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ECR Plasma in CH_4/H_2 Gas Mixture And Film Deposition

S. MIYAKE*, W. CHEN**, N. WATANABE*** and T. ARIYASU****

Abstract

An ECR plasma in CH_4/H_2 gas mixture was studied experimentally in comparison with the hydrogen plasma reported previously. Formation of a-C: H films was also performed in a gas pressure range of 7×10^{-1} to 15 Pa. Efficient film formation was achieved near the resonance region and a good correlation between optical emission and the film deposition rate was verified. The infrared absorption and electron spin resonance characteristics of prepared films indicated that their compounds wer governed by sp^3 structures of CH_n (n=1 to 3) radicals.

KEY WORDS : (ECR Plasma) (Plasma CVD) (a-C: H Film) (Electron Spin Resonance, ESR) (Optical Gap).

1. INTRODUCTION

ECR plasmas have widely been used for and are playing a potentially role in various thin film synthesis, since they typically reveal various comfortable characteristics for the material processing[1-4].

In a former report[5], we studied the characteristics of an ECR process plasma in hydrogen gas, taking into account the spatially localized property of ECR phenomenon in a non-uniform magnetic field. The spatial distribution of the plasma parameters were studies in detail in various vacuum chamber and magnetic field configurations in the pressure range of 10^{-2} to 10^{-1} Pa. A strongly non-uniform axial distribution of electron energy and electron density was obtained with a peak value near the resonance zone, due to the local feature of the ECR phenomenon at a high gas pressure over 1×10^{-1} Pa. This result made us suggest that the reaction process would also be different in space causing different effects on the film property. We made an experiments in CH_4/H_2 gas mixture with a-C: H film formation.

In this paper experimental results on the study of the correlation between the ECR plasma behavior and the film deposition in H_2+CH_4 gas mixture are reported.

2. Experimental Procedure

The experimental apparatus used is shown schematically in **Fig. 1**. Two kinds of the discharge chamber were used as shown in a) and b) of the figure. The detailed configuration of the vacuum chamber was described in the previous paper[5]. The operating gas is H_2 and CH_4 mixture in the pressure range of 10^{-1} to 15 Pa. The plasma behaviors were studied by using Langmuir probes and optical emission spectroscopy method. To avoid an influence of the deposition of the film on the probe surface to V-I characteristics, the measurement was performed rapidly within one minute after the inclusion of methane into hydrogen discharge and the probe was cleaned at each data acquisition verifying to obtain the same characteristics in the hydrogen discharge. The optical emission spectroscopy was applied to monitor H atoms and CH radical species and so on in the plasma.

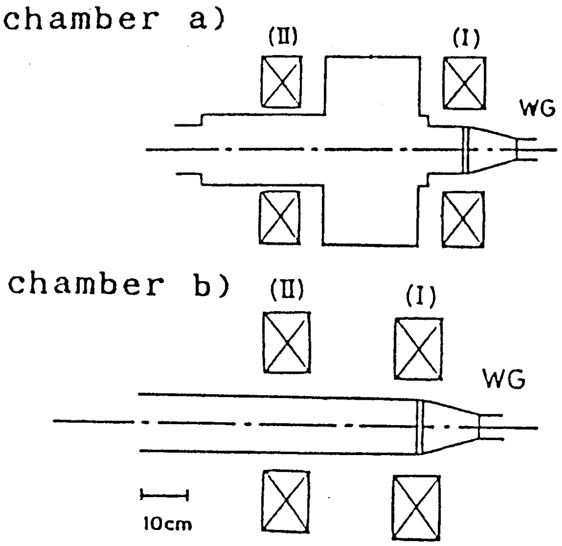

Fig. 1 Schematical diagram of experiment apparatus.

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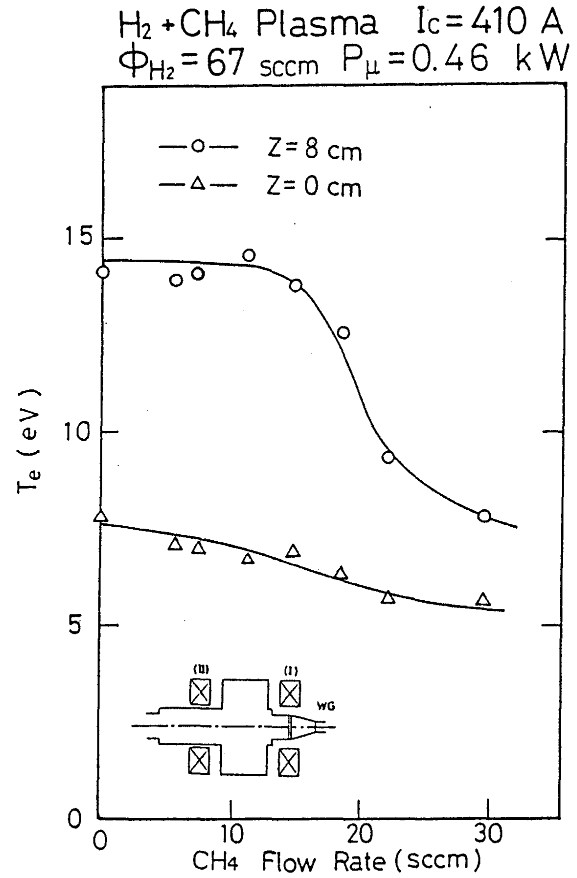


Fig. 2 Variation of the electron temperatures T_e in the vacuum chamber (a) by the admixture of CH_4 gas into the H_2 plasma.

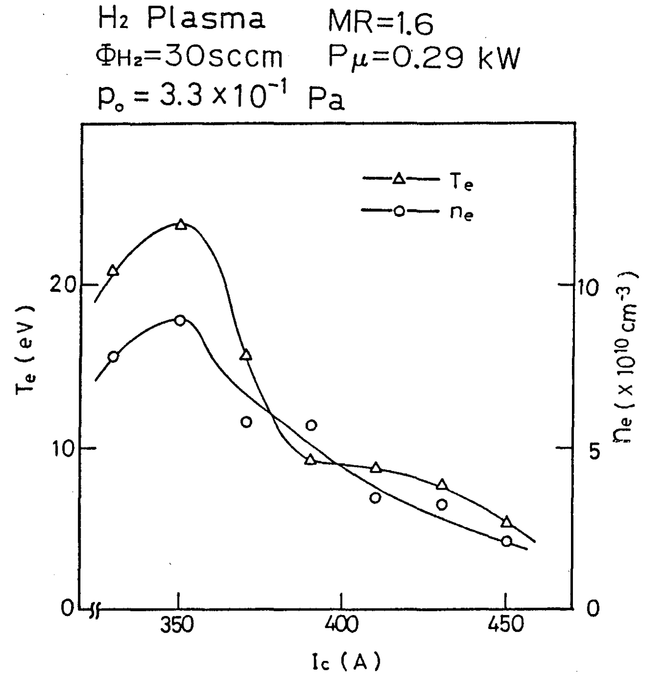
For the carbon film deposition, quartz plate and silicon wafer were used as substrates. The substrate holder was water cooled and the temperature of the substrate during the film synthesis was monitored by a thermocouple. The property of prepared films was evaluated with, ESR spectroscopy (Bruker ESP300), visible and ultra-violet absorption characteristics, and infrared absorption characteristics (JEOL JIR-AQS20M).

3. RESULTS AND DISCUSSION

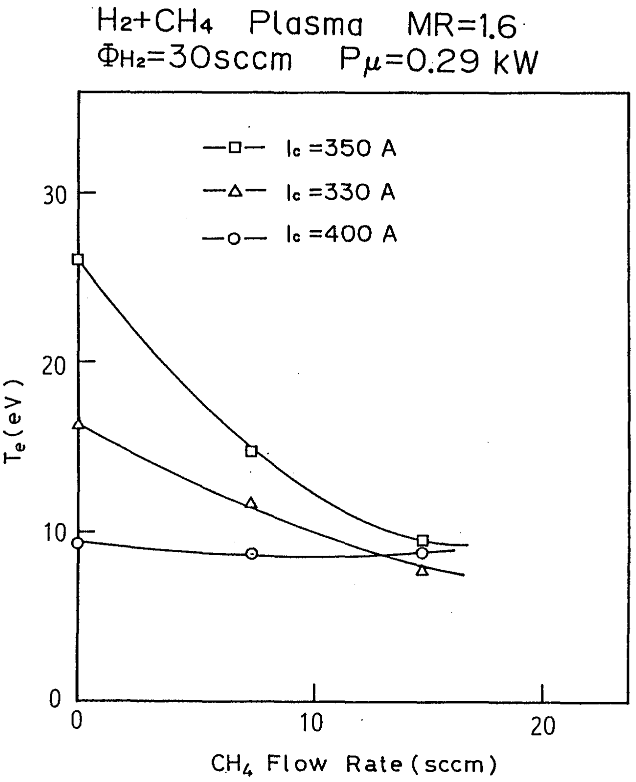
3.1 PLASMA PROPERTY

In our previous study$^{5)}$ the axial distribution of electron temperature T_e and electron density n_e of hydrogen plasma was measured at a pressure of 3.3×10^{-1} Pa in the chamber a). The result gave a strongly non-uniform distribution, and the highest temperature was obtained around the resonance zone of the microwave input side.

To know the variation of this character in CH_4/H_2 gas mixture, we admixed CH_4 gas into the hydrogen plasma. The distribution changed remarkably as shown in **Fig. 2**.



(a) Dependence of the electron temperature T_e in the vacuum chamber (b) on the magnetic coil current in the case of the hydrogen plasma.



(b) Variation of the electron temperatures T_e by the admixture of CH_4 gas into the H_2 plasma for three values of the magnetic coil current.

Fig. 3

The variation of T_e in the vacuum chamber a) with the flow rate of CH_4 is given. It is clear that T_e diminishes by increasing the flow rate. The data at $z=8$ cm corresponds to that near the resonance zone, where the highest T_e is obtained in the H_2 plasma. This figure indicates that T_e is diminished mainly around the resonance zone to a value nearly equal to that at $z=0$ cm.

Figure. 3(a) shows the dependence of T_e and n_e, measured at the center of the hydrogen plasma, on the magnetic coil current I_c in the case of the vacuum chamber b). The electron temperature and electron density rise with increasing I_c and show a peak value at $I_c = 350$ A, corresponding to the fact that the resonance zone moves in space by changing the coil current I_c. When I_c is higher than 400 A the resonance zone moves towards the radial direction on the midplane of the plasma. It gives a rapid decrease of T_e and n_e as is clearly found in the figure.

As shown in Fig. 3(b), mixing CH_4 gas to the hydrogen plasma gives a similar dependence of T_e on the flow rate of methane; the temperature measured at the center of the plasma again decreases drastically at $I_c=350$ A, where the highest T_e is obtained in the hydrogen plasma.

From these results it was concluded that the efficient dissociation and/or resolution of CH_4 gas was performed near the resonance zone, where the most effective energy gain of electrons from the microwave was obtained. It in turn gave the cooling of electrons by the admixture of CH_4 into H_2 gas. This point was further checked by the emission spectroscopy.

Fig. 4 shows the dependence of radially integrated emission intensity of the H_γ line from the central part of the plasma on the input microwave power P_μ in the case of the chamber b). In the hydrogen plasma the intensity shows a linear increase with P_μ . When we admix CH_4 into this plasma, the H_γ line emission becomes weaker by increasing the flow rate of CH_4 at a power input below 0.4 kW, and it is reversed over 0.4 kW. This result well reflects the above described interpretation of electron cooling. The energy of electrons near the resonance zone is dissipated most efficiently by multiple dissociation processes of CH_4 gas mixed into the hydrogen plasma and the axial nonuniformity of the electron energy becomes weak.

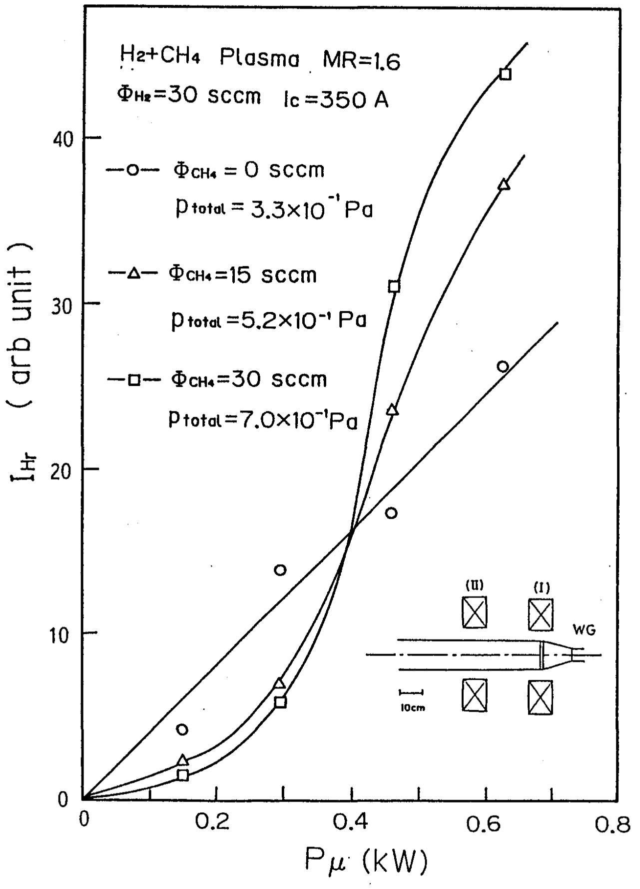


Fig. 4 Dependence of emission intensity of the H_γ line on the microwave power in H_2 and CH_4/H_2 plasmas.

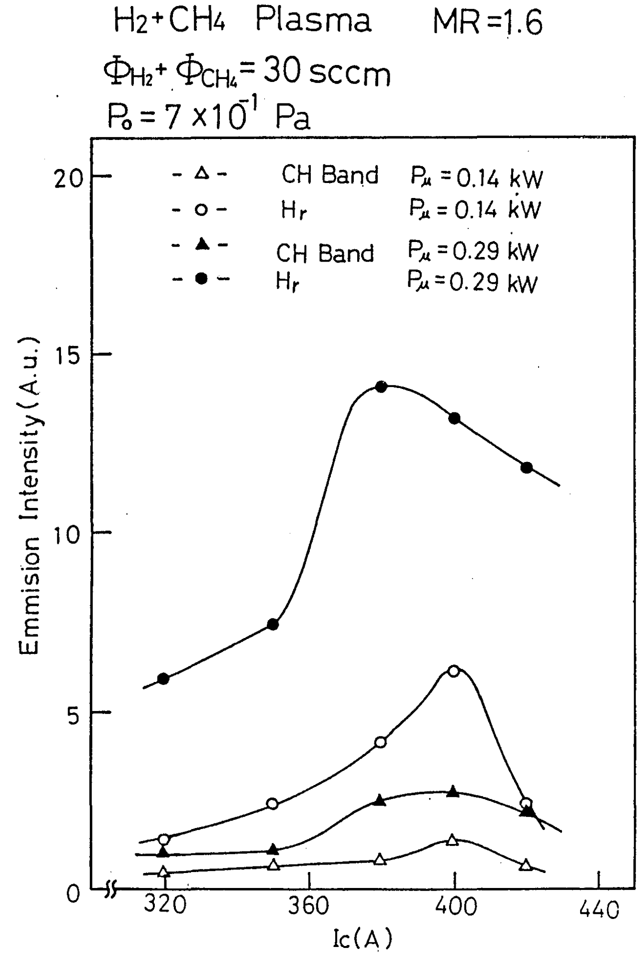


Fig. 5 Dependence of emission intensity of the H_γ line on the magnetic coil current inhthe H_2 and H_2+CH_4 plasma.

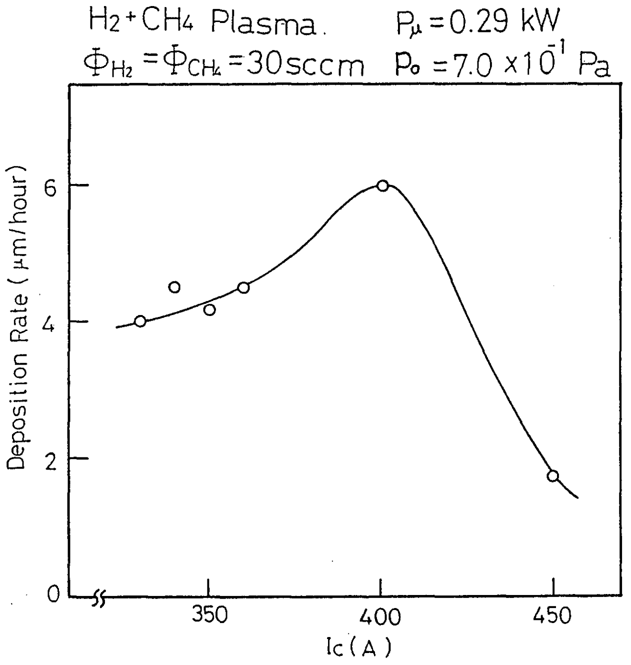


Fig. 6 Dependence of the deposition rate of the a-C: H film on the magnetic coil current in the CH_4/H_2 plasma.

The emission intensity of H_γ line and CH band head spectra as a function of the magnetic coil current is shown in **Fig. 5** for two microwave powers. In the figure the emissions have peak values around $I_c = 370 - 400$ A, where the resonance regions are positioned near the central part of the plasma. Dependence of the intensity on the microwave power input has the same tendency as that in Fig. 4. It is interesting to note that the intensity ratio of CH band to H_γ line in the ECR plasma is much lower than *rf* plasma reactors$^{6)}$. Here we also notice that the peak value of the emission intensity in this figure and eleftron temperature in Fig. 3(a) appears at different coil currents. Indeed this is because the probe measurement only indicates the information at a point on the midplane of the plasma while emission specturm is obtained as the integrated intensity in the radial direction.

3.2 SYNTHESIS OF a-C: H FILMS

Amorphous hydrocarbon films were prepared on silicon wafers and quartz glasses with a thickness of 1 mm and a diameter of 2 cm. The substrate temperature was controlled at around 100 °C by the water cooling. A typical example of the deposition rate of the synthesized films at $z = -2$ cm on the plasma axis as a function of the magnetic coil currents is shown in **Fig. 6.** It is clear that the deposition rate has a dependence on the coil current in good correspondence with the optical emission data given in Fig. 5, indicating that the deposition rate is higher near the resonance region of the plasma.

The data mentioned above was obtained in a simple mirror magnetic field. The data obtained in an expanding plasma in a divergent magnetic field, where the magnetic current of the left side coil II was set to be zero, also indicated the same tendency.

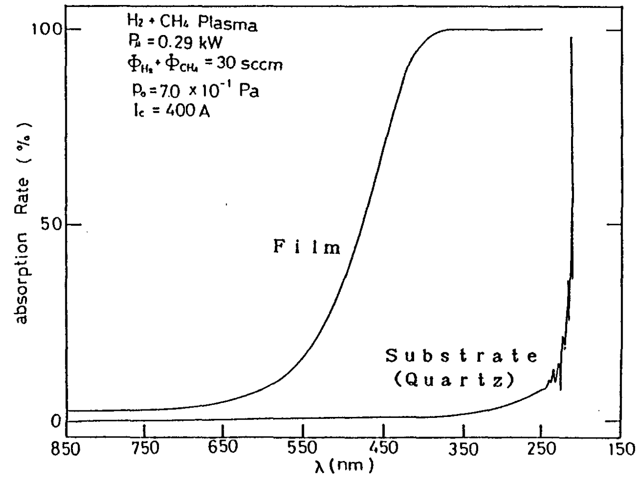


Fig. 7 Visible-ultraviolet absorption spectra of the a-C: H film.

These results well reflect that the dissociation and/or resolution of CH_4 has a spatially non-uniform character causing the non-uniform deposition rate of the carbon film by the local feature of the ECR phenomenon.

The prepared films were analyzed by visible-ultraviolet and infrared absorption measurements. **Figure 7** shows a typical visible-ultraviolet absorption spectrum of the film. The absorption starts from around 650 nm and almost fully developed below about 400 nm. The absorption above the band edge of crystalline compounds is usually described$^{7)}$ by

$$E_{h\nu}\,\alpha = \text{constant} \times (E_{h\nu} - E_G)^n \qquad (1)$$

where $E_{h\nu}$ and E_G are the energies of photons and the band gap respectively. Factor α is the absorption coefficient and n is a index of the equation which changes for different crystalline compounds. When the bands are both parabolic this equation reduces to

$$E_{h\nu}\,\alpha = \text{constant} \times (E_{h\nu} - E_G)^2\,. \qquad (2)$$

This equation was applied for the evaluation of the a-C:H film spectrum. Plot of $(E_{h\nu}\,\alpha)^{1/2}$ versus $E_{h\nu}$ frequently yields a straight line. By this method we obtained the optical gap of the film estimated to be about 2.5 eV. Typically the optical gap of the a-C:H film prepared by an *rf* discharge is between 1.2 and 2.0 eV$^{8)}$ and for the diamond film it is about 5.5 eV.$^{9)}$

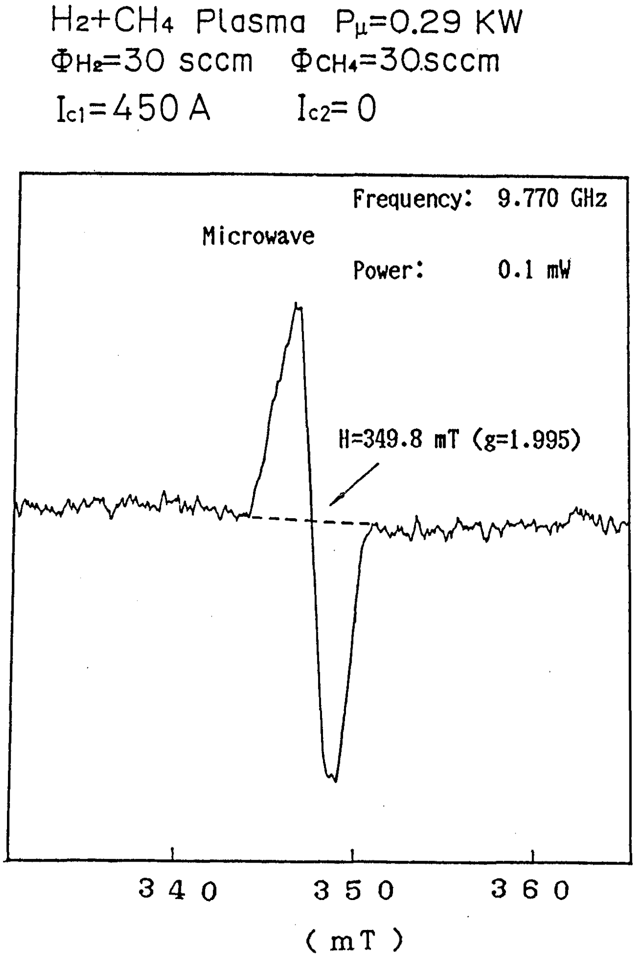
In order to understand the film property correlated with the plasma character, we have estimated the structure and the composition of the films by ESR

(Electron Spin Resonance) and FT-IR (Fourier-transform Infrared Spectroscopy) methods. The result is shown in **Fig. 8.** The ESR measurement as shown in Fig. 8(a) was obtained at a microwave frequency of about 9.77 GHz and we obtained the *g* factor of 1.995. This indicates the compound of the film is governed by the sp^3 structure.

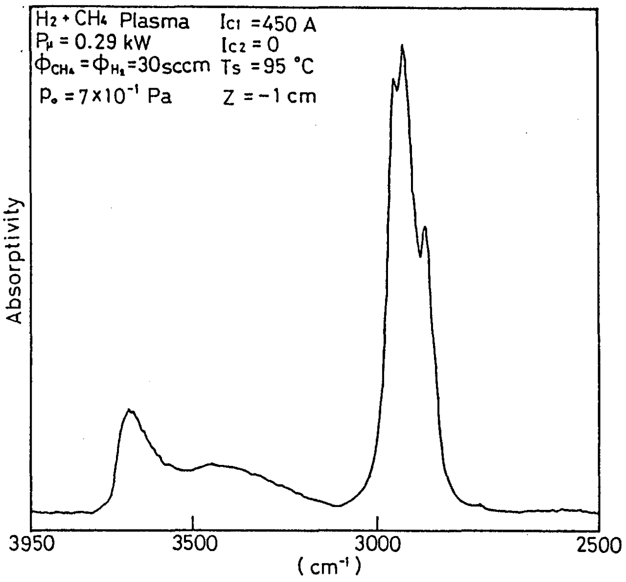
For the same film, the IR absorption spectra was obtained as shown in Fig. 8(b). We find three peaks in the absorption profile between 2800 cm^{-1} and 3000 cm^{-1}. This result corresponds well to ESR characteristics. The observed three peaks at about 2957 cm^{-1}, 2928 cm^{-1} and 2872 cm^{-1} indicate that the compound of the film has almost sp^3 structure as the reference data[9)] shows in **Tab. 1.**

4. CONCLUSION

Characteristics of an ECR plasma in CH_4/H_2 gas mixture and its correlation with the a-C:H film deposition were studied experimentally taking into account the local effect of the ECR phenomenon. In the hydrogen plasma, the electron temperature T_e was axially



(a) Electron spin resonance spectrum of the prepared a-C: H film.



(b) IR absorption spectrum of the C-H stretch bands of a-C: H film.

Fig. 8

Table 1 C-H stretch absorption bands, predicted.

Band	Conifguration	predicted frequency (cm^{-1})
1	sp^1CH	3305
2	sp^2CH(arom.)	3050
3	sp^2CH_2(olef.)	3020
4	sp^2CH(olef.)	3000
5	sp^3CH(asym.)	2960
6	sp^2CH_2(olef.)	2950
7	sp^3CH_2(asym.)	2925
8	sp^3CH	2915
9	sp^3CH_3(sym.)	2870
10	sp^3CH_2(sym.)	2855

non-uniform with a peak value near the resonance zone as reported in the previous paper. By the admixture of CH_4 gas into the H_2 plasma, T_e was decreased remarkably due to the efficient dissipation of electron energy by the multiple dissociation and/or resolution processes of CH_4. The decrease of T_e was dominated near the resonance zone, and the emission intensity of the H_γ line and CH band spectrum head gave a stronger value near the resonance zone in comparison with other regions. The deposition rate of the a-C:H film was also higher when this zone moves close to the substrate by the change of the magnetic coil current. The compound of the prepared films was almost in the sp^3 state of $CH_n(n=1,2,3)$.

It is demonstrated that the detailed study of the spatial structure of the ECR plasma inherent to the local ECR phenomenon in a nonuniform magnetic field is one of the key problems in the film deposition.

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