

Gas Temperature Determination from C₂ Swan Band Emission of Plasma and Hot Filaments Assisted CVD Process of Carbon Nanotubes Growth

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Abstract: The C₂ radical in DC plasma and hot filaments assisted catalytic chemical vapor deposition (DC HF CCVD) process of carbon nanotubes growth has been studied by means of optical emission spectroscopy. The rotational temperature was evaluated from the emission spectra of the (0-0) C₂(d³ g_g) - C₂(a³ u_g) transition using numerical simulation of the spectra. The rotational temperature as a function of the C₂H₂ content in a C₂H₂ + H₂ mixture was measured. The rotational temperature strongly decreases with the H₂ content.

1. Introduction

Different types of DC plasma and hot filaments enhanced chemical vapor deposition apparatus are successfully used for diamond, diamond like carbon (DLC) or carbon nanotubes growth [1,2]. Also microwave plasma can be used for CVD growth process of carbon nanotubes [3]. Plasma conditions for carbon nanotubes growth are practically the same as for diamond or DLC deposition, only the carbon precursor is different (C₂H₂ is used instead of CH₄). The absolute densities of different active species and the substrate and surrounding gas temperature are important growth parameters. Optical diagnostic seems to be pertinent to study C₂ radical density as it plays an important role during nanotubes growth. Absolute density values can be obtained by different optical methods e.g. optical emission spectroscopy in combination with actinometry [4] or by laser induced fluorescence [5]. The aim of this contribution is the gas temperature determination using the emission spectroscopy.

2. Experiment

In our experiment we studied DC plasma and hot filaments assisted catalytic chemical vapor deposition (DC HF CCVD) process of carbon nanotubes growth. Plasma burnt between two grids, placed above the substrate, and two pairs of perpendicularly oriented

tungsten wires were placed in-between the grids. Wires were heated up to 2450 K and the substrate at 973 K. The substrate was heated separately by an IR halogen lamp placed directly in the vacuum chamber. Another DC plasma burnt between the substrate ($\text{SiO}_2/\text{Si}(100)$) and the cathode. More experimental details about carbon nanotubes growth process are reported in [6].

Plasma emission gives information about present radicals and their population, from which the rotational temperature can be deduced. Unfortunately plasma emission is shielded by the strong continuous hot filament emission. In order to obtain the emission from plasma only, two spectra of hot filament process with and without DC plasma resp. were measured at the same experimental conditions. The optical spectra (ranging from 300 nm to 700 nm) were taken 5 mm above the substrate from the plasma as a function of gas mixture. Small Jobin Yvon grating spectrometer equipped with optical fiber and photomultiplier as detector was used to measure the spectra. Emission spectrum from plasma was obtained after subtraction of the continuum spectra of hot filaments (examples of spectra are presented in Fig. 1).

At the same time the measured hot filaments emission in comparison with simulated one was used to calibrate spectral response. For theoretical emission simulation the filaments temperature was measured (2450 K) and the tungsten carbide top layer emissivity was used [7].

In the example of emission spectra (Fig. 1) of DC plasma from the DC HF CCVD process in pure C_2H_2 dominates 4 systems of the C_2 (d-a) Swan bands from $v = 2$ to $v = -1$ at 437 nm, 469–473 nm, 509–516 nm and 546–563 nm, 0-0 CH (A-X) band at 430 nm and the H line at 486 nm. In the case of hydrogen addition the intensity of C_2 (d-a) Swan bands decreases, H atomic line intensity increases and some new bands appears; e.g. new bands at 417 nm and 462 nm, which can be attributed to the 0-3 and 0-4 transitions of CH (C-X) band [8]. The next 0-5 transition of this system appears at 515 nm and so partially overlap the C_2 (d-a) Swan band at 516 nm.

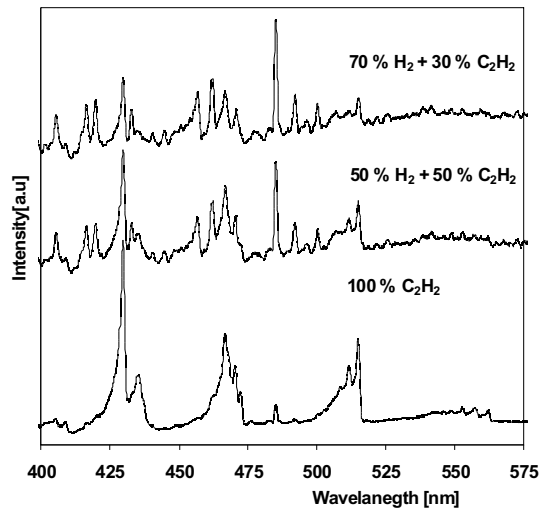


Fig. 1. Optical emission spectrum of DC plasma and hot filament assisted catalytic CVD in pure C_2H_2 after subtraction of hot wires emission.

The most dispersed C_2 (d-a) Swan bands are for $v = -1$ at 540–560 nm, but the intensity is low and disappears after dilution with hydrogen. Systems for $v = 1$ and $v = 2$ are not enough dispersed for the determination of rotational temperature. System for $v = 0$ at 500–516 nm is not overlapped for high C_2H_2 content. For the lowest C_2H_2 content (10%) very small band attributed to the 0-5 CH (C-X) transition overlaps the tail of the 0-0 transition of Swan band, however the overlapping band can be isolated and subtracted. So finally the 0-0 transition of C_2 (d-a) Swan bands was chosen for an evaluation of the rotational temperature.

3. $C_2(d^3_g - a^3_u)$ Swan band spectrum simulation and determining the rotational temperature

The rotational temperature determination was based on the comparison of measured and simulated rotationally non resolved spectra of the Swan band. The 0-0 transition at 516 nm wavelength was chosen as a good compromise between intensity, isolation from other systems and spectral dispersion. Similarly as in our previous paper [9], the spectra simulation was based on the following steps:

- (I) Simplification to the $^1 - ^1$ transition.
- (ii) Calculation of line wavelengths using a known rotational constant (Table 1) up to $J = 60$ for 3 branches P, Q, R [10].

Table 1: Parameters of $C_2(d^3_g) - C_2(a^3_u)$ [10].

Parameter	$C_2(d^3_g)$	$C_2(a^3_u)$
T_e [cm^{-1}]	20022.50	714.24
ϵ [cm^{-1}]	1788.22	1641.35
$w_e \times \epsilon$ [cm^{-1}]	16.440	11.67
B_e [cm^{-1}]	1.7527	1.6324
ϵ [cm^{-1}]	0.01608	0.01661

- (iii) Calculation of $C_2(d^3_g, v = 0, J)$ state relative density and intensity of individual spectral lines assuming that the population obeys the Boltzmann law:

$$I_{jj} \sim S_{jj} \exp(-F_j / kT_r)$$

where λ is the wavelength of a spectral line, S_{jj} the Höln–London factor, F_j the rotational energy of molecules in upper state at temperature T_r .

- (iv) Convolution of the non-broadening lines with the instrumental function of the spectrometer approximated by the asymmetric trapezoidal shape with 1.25 nm width (FWHM) – presented in the Fig. 2.

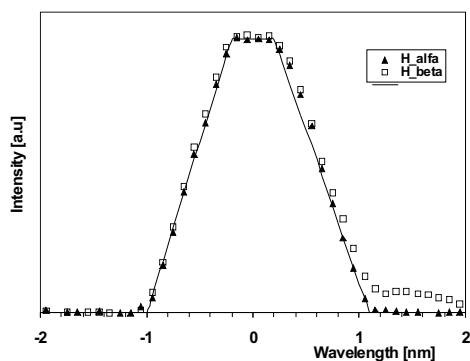


Fig. 2. The spectrometer's instrument function determination from the H line at 656.3 nm.

The instrumental function was determined from the broadening of H line at 656.3 nm. The H line centered at 486.2 nm could not be used, because it was slightly overlapped by the 0-1 CH(A-X) band at 488.2 nm. As we are only interested in low resolution of the spectrometer, exact knowledge of the line profiles is not necessary. In Fig. 3, calculated spectra for different rotational temperature ranging from 600 K to 2200 K are shown.

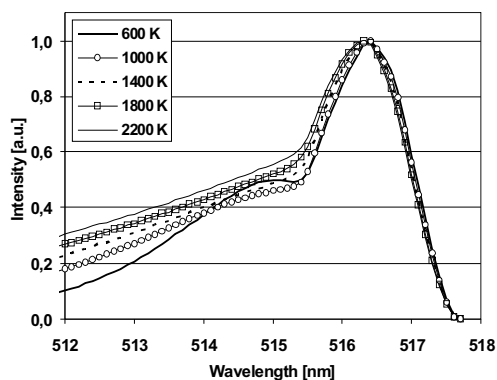


Fig. 3. Simulated emission spectra of the (0-0) $C_2d^3_g - C_2a^3_u$ transition as a function of temperature.

3. Results and Discussion

The rotational temperature was determined by the comparison of experimental and simulated spectra using least square method in two regions (region of band tail and band head respectively). The sum of these two contributions with the same statistical weight was minimized.

Examples for pure C_2H_2 and for the lowest content of C_2H_2 in H_2 (10 %) are presented in Fig. 4 and Fig. 5 respectively. Rotational temperature evolution as a function C_2H_2 content in the mixture is presented in Fig. 6. The temperature decreases with increasing H_2

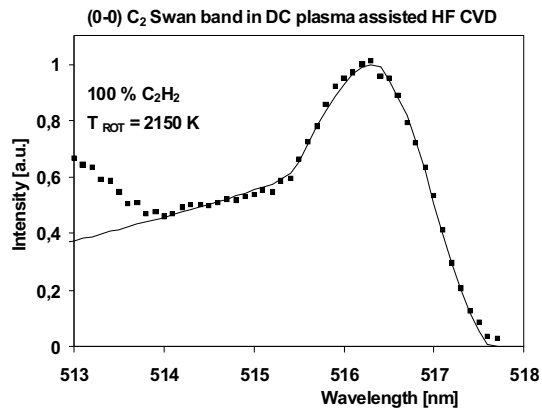


Fig. 4. Measured and simulated emission spectrum of the (0-0) $C_2d^3_g - C_2a^3_u$ transition in pure C_2H_2 .

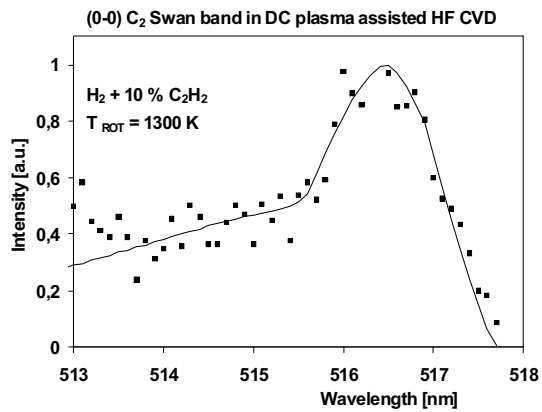


Fig. 5. Measured and simulated emission spectrum of the (0-0) $C_2d^3_g - C_2a^3_u$ transition in the mixture of H_2 with 10% C_2H_2 .

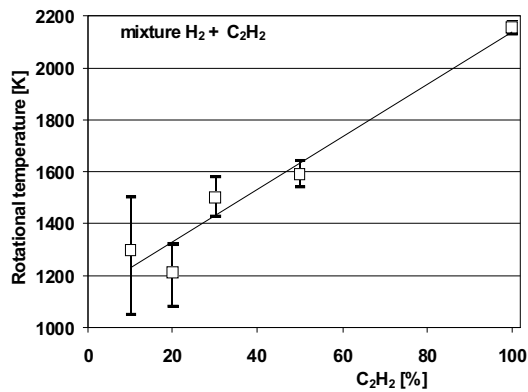


Fig. 6. Rotational temperature of (0-0) C_2 Swan band as a function of C_2H_2 content in mixture with hydrogen.

content. But the temperature evaluation seems to be less precise in more complicated mixture with low C_2H_2 content due to the overlapping bands. In future, rotational temperature determination in more complex gas mixtures of carbon nanotubes growth process will be necessary to verify method by the use of other bands.

Acknowledgements

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