C/H/O plasmas for diamond growth: density measurements of key plasma species using cavity ring down and optical emission spectroscopy

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A comprehensive study of (MW) activated C/H/O plasmas used for the chemical vapour deposition of diamond is reported. Absolute column densities of electronically excited H(n = 2) atoms, CH, C_2 and OH radicals have been determined by cavity ring down spectroscopy, as functions of height (z) above a molybdenum substrate and of the plasma process conditions ($CH_4/CO_2/H_2$ ratios; total pressure, p; and supplied MW power, P). Optical emission spectroscopy has also been used to explore variations in the relative densities of electronically excited H atoms, CO, OH, CH, and C_2 radicals, as functions of the same process conditions. These experimental data are complemented by extensive 2D(r, z) modeling of the plasma chemistry.

Plasma enhanced chemical vapour deposition (CVD) is a well established method for producing diamond films.[1] The composition of the plasma affects the rate and quality of the diamond film grown. C/H/O plasmas provide a means for producing high quality diamond films at lower input powers [2-4] in comparison to conventional C/H gas mixtures[1] but there is, as yet, rather little detailed mechanistic information in the literature relating to the use of $CO_2/CH_4/H_2$ gas mixtures under the high temperatures and pressures relevant to typical microwave (MW) reactors used for diamond CVD.

To gain a better understanding of the gas processing and species distributions in MW activated C/H/O plasmas, experimental measurements are used to test, tension and validate a 2-D(r, z) computational model. Optical emission spectroscopy (OES) and cavity ring down spectroscopy (CRDS) have been used to measure, respectively, H, C_2, CO, CH and OH species emissions, and absolute column densities of H(n = 2), C_2, CH and OH in $CO_2/CH_4/H_2$ plasmas as functions of process conditions (*e.g.* species flow rates, pressure, and microwave power) and of height (z) above a substrate. Such spatially resolved experimental measurements are compared with results (local number densities, temperatures, *etc*) from the 2-D model, allowing detailed insight into the input gas processing, power utilisation, and the effects of changing plasma parameters like feed gas mixing ratio, input power, and total pressure on the radical (and electron) density distributions within the plasma – as illustrated in fig. 1 – and at the growing diamond surface.

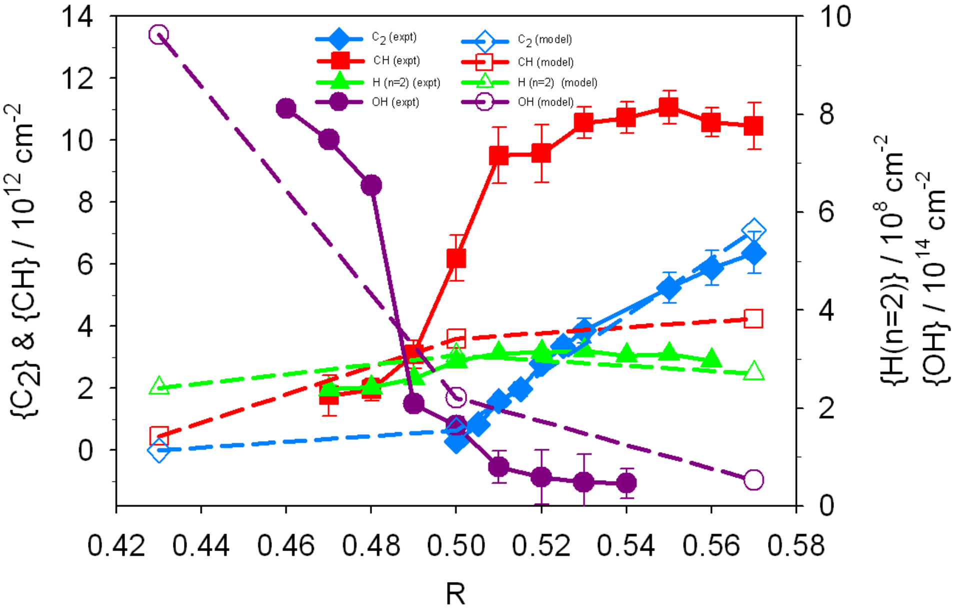

Fig 1: Solid curves: absolute column densities of H(n = 2) atoms and C_2, CH and OH radicals measured at z = 10 mm above the substrate surface for a $CO_2/CH_4/H_2$ plasma operating at P = 1 kW and p = 150 Torr. For this data set, the $(CH_4+CO_2)/H_2$ ratio in the input gas mixture was held fixed at 70:30, but the ratio R = $[CH_4]$ / $([CH_4]+[CO_2])$ was varied. Dashed curves: corresponding column densities predicted by the 2-D(r, z) model.

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