Optical measurements of gas temperatures in atmospheric pressure RF cold plasmas

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Abstract

Rotational temperatures can be estimated directly from the ratios between peaks in the ultra violet (UV) band of OH molecular spectra. With a relatively poor spectral resolution of approximately 0.4 nm, ratios between two broad band peaks near 308 and 309 nm are identified to be sensitive to the gas temperatures in the range of $350 \sim 1000$ K. In cold radio frequency (RF) generated atmospheric plasmas, rotational temperatures of molecules are measured to be in a relatively low temperature range of $400 \sim 700$ K. These temperatures are confirmed to be in good agreement with gas temperatures measured by thermocouples. This simple emission spectroscopy can be used to monitor gas temperatures in cold atmospheric plasmas without any expensive spectrometer.
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1. Introduction

Atmospheric pressure RF plasmas are widely used in the industries for surface modification, decontamination, cleaning, etc. [1]. Gas temperatures as well as plasma parameters such as electron temperature and electron density are very important for plasma processing. Although high gas temperatures are favored in most applications because of their strong reactivity, maintaining gas temperature low in atmospheric plasmas is a crucial condition for polymer processing [2]. To avoid thermal damage at polymer surfaces, the gas temperature of ejected plasmas need to be monitored and controlled to be within a certain limit. In addition, the gas temperature inside the discharge region is also important to estimate the input power distribution, which affects dissociation of molecules significantly.

There are several methods to measure the gas temperatures in atmospheric pressure plasmas. Among them, the most simple and easy technique for relatively low temperatures is considered to be using a thermocouple. However, the thermocouple has to be used carefully because it can disturb the flow of plasma gas. In certain plasma source configurations such as capacitively coupled plasmas, it can be self-heated significantly by accepting charged particles since it can also function as a ground electrode. Absorption spectroscopy has also been developed as a non-intrusive method to measure the gas temperature. Boltzmann plots of individual rotational lines near infrared can be used to infer the rotational temperature. However, this technique requires an expensive spectrometer with a good spectral resolution and a wide spectral range. On the other hand, the rotational temperature, which is strongly correlated with a gas temperature, can be quickly determined by simple comparison of the theoretical and experimental spectra from spectrometer with various spectral resolutions [3]. The UV OH band spectra have been used to measure the gas temperatures in the range of $2000 \sim 8000$ K [4].

In this paper, the rotational temperature of OH molecule has been used for much lower gas temperatures in the range of $400 \sim 700$ K which appears in the very cold RF-generated atmospheric plasmas. Only with the spectrometer of relatively poor spectral resolution the UV OH band makes only few peaks, and they are considered to be very sensitive to the gas temperature. Direct estimation of rotational temperatures from the ratio of these peaks ratio can be developed as an

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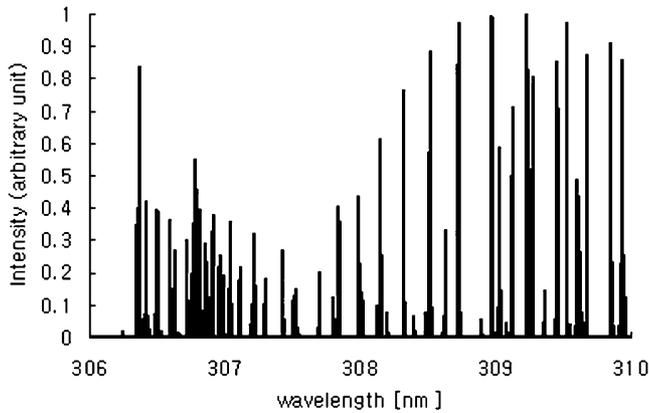*E-mail address:* yhwang@snu.ac.kr (Y.S. Hwang).

Fig. 1. Plot of the rotational lines of OH spectrum represented as Dirac impulses for the reference temperature $T^* = 3000$ K. Reference data are from the paper by Dieke and Crosswhite [6].

economical and fast monitoring system of gas temperatures even without high-resolution spectrometer.

2. Theoretical backgrounds

2.1. UV OH band spectrum [5]

Molecular spectra can be used in temperature measurements when atomic spectra are not strong enough to give significant information. The intensity I_{nm} of a spectral line corresponding to a transition $(n \rightarrow m)$ between two levels is given by:

$$I_{nm} = N_n A_{nm} h \nu_{nm} \tag{1}$$

where h is Planck's constant, ν_{nm} the frequency of the transition, A_{nm} the spontaneous transition probability and N_n particle density in the initial state n. Assuming thermodynamic equilibrium and Boltzmann's law, N_n will be given as a function of the temperature T.

$$N_n = \frac{N_0 g_n}{Q(T)} \exp\left(\frac{-E_n}{k_B T} \right) \tag{2}$$

where k_B is Boltzmann constant, $Q(T)$ the partition function, N_0 the particle density, and g_n and E_n the statistical weight and the energy of state n, respectively. From Eq. (1) and Eq. (2), I_{nm} is:

$$I_{nm} = \frac{K_{nm}}{Q(T)} \exp\left(\frac{-E_n}{k_B T} \right) \tag{3}$$

where $K_{nm} = N_0 A_{nm} g_n h \nu_{nm}$ is a constant for given transition $(n \rightarrow m)$. When I_{nm}^* is known for a given reference temperature T^*, we can write;

$$I_{nm} = I_{nm}^* \exp\left(\frac{-E_n(T^* - T)}{T T^*} \right) \frac{Q(T^*)}{Q(T)} \tag{4}$$

Since the term $Q(T^*)/Q(T)$ will remain unchanged for a certain temperature T, the general procedure of temperature measurements from molecular band spectra does not need to consider the absolute values of the intensities.

The UV OH band $(A^2\Sigma^+, \nu = 0 \rightarrow X^2\Pi, \nu' = 0)$ has been completely studied by Dieke and Crosswhite [6]. Fig. 1 shows the reference UV OH spectrum as Dirac impulses. These lines can be used to estimate rotational temperatures from those Boltzmann plots with high-resolution spectrometer.

2.2. Convoluted spectrum with instrumental broadening

For an accurate analysis of emission spectroscopy, it is very important to include instrumental broadening of the spectrometer used in the experiment. Instrumental broadening has been measured from the reference single wavelength source such as a mercury lamp. In most experimental conditions, the apparatus function with instrumental broadening can be successfully expressed with a Gaussian profile as a function of the wavelength λ.

$$G(\lambda_0) = \frac{2}{\Delta \sqrt{\pi}} \exp\left(- \frac{(\lambda - \lambda_0)^2}{(\Delta / 2)^2} \right) \tag{5}$$

where Δ is the instrumental broadening, i.e. full width at $1/e$ of the maximum intensity measured at the wavelength λ_0.

Fig. 2 shows plots of convoluted spectrum of OH band for various temperatures with the instrumental broadening of $\Delta = 0.4$ nm. Three prominent peaks such as G_1 (~ 307 nm), G_2 (~ 308 nm) and G_{ref} (~ 309 nm) are identified. When those two peaks of G_1 and G_2 are normalized with the reference peak G_{ref}, normalized
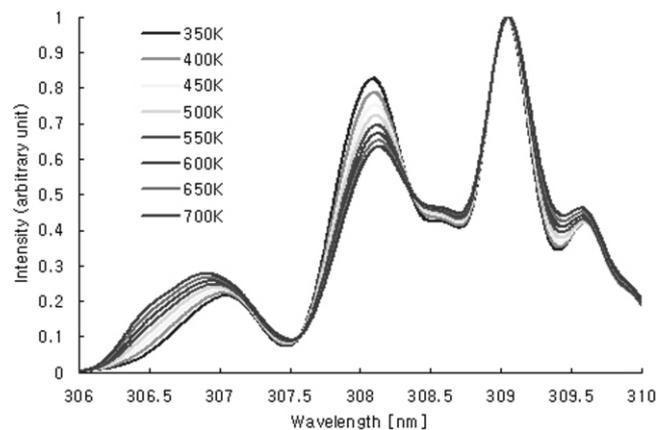

Fig. 2. Plot of the UV OH spectrum for the rotational temperature varying from 350 K to with the instrumental broadening of $\Delta = 0.4$ nm.
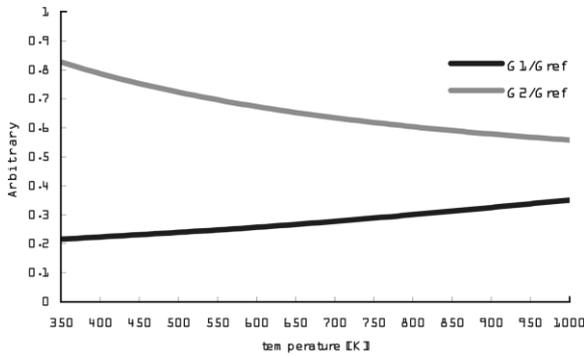
Fig. 3. Plot of the maximum amplitude of the unresolved peaks as a function of the temperature for the full width at $1/e$ of the maximum $\Delta = 0.4$ nm.

intensities are varying as a function of T as shown in Fig. 3. The ratios of G_1/G_{ref} and G_2/G_{ref} are shown to be sensitive to the gas temperature in the range of $350 \sim 1000$ K.

3. Experimental setup

3.1. Atmospheric pressure ejected plasma ejection source

Low-temperature glow-like atmospheric pressure plasmas are generated with RF power in the form of plasma ejection source. The structure of the plasma source is described in Fig. 4. The discharge is generated between two coaxial electrodes. The central hot electrode of 13 mm diameter is made of aluminum and anodized, and the ground electrode of 20 mm inner-diameter is covered with alumina ceramic layer of 15 mm inner-diameter. The plasma source of this type has advantages that it can treat the arbitrary shaped objects with ejected plasma, regardless of material properties, i.e. for both insulator and conductor.

3.2. Experimental set-up with diagnostic arrangement

Overall experimental setup is shown in the Fig. 5. With two mass-flow-controller units, various gas mixtures are provided to generate glow-like plasmas with the gas composition of helium and argon. A personal computer (PC) plug-in type spectrometer of AVS-PC2000S-ISA from Avantes with the spectral resolution of 0.4 nm covers a spectral range of $250 \sim 400$ nm. The spectrum of the ejected plasma region is obtained from the side view with a collimating lens COL-UV (transparent in the wavelength range of $200 \sim 2000$ nm) from Avantes because of its low light intensity. The spectrum of the discharge region is obtained from the integrated lights by looking directly into the plasma vertically.
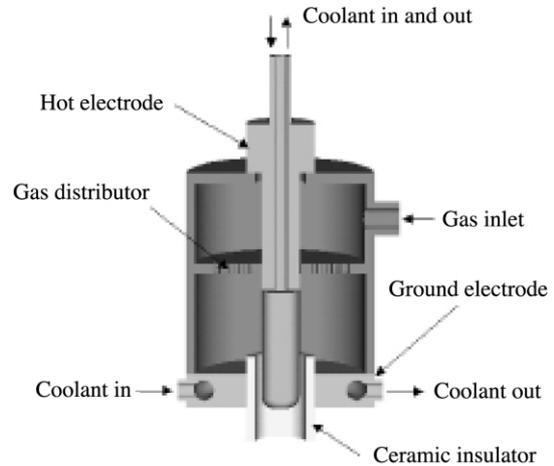

Fig. 4. Schematic diagram of plasma source.

In order to verify the validity of the rotational temperature using UV OH band as a gas temperature, a thermocouple has been installed in the downstream region of the plasma source. Of course, the thermocouple cannot be located in the discharge region because it can cause arcing there. Therefore the verification is performed only in the ejected region.

4. Experimental results

Rotational temperatures are calculated from two different unresolved peaks near 307 nm (G_1) and 308 nm (G_2) as identified in the Fig. 2, where the 309 nm (G_{ref}) peak is used as a normalizing peak. In the discharge region, rotational temperatures from the ratio G_1/G_{ref} are compared with those from the ratio G_2/G_{ref} as a function of input power. Although both temperatures increase slightly with increasing input power, the temperature from the ratio G_1/G_{ref} is much higher than that from the ratio G_2/G_{ref} as shown in Fig. 6a. In the ejected region, the ratio G_1/G_{ref} is still higher than that from the ratio G_2/G_{ref} as shown in Fig. 6b.
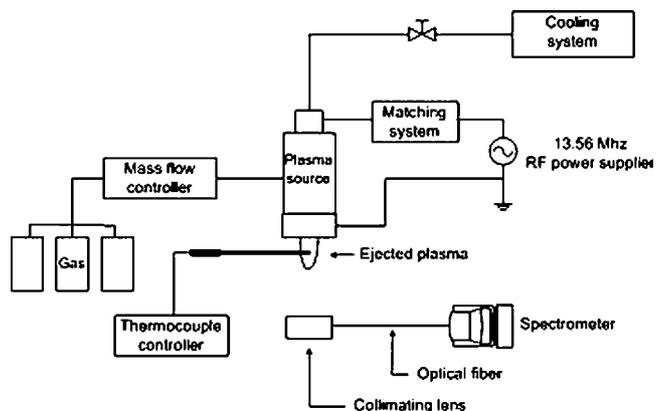

Fig. 5. Schematic diagram of the experimental set-up.

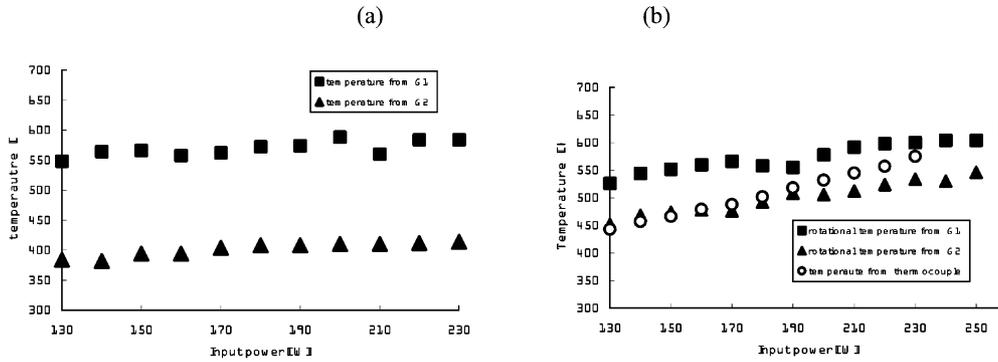(a)   (b)

Fig. 6. (a) Comparison of OH rotational temperatures from G_1 and G_2 in the plasma generation region (He: 10 lpm, Ar: 0.4 lpm). (b) Comparison of OH rotational temperatures from G_1 and G_2 with the temperature from thermocouple in the ejected plasma region (He: 10 lpm, Ar: 0.4 lpm with insufficient cooling.

To find out appropriate OH rotational lines, these rotational temperatures are compared with gas temperatures measured with thermocouples in the ejected region. The rotational temperatures obtained from the ratio G_2/G_{ref} are in good agreements with the gas temperature obtained from the thermocouple in the limited power ranges of less than 180 W as shown in Fig. 6(b). With higher input power above 180 W, even these two temperatures become different from each other. This is because discharges are formed between hot electrode and grounded thermocouple probe. The thermocouple seems to be overheated by the impact of charged particles more from these extra discharges. Above 240 W of input power, even arc transition has occurred between them. Based on these results, the ratio G_2/G_{ref} has been confirmed to give more reliable gas temperatures in this kind of plasma sources.

The only problem to be resolved is why the ratio G_1/G_{ref} is overestimating the temperature compared to the other ratio. This discrepancy can be explained from the experimental spectrum shown in Fig. 7. Near the unresolved peak G_1 a few extra peaks are observed in the range of $306 \sim 307.5$ nm, indicating the existence of extra lines, for example, other atomic or molecular lines, which are not included in UV OH band calculation. This can lead to the overestimation of temperatures obtained from the ratio G_1/G_{ref}. Although these lines are difficult to be identified without high-resolution spectrometer, the ratio G_2/G_{ref} can be chosen as a reliable data to provide gas temperature reasonably well.

5. Conclusions

The emission of OH band has been used to measure the gas temperature in the glow-like atmospheric pressure plasma generated with RF power. The OH band has three distinct unresolved peaks when the full width at $1/e$ of the maximum is $\Delta = 0.4$ nm. Two unresolved peaks in the UV OH band can be used to calculate the

gas temperature after normalizing with the reference peak near 309 nm (G_{ref}). According to the simulation, the peak ratios are sensitive to the gas temperature.

It is shown that rotational temperatures from the ratio G_2/G_{ref} agree very well with the gas temperatures from thermocouple in the ejected plasma region. When the thermocouple fails to give reliable gas temperature measurements with increasing input power because of extra discharge channels between the hot electrode and the grounded thermocouple probe, this emission spectroscopy is believed to be a very attractive tool for measuring gas temperatures. Moreover, the method of using UV OH spectra can take the place of thermocouple inside the discharge region. However, the other ratio G_1/G_{ref} always overestimates the gas temperatures because of the existence of several unidentified spectral lines from other atoms or molecules, which are not included in UV OH band calculation.

In conclusion, it is shown that the peak ratio in the poorly resolved UV OH band can give a reliable time-averaged gas temperature directly in the RF generated atmospheric pressure plasmas in the range of $400 \sim 700$ K.
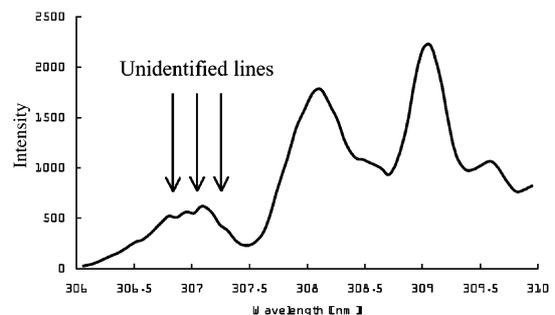

Fig. 7. Experimental spectrum of UV OH band ($\Delta = 0.4$ nm).

Acknowledgments

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