown in Fig. 5. The production of μc-Si was clearly observed only at the microwave power between 1.25 kW and 1.75 kW. The best crystallinity was obtained at 1.5 kW as shown in Fig. 6. Then, the volume fraction I_c/I_a was 2.1 and μc-Si was prepared homogeneously in the radial direction of r = ±2 cm from the center of substrate.

4. Discussion

Here, we discuss the correlation between the electron temperature and the film property.

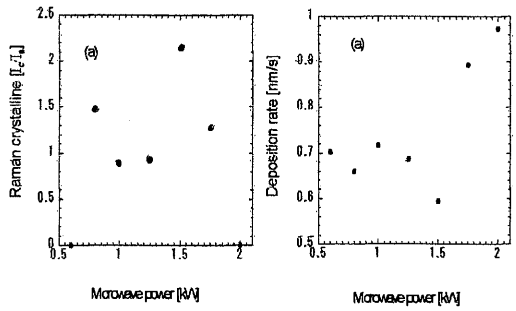

Fig. 7. Dependence of μc Si film on the microwave power. (a) Volume fraction (b) Deposition rate

Figures 7 show the dependence of the film property on the microwave power. The volume fraction of μc-Si was evaluated using I_c/I_a obtained from the Raman scattering intensity. I_c and I_a indicates the Raman intensity at a wave number of 520 cm^{-1} and 480 cm^{-1}, respectively. The deposition rate was evaluated from the film thickness measured using a spectrophotometer. From the comparison between Fig.4

(a) and Figs. 7, we notice that the volume fraction is maximum and the deposition rate is minimum when the T_e has a local maximum value at 1.5 kW. In general, it is said the following reactions are especially important for Si thin film deposition process [13].

$$e + SiH_4 \rightarrow e + SiH_3 + H. \quad (1)$$

$$SiH_4 + H \rightarrow SiH_3 + H_2. \quad (2)$$

When reaction (1) proceeds due to the increase of T_e, the density of SiH_3 molecules which are main precursors increases and the crystallization proceeds under the adequately supplied H. However, when this reaction proceeds too much, the depletion of SiH_4 occurs due to reaction (2). As a result, the excessive H works to etch the film surface and the film deposition rate decreases. This mechanism has been often confirmed in the a-Si film preparation using the conventional capacitive coupled plasma [13]. In our case, thin film of interest is μc-Si and the plasma is generated by microwaves under low gas pressure. The same mechanism cannot be always applied. In order to make clear the mechanism, we need further research such as measurement of radicals and numerical simulation taking important physical and chemical reactions into account.

Next, we considered why Te increased. Figure 8 show the I-V curves of the heated Langmuir probe which correspond to Fig. 4(a).

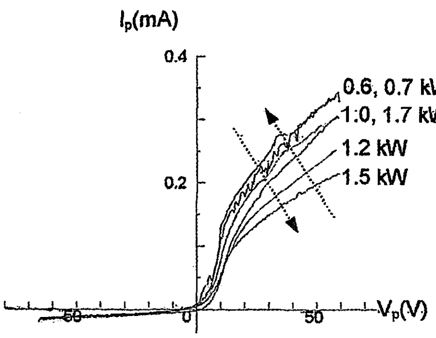

Fig. 8. I-V curves from the heated Langmuir probe

As shown in the figure, electron saturation current became lowest value at 1.5 kW where the T_e was maximum. This result suggests the production of negative ions. Therefore, we can infer that increase of T_e was caused by the loss of electrons due to the electron attachment. In the ECR plasma, however, the microwave power deposition also influences directly on T_e. Further research is necessary in order to clarify the reason.

5. Conclusion

Plasma parameters in a 915 MHz ECR plasma with H_2 and SiH_4/H_2 mixtures were measured successfully using a heated Langmuir probe. From the data analysis, we found that we can explain the relationship among electron temperature, crystallinity of μc-Si and deposition rate of the film. This mechanism should be confirmed by the further investigation.

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