

Optical emission spectroscopy for diagnosis of diamond growth and etching processes in microwave plasma

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For a better control and understanding of growth process of CVD single crystal diamond in microwave (MW) plasma it is important to monitor a large number of the gas phase parameters (chemistry, temperature, concentrations, etc.). A relatively simple and non-perturbing method to measure the plasma parameters is the optical emission spectroscopy (OES) [1, 2]. The OES advantage is also in a fast response to variation of the plasma parameters in the reactor. Here we present the results of OES application to characterize the MW plasma (2.45 GHz) in course of diamond deposition in H₂-CH₄ mixtures and etching in pure H₂.

The emission from the plasma passed through a quartz window in the CVD reactor chamber and an image was formed by a lens onto a matted silica plate (OES configuration (I)). The emission collected by a 0.6 mm diameter quartz fiber was directed to a spectrometer (Ocean Optics HR 4000, wavelength range of 400–800 nm, spectral resolution 0.6 nm). The fiber tip was translated across the image of the plasma to record spatially resolved emission spectra along X or Z axes, parallel and perpendicularly to the substrate, respectively, with the distance of –25 to +25 mm along the X axis (counting from the plasma center), and from zero (the substrate position) to 50 mm along Z axis. The probed volume was a cylinder with diameter of 1.5–2 mm directed along the plasma ball diameter (Y direction), thus the spatial resolution of ~1.5 mm in the OES was obtained both for X and Z axes [2].

In another OES configuration (II) a M833 spectrometer (Solar Laser System) with high spectral resolution of 0.01 nm, equipped with a double grating with 2400 lines/mm and CCD image sensor Hamamatsu S10420-1006, was used. The optical fiber system collected the emission from a cylinder of 12 mm diameter directed horizontally along the plasma ball diameter (Y direction). The gas temperature was evaluated from OES data measured in the central region of plasma by the analysis of the (0,0) band of C₂ Swan system (d³Π_g → a³Π_u) following the procedure described in [3, 4]. A thermal equilibrium between heavy species' translational and rotational modes, and a Boltzmann distribution of the rotational levels of the considered vibrational state are assumed.

The spectroscopy of the Swan transitions of the C₂ molecule (λ = 516 nm) with well-resolved rotational components was used to measure the gas temperature with accuracy of ±150 °C upon wide variation, 1–13%, in methane concentration [5]. The rotational temperature T_{rot} only weakly depends on the absorbed MW power (Fig.1). It increase from ~3000 K at low (2%) CH₄ content to 4000–4500 K at higher (7–13%) CH₄ concentrations.

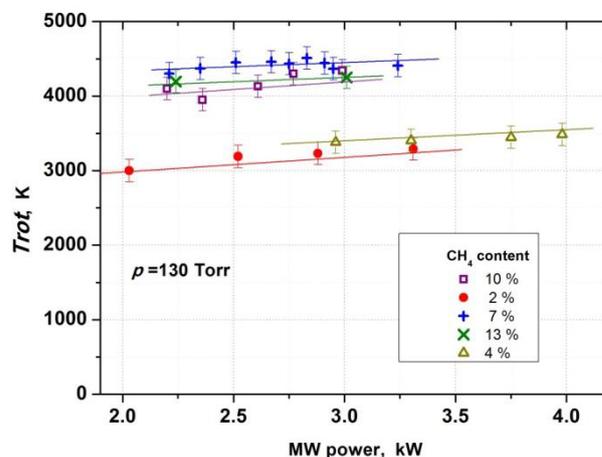


Fig. 1. Rotational temperature T_{rot} in the core of plasma cloud measured from C₂ fine structure spectrum vs MW power at CH₄-concentrations: 2, 7, 4 10, 13, 10%, and pressure $p = 130$ Torr

The EOS data are useful for estimation of MW power density in the discharge. As the atomic hydrogen line H_α is excited mainly by electron impact, the intensity of H_α line gives an information about the plasma size [6]. With spatially resolved EOS for atomic hydrogen line H_α the intensity profiles of plasma glow were reconstructed in different cross sections. This, in turn, allows correct assessment of the MW power density, which eventually governs the rates of all chemical reactions in the plasma [1, 7].

We used two different approaches to measure H_α profiles in vertical (Z) and horizontal (X) directions of the discharge. The first one was based on spatially-resolved EOS in configuration (I) and spectrometer measured H_α line intensity. The second method implies using photographs of the plasma captured with a digital mirror camera Canon EOS 650D through a red H_α-filter passing only the H_α line emission (λ = 656.5 nm ± 6 nm). The spatial profiles of the H_α line emission along X and Z axes were determined from those images, and the shape of the plasma was very well fitted with Gaussian profiles, with further calculation of the volume and microwave power density (MWPD) values. It was important to save images as a RAW-data, that keep linearity in intensity in the photo [1]. The both approaches gave consisted results and very good fits with Gaussian profiles.

Diamond etching with atomic hydrogen in a microwave plasma is an important process in preparation of hydrophobic surfaces, highly stable interfaces modified with a variety of biomolecules, in pre-treatment of single crystal (SC) substrates in a H₂ or H₂-O₂ mixtures to eliminate defects before homoepitaxy. Due to low etching

rates the etching kinetics measurements may take much time, and these data still are rather rare.

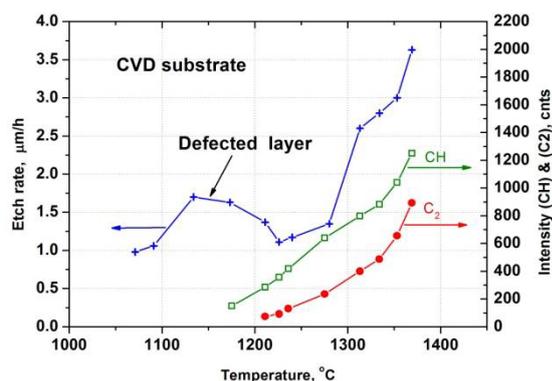


Fig. 2. Etching rate for CVD sample (crosses) in pure H₂ plasma and intensities of CH (open squares) and C₂ (filled circles) lines in OES spectra of the plasma vs substrate temperature at pressure 130 Torr

The EOS is also interesting for study diamond etching in pure hydrogen, which is relevant for substrate pre-treatment in diamond growth technology. Since the etching of diamond supplies carbon species into the plasma, OES is able to monitor the emission lines from CH and C₂ radicals. High resolution OES configuration (II) was used in such experiments. Simultaneously, the etching rate of (001) plane of SC diamond was measured with a low coherent interferometry [7]. The etch rate increases with the substrate temperature T_s , however, non-monotonically (Fig. 2). The etching rate spike in the temperature range of 1170–1230 °C is caused by enhanced etch of a defective surface layer formed by the sample polishing. At higher T_s the etching rate follows Arrhenius law with activation energy of 43 ± 5 kcal/mol.

At the lower T_s of 1092 °C only the hydrogen lines H _{β} and H _{γ} are seen in OES spectra, but with the temperature increase to $T_s = 1369$ °C the CH line at 431 nm and the C₂ peak (516 nm) are revealed, as the supply of carbon to the plasma becomes significant. While the primary etching products of CVD sample are hydrocarbons C_xH_y, the CH and dimer C₂ radicals observed in OES, form by further reactions in the plasma.

Both I_{CH} and I_{C_2} intensities monotonically increase with etch temperature, following in general the enhanced etch rate. The CH_x radicals are assumed to be primary etching products, which are then consumed in a part for conversion to a number of carbon-containing species, such as C₂H₂, CH₄, C₂, and others to reach an equilibrium in the plasma [8]. We checked that CH and C₂ lines appeared in OES spectra only in presence of a hot diamond substrate in the reactor. No lines associated with carbon-containing species were observed in the plasma optical emission spectra in absence of the substrates under identical MW power and pressure. Therefore the CH and C₂ emission we monitored was surely not due to the plasma

etching of carbon contamination from the reactor chamber walls.

As the substrate temperature in the present work was tuned by variation of microwave power P , rather than by an independent heating/cooling, a question arises if the plasma chemistry (concentration of atomic H) contributes to the etching kinetics in addition to the main effect of the substrate temperature. The elementary processes and concentration of species in the plasma are determined by the microwave power density (MWPD) P/V , where V is the plasma volume. We checked how the MWPD depends on the absorbed power, using spatial profiling of H _{α} line intensity, and we found the MWPD to be almost constant. This suggests a stability of plasma chemistry and atomic hydrogen flux towards the diamond surface, therefore we assign the observed etch effects solely to the temperature-dependent surface chemical reactions.

The measurement of OES intensities of CH and C₂ lines could be a simple and convenient qualitative indicator of etching rate of diamond in H₂ plasma, and presumably also in plasmas with more complex compositions, such as H₂-O₂ or H₂-Ar.

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