COMPARISON OF PROCESSES IN RADIO- AND MICROWAVE FREQUENCY PLASMAS BY OPTICAL EMISSION SPECTROSCOPY

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1. INTRODUCTION

Important effects of excitation frequency on low pressure plasma processes have been reported in several recent studies /1-4/, most often devoted to a comparison of microwave (MW) and lower frequency (for example radio frequency - RF) /1,3,4/. MW discharges are found to be characterized by an electron energy distribution function (EEDF) which is close to maxwellian, in contrast to that at lower (eg RF) frequencies. This leads to a higher population of electrons in the energetic tail of the MW EEDF, which in turn results in higher reaction rates observed for MW discharges /4/.

For some time now, we have been using "dual-frequency" (MW/RF) plasma for materials processing /5,6/, in which substrates are exposed to a MW discharge while RF power, applied to the capacitively coupled and electrically isolated substrate holder, results in the formation of a negative dc substrate bias voltage V_B. In this case, MW/RF volume processes in the plasma and ion bombardment effects due to V_B can be controlled independently; applied to plasma deposition of thin films, for example, more densely packed films can be grown at high rates, due to the effects of the high ion flux /6,7/. In the present work we use optical emission spectroscopy (OES) to study gas phase reactions in MW, RF and MW/RF plasmas. Particular attention is devoted to those species considered to be major contributors to surface nitridation of polymers and to the growth of hard hydrogenated amorphous carbon (a-C:H) films.

2. EXPERIMENTAL DETAILS

The experiments were carried out in a "dual-frequency" (MW/RF) plasma reactor described in more detail elsewhere /6/. The MW power (2.45 GHz) was applied from a periodic slow wave structure through a fused silica window. The RF powered electrode (15 cm in diameter), at a distance of 4 cm from the silica window, was capacitively coupled to an RF (13.56 MHz) power supply. While the applied MW power was kept constant at 100 W throughout, the RF power value was varied from 0 W to 200 W resulting in V_B values from 0 V to -800 V, respectively. Flows of N_2, NH_3, CH_4, or CH_4/Ar mixtures were introduced into the reactor at a pressure of 100 mTorr (13.3 Pa), at flow rates of 10, 40 or 80 sccm. Spectra emitted from the plasma were monitored and recorded using a Princeton Instruments ST 120 optical multichannel analyzer, with a SPEX 1681C spectrograph. The plasma zone from which the spectra were taken, coincides approximately with the edge of the sheath region in front of the RF electrode.

3. RESULTS AND DISCUSSION

3.1 OES of Discharges in Nitrogen and Ammonia

Important, systematic differences have been observed in the emission spectra from MW and RF discharges in N_2 and NH_3, selected examples of which are shown in Figs. 1 and 2. For example, the 1^+N_2 (first positive) system, between 500 nm and 650 nm, is more intense in the MW case (see Fig. 2). The 1^+N_2 bands can result from the reaction

$$N + N + (M) \rightarrow N_2 + (M) + h\nu$$

where a third body (M) (ion, molecule, wall) may or may not participate /8/. This can serve as a direct confirmation of a higher concentration of atomic nitrogen [N] in the MW discharge, since the 1^+N_2 band intensity has been found to be proportional to $[N]^2$ /9/. Relating the 1^+N_2 band structure to the rotational temperature T_R /9/ we typically find T_R values of 300 K and 500 K in the RF and MW discharges, respectively. Lower band intensities due to N_2^+ in the N_2 plasma (in particular, at 354.9, 356.4, 391.4, 423.7, and 427.8 nm) in the RF case also confirm the differences in the EEDFs. Chemical reactivity is illustrated in Fig. 1, where even a trace of contaminant such as oxygen (for example, desorbed from the reactor walls) can result in a very intense band structure due to NO /8/; (215-281 nm) found to be very pronounced in the RF discharge (see Fig. 1a). In the MW plasma, however, this system is practically absent due to the reaction

$$NO + N \rightarrow N_2 + O$$

which has frequently been used to measure [N] /9/. Finally, higher H_α and H_β emission line intensities in the NH_3 MW plasma (see Fig. 2) also underscore the more pronounced fragmentation than in the RF case.

The discharge emission intensities are coupled to changes in the EEDF (for example, in going from RF to MW) via the parameter Θ/p, the average energy absorbed by an electron per unit density of the gas /4/. The value of Θ/p decreases with increasing excitation frequency f, since the electron density n_e at fixed pressure and absorbed power values rises with f. This rise in n_e, combined with the higher population of energetic electrons in the EEDF, more than compensate the reduction in Θ/p; this gives rise to the observed enhancement in total optical emission intensity in MW or MW/RF plasmas. This is, of course, also the reason for the more intense atomic lines having higher excitation potentials, and for the more abundant ionzing events in MW plasma (see Figs. 1 and 2). As a consequence, the process rates in deposition /5-7,10/, etching /4/ and surface modification reactions are more efficient in MW discharges.

3.2 OES of Discharges in Methane

In the second part of this study we focus on glow discharge processes in CH_4 and CH_4/Ar mixtures, and we relate the observed spectral features to the deposition and characteristics of a-C:H films. The main peaks identified in the region 300-700 nm are illustrated in Fig. 3; the most intense emissions, discussed below, are /11/: CH (431.4 nm), C_2 (516.5 nm), C_3 (405.0 nm), H_α (656.3 nm), H_β (486.1 nm), and Ar (420.1 nm). The intensities have been found to depend strongly on the plasma excitation mode, and their variations with substrate bias voltage V_B, and with argon concentration C_{Ar} are shown in Figs. 4 and 5, respectively.

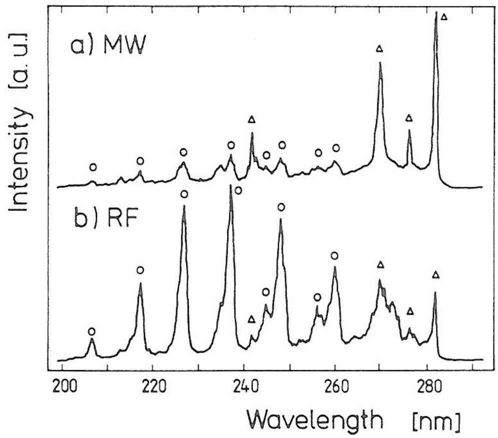

Fig. 1: Spectra emitted from a discharge in nitrogen at a flow rate of 10 sccm: a) MW - 100 W, b) RF - 100 W; (o) NO_γ bands, (▲) N_2 bands.

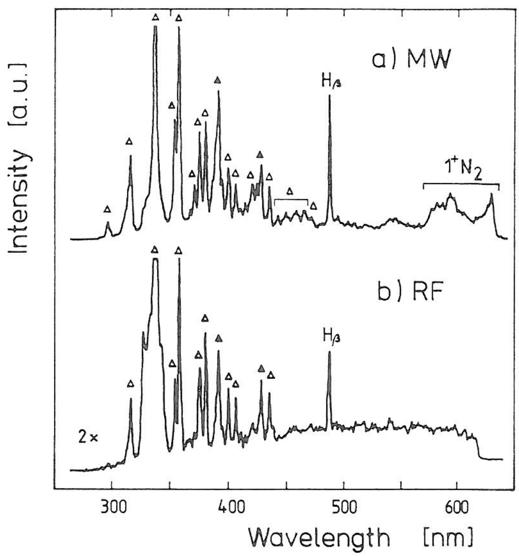

Fig. 2: Spectra emitted from a discharge in ammonia at a flow rate of 10 sccm: a) MW - 100 W, b) RF - 50 W; (△) N_2 bands, (▲) N_2^+ bands.

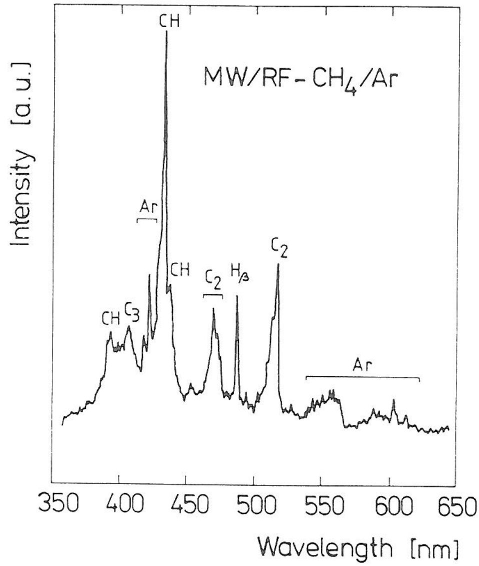

Fig.3: Spectrum emitted form a CH4/Ar (50/50 vol.%) mixture in a MW/RF discharge (flow rate: 80 sccm)

In the dual frequency MW/RF plasma (Fig. 4a), in which P_{MW} = 100 W is kept constant while V_B is increased by raising P_{RF}, the emission intensities are seen to remain unchanged. This means that practically all the species which contribute to film growth are created in the gas phase by the absorbed MW power. An increase in applied RF power (the means for raising V_B) does not appear to influence the abundance of light emitting species, but it does provide an independent means to control the energy and flux of ions bombarding the substrate surface /6,7/. In the RF plasma (Fig. 4b), on the other hand, CH and H_β intensities increase appreciably with rising P_{RF} and V_B, whereas C_2 and C_3 do not vary. From a comparison with the MW/RF results, where the deposition rates are systematically higher /10/, CH and C_2 are deduced to be the main growth precursors detectable by OES, in agreement with Koidl's suggestion /12/, while C_3 is considered to contribute mainly to the formation of crystalline diamond /13/. MW/RF displays a systematically higher H_β emission intensity, symptomatic of a higher atomic hydrogen concentration, which contributes to etching of the sp^2 component in the a-C:H films. Indeed, films possessing the highest microhardness and the most pronounced sp^3 features have been grown in MW/RF plasma at V_B = -200 V /10/. This V_B value corresponds to conditions which favour formation of the sp^3 phase, in agreement with the "preferential displacement" model of a-C:H film growth /14/.

Addition of argon has been found to promote CH_4 fragmentation in the gas phase and, somewhat like MW plasma, it enhances formation of the precursors (Fig. 5). Systematically higher CH, C_2 and C_3 intensities are observed in the MW/RF case, when C_{Ar} is increased in the CH_4/Ar mixture. This correlates well with the enhancement of the sp^3 features, microhardness, and particularly the deposition rates of a-C:H films grown from CH_4/Ar mixtures /10/.

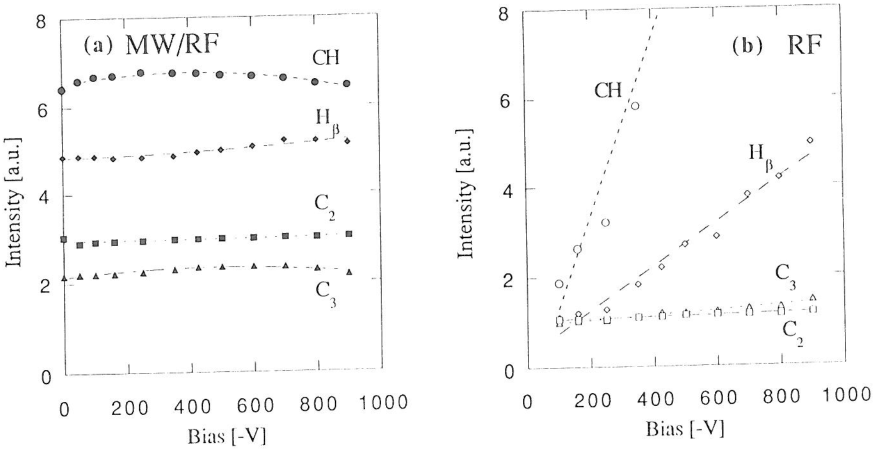

Fig. 4: Emission intensities of selected species in MW/RF (a) and RF (b) discharges in CH_4, as a function of substrate bias (flow rate of CH_4: 40 sccm).

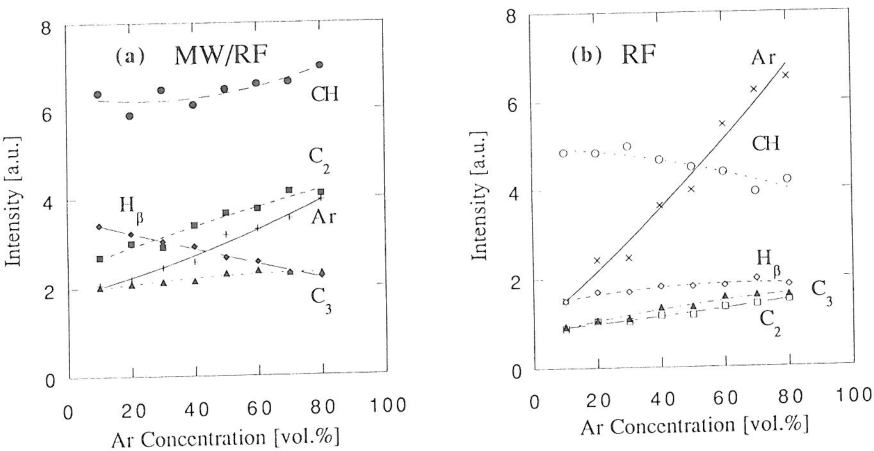

Fig. 5: Emission intensities of selected species in MW/RF (a) and RF (b) discharges as a function of Ar concentration in the CH_4/Ar mixture (flow rate: 80 sccm).

4. CONCLUSIONS

The optical emission spectroscopy (OES) study reported here clearly demonstrates that physical and chemical processes requiring higher excitation energies are more pronounced in MW than in RF plasmas. For example, in N_2 and NH_3 discharges, this leads to a higher concentrations of atomic nitrogen and of ions. During the growth of a-C:H films, MW power absorption by the plasma is an efficient source of growth precursors (e.g. CH, C_2) and of atomic hydrogen in the gas phase. When RF power-induced bias V_B is applied simultaneously (in the MW/RF operating mode), the emission characteristics are not affected appreciably, but the average ion energy can be controlled independently. Conditions leading to an enhancement of sp^3 features in the a-C:H films have been found in this way.

Acknowledgements

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