Optical emission diagnostics of H_2+CH_4 50-Hz–13.56-MHz plasmas for chemical vapor deposition

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The emission spectra of $H_2 + CH_4$ plasmas excited at 50 Hz–13.56 MHz were measured. The emission intensity ratios of H_α/H_2^* ($^3\Sigma g \rightarrow {}^3\Sigma u$) from $H_2 + CH_4$ plasma at 50 Hz and 13.56 MHz were about 0.7 and 0.05, respectively. The electron temperature was obtained from the two-line radiance ratio method using the Balmer lines (H_α and H_β), and rapidly decreased with an increase above 200 kHz. The electron temperature for $H_2 + CH_4$ plasma is 16 000 K at 1 kHz and 8200 K at 13.56 MHz. The plasma-maintaining voltages for H_2 and $H_2 + CH_4$ mixtures were also measured. The maintaining voltages were constant below 200 kHz, and rapidly decreased between 200 kHz and 13.56 MHz. The position dependence of emission intensity was also measured for H_α, H_β, and H_2^* at 50 Hz and 13.56 MHz. The results are interpreted in terms of the electron distribution in the plasma.

I. INTRODUCTION

Silicon nitride (SiN_x) and amorphous carbon (a-C:H) used in semiconductor devices are generally deposited with high-frequency (e.g., 13.56 MHz and 2.56 GHz) plasma chemical vapor deposition (CVD) under conditions that include a substrate temperature of about 300 °C.[1,2] It was found that high-quality silicon nitride and amorphous carbon thin films can be deposited on room-temperature substrates with a 50-Hz plasma CVD method using $N_2 + SiH_4$ and $H_2 + CH_4$ mixtures, respectively.[3–5] In a previous paper,[4] the authors report that no difference was found in the film properties (refractive index, resistivity, and dielectric strength) with different plasma frequencies in the 50-Hz–10-kHz range. With the 50-Hz plasma CVD method, there is no need for a high-frequency power supply, which results in an inexpensive plasma CVD apparatus with low overall power consumption.[3] Moreover, high-quality silicon nitride and amorphous carbon thin films have not been deposited with 13.56-MHz frequency plasma CVD on an unheated substrate. Clearly, there are differences in the characteristics of low- and high-frequency plasma that must be understood.

This paper reports on the characteristics of plasmas at various frequencies that are derived from optical emission measurements. The deposition mechanism of high-quality thin films using low-frequency plasma CVD without substrate heating is discussed in light of the experimentally measured electron temperatures in low- and high-frequency plasmas.

II. EXPERIMENTAL

The experimental apparatus for this study is the same as that previously used for the deposition of amorphous carbon films.[5,6] Briefly, the plasma discharge chamber was made of stainless steel and pumped by a turbomolecular pump to a background pressure of 5×10^{-7} Torr. The stainless-steel electrodes had a 12-cm diameter with a 2-cm gap. The gases used in the experiment, H_2 (99.999 99%) and CH_4 (99.99%) were introduced into the chamber at flow rates of 250 and 5 sccm, respectively. The total pressure (1.0–1.5 Torr) was measured with a Baratron pressure gauge. Low-frequency (50 Hz–200 kHz) and high-frequency (13.56 MHz) plasmas were excited between the two parallel electrodes by applying about 80–250 V to the upper electrode with the lower electrode grounded. The plasma current was about 5 mA (45 μA/cm^2).

The plasma emission spectra were observed with a monochromator and photomultiplier over a range of 180–670 nm. The variation of the emission intensity was measured against the plasma frequency (50 Hz–200 kHz, 13.56 MHz) and position in the plasma. The photomultiplier had adequate sensitivity in the wavelength range of 180–800 nm. Sensitivity of the optical measurement apparatus system against wavelength was measured using a standard lamp, and the emission intensities of H_α and H_β were collected for calculation of the electron temperature.

III. RESULTS AND DISCUSSION

The emission spectra from 50-Hz plasma for CH_4, 50-Hz plasma for $H_2 + CH_4$, and 13.56-MHz plasma for $H_2 + CH_4$ are shown in Figs. 1(a)–1(c). The major light emission lines from excited states of $H_2^*(^3\Sigma g \rightarrow {}^3\Sigma u)$ (peak wavelength: 220 nm), H_α (656 nm), H_β (486 nm), H_γ (434 nm)[7] and CH*($A\,^2\Delta \rightarrow X\,^2\Pi$:431 nm, $B\,^2\Sigma \rightarrow X\,^2\Pi$:389 nm, $C\,^3\Sigma \rightarrow X\,^2\Pi$:315 nm),[8] and C* (excited C atom) were observed. It was found that the emission intensity of CH* was larger than that of C* from 50-Hz plasma for CH_4 in Fig. 1(a). Figures 1(b) and 1(c) show the emission spectra from 50-Hz and 13.56-MHz plasmas for the $H_2 + CH_4$ mixture. In 50-Hz plasma for a 2%CH_4 + H_2 mixture, light emission lines from CH-excited molecules can be seen. However, the emission intensity from H* (excited H atom) and CH* (excited CH molecule) in

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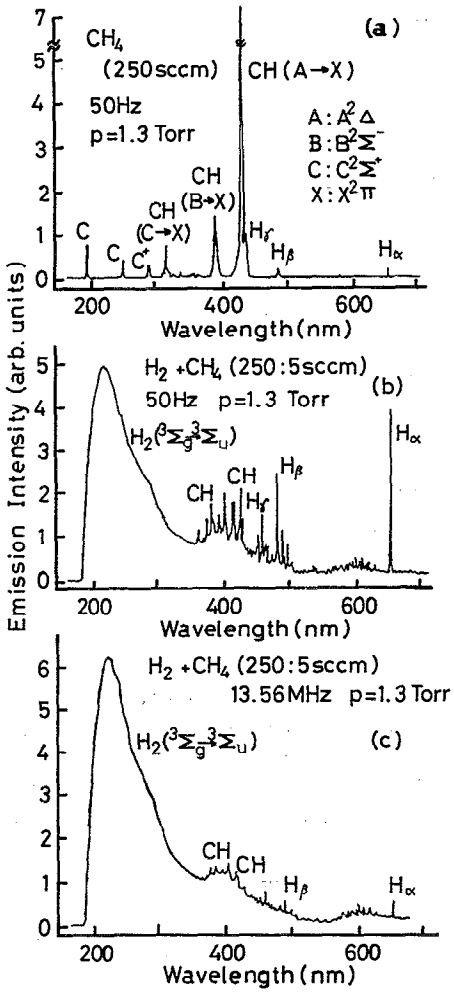

FIG. 1. The emission spectra of (a) 50-Hz plasma for CH_4, (b) 50-Hz plasma for $H_2 + CH_4$, and (c) 13.56-MHz plasma for $H_2 + CH_4$.

13.56-MHz plasma were much smaller than that from H_2^*. Accordingly, it appears that the CH_4 molecule was dissociated with high efficiency by the 50-Hz plasma. The H_α/H_2^* emission intensity ratios for 50-Hz and 13.56-MHz plasmas were about 0.7 and 0.05, respectively. The H_α and H_2^* emission originated from dissociation and direct excitation by electron impact with energy greater than 16.6 (Ref. 9) and 12 eV, respectively. Our interpretation is that the electron mean energy in low-frequency plasmas is higher than that in 13.56-MHz plasmas.

The electron temperature in H_2 and $H_2 + CH_4$ plasmas was obtained from the two-line radiance ratio method using the Balmer lines (H_α and H_β). For a Boltzmann population distribution, the electron temperature T_e is related to the emission intensity by[10–12]

$$\frac{I_{ij}}{I_{kl}} = \frac{\lambda_{kl} A_{ij} g_i}{\lambda_{ij} A_{kl} g_k} \exp\left(-\frac{E_i - E_k}{kT_e} \right). \quad (1)$$

Here, I_{ij} and I_{kl} are the spectral intensity, λ_{ij} and λ_{kl} are the wavelength, A_{ij} and A_{kl} are the transition probability, g_i and g_k are the statistical weight,[13] E_i and E_k are the excitation energy, and k is the Boltzmann constant. Figure

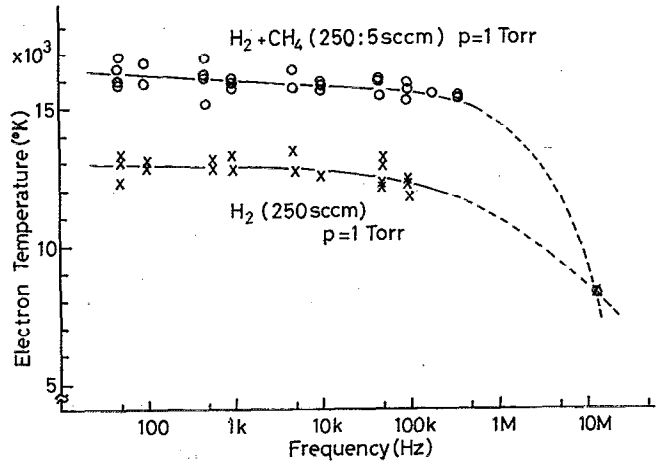

FIG. 2. The electron temperature vs plasma power frequency in H_2 and $H_2 + CH_4$ plasmas.

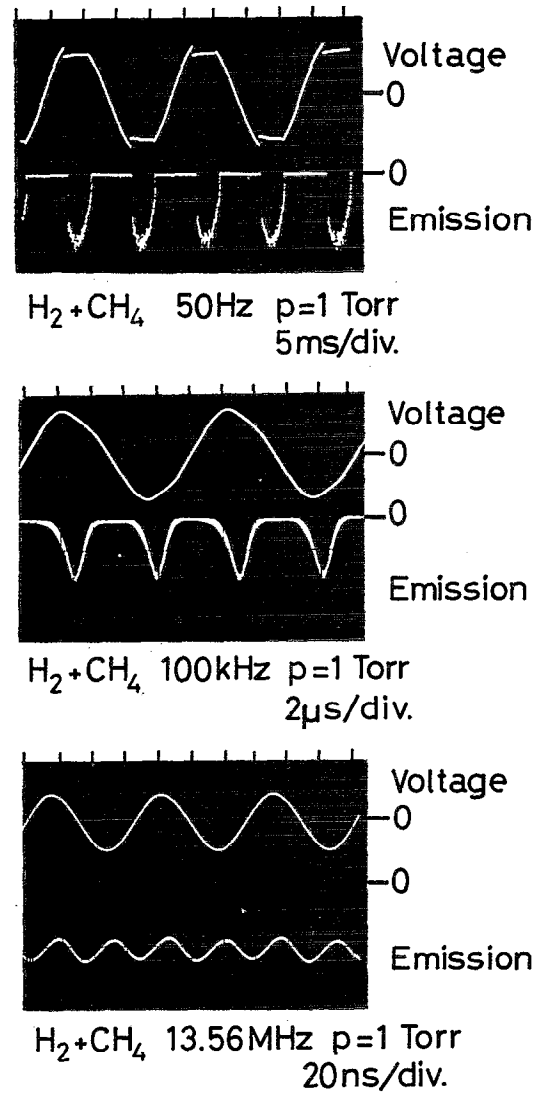

FIG. 3. The emission intensity and applied voltage waves at various frequencies.

2 shows the electron temperature versus plasma power frequency in H_2 and $H_2 + CH_4$ plasmas. In this figure, the electron temperature slowly decreases with increasing frequency below 200 kHz, but rapidly decreases with increasing frequency between 200 kHz and 13.56 MHz. The electron temperature for a $H_2 + CH_4$ plasma is 16 000 K at 1 kHz, and 8200 K at 13.56 MHz. We interpret the data of Fig. 2 to show that the electron mean energy in a 13.56-MHz plasma is lower than that in a low-frequency (<200 kHz) plasma.

Emission intensity and applied voltage waves are shown in Fig. 3 at various frequencies. The emission from 50-Hz and 100-kHz plasmas was intermittent every half-cycle, but the 13.56-MHz plasma showed continuous photoemission. It appears that many active species remain in the gap of the two electrodes at the instant at which the applied voltage is zero.

Figure 4 shows minimum values of the maintaining voltage versus frequency for H_2 and $H_2 + CH_4$ plasmas at 1.2 Torr and 2.0 cm gap length. The maintaining voltage was constant below 200 kHz, and rapidly decreased between 200 kHz and 13.56 MHz. The maintaining voltage for a $H_2 + CH_4$ plasma (260 V) is higher than that for H_2 (210 V) at frequencies below 200 kHz. Similar results were seen for the electron temperature of the H_2 and $H_2 + CH_4$ plasmas (in Fig. 2). We believe that the reason for the rapid decrease of the electron temperature and the maintaining voltage with increasing frequency is the nonintermittent nature of high-frequency plasmas, as seen in Fig. 3.

Figure 5 shows the emission intensity of the excited state of H_2^* molecules and the excited state of H* atoms (H_α and H_β) against plasma position for $H_2 + CH_4$ plasmas at 50-Hz and 13.56-MHz frequencies. The greater part of the photoemission intensity from the 13.56-MHz plasma was from the neutral excited molecule H_2^*, while the H_α and H_β intensities were about 6% of the H_2^* intensity at the midpoint of the discharge axis. The H_α and H_β emission intensity from 50-Hz plasmas were about half of the H_2^* intensity. Moreover, the emission intensity of H* in the

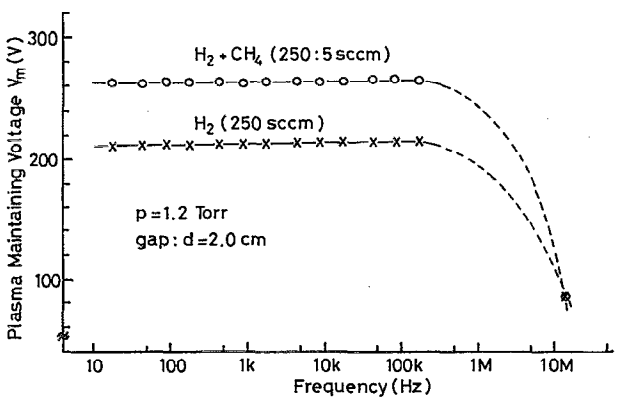

FIG. 4. The minimum value of the plasma maintaining voltage V_m vs frequency for H_2 and $H_2 + CH_4$ plasmas at 1.2 Torr and 2.0 cm gap length.

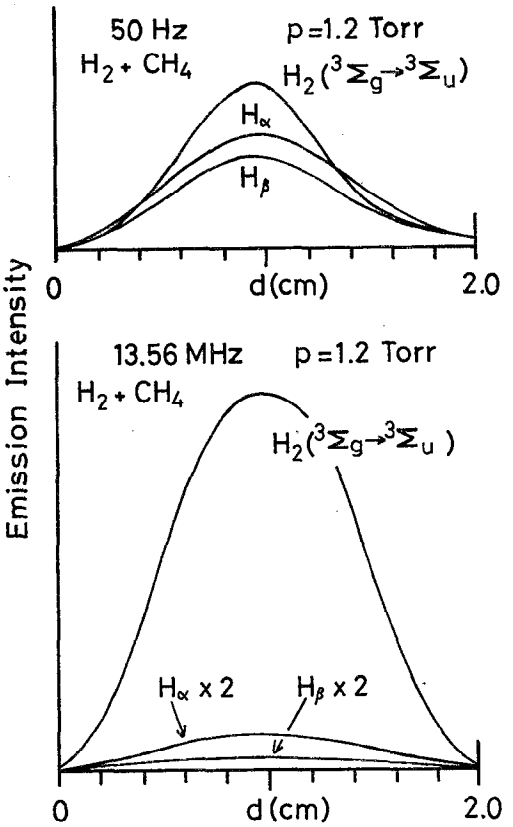

FIG. 5. The emission intensity of the excited state of H_2^* molecules and excited state of H* atoms (H_α and H_β) against plasma position for $H_2 + CH_4$ plasmas at 50-Hz and 13.56-MHz frequencies.

50-Hz plasma near the electrodes was much larger than that of H_2^*.

From our study, we conclude that dissociation of CVD gases such as H_2 and CH_4 is accelerated by high-temperature electrons in low-frequency plasmas. Our view is that, in low-frequency plasmas, ions are not trapped by the applied electric field, and are free to bombard the deposited film. We assume that the mechanism by which the bombarding ion energy can be consumed is as migration energy for rearrangement of deposited atoms. It is by this mechanism that thin films deposited with low-frequency plasmas can achieve good material properties without substrate heating.[3-5]

IV. CONCLUSIONS

The emission spectra of 50-Hz and 13.56-MHz plasmas for $H_2 + CH_4$ mixtures were measured. The emission intensity ratios of H_α/H_2^* ($^3\Sigma g \rightarrow {}^3\Sigma u$) in 50-Hz and 13.56-MHz plasmas were about 0.7 and 0.05, respectively. Electron temperature in H_2 and $H_2 + CH_4$ plasmas was obtained from the two-line radiance method using the Balmer lines. The electron temperature slowly decreased with increased plasma frequency below 200 kHz, but rapidly decreased between 200 kHz and 13.56 MHz. In a $H_2 + CH_4$ plasma, the electron temperature was 16 000 K at 1 kHz and 8200 K at 13.56 MHz. The emission from 50-Hz and 100-kHz plasmas was intermittent with every

half-cycle, but 13.56-MHz plasmas exhibit continuous photoemission. The emission intensity from $H_2 + CH_4$ mixtures versus plasma position were also measured. Emission intensities from H* at 13.56 MHz in $H_2 + CH_4$ plasma were only 7% of that from neutral excited molecular H_2^*. From these results, it was deduced that the electron temperature of low-frequency plasmas is larger than that in high-frequency plasmas.

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