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Remote Microwave Plasma Enhanced Chemical Vapour Deposition of Amorphous Carbon: Optical Emission Spectroscopy Characterisation of the Afterglow and Growth Rates

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Abstract : Amorphous carbon films were obtained by remote microwave plasma enhanced chemical vapour deposition (RMPECVD). In this process, a mixture of argon and hydrogen is excited in the microwave discharge while methane is injected in the afterglow. The substrates are radio-frequency (RF) biased in order to improve the film properties. Three configurations have been compared : microwave, RF, and mixed microwave-RF coupling. Optical emission spectroscopy allowed to compare intensities of a few spectral lines in the afterglow (CH, C₂, H, and Ar lines) as a function of process conditions. Films have been characterised by infra-red (IR) spectroscopy and electron recoil detection analysis (ERDA). Stress in the films is in the range of -0.7 to -0.3 GPa (compressive). The influence of the hydrogen presence in the plasma, microwave power and radio-frequency bias voltage is discussed.

1. INTRODUCTION

Amorphous carbon is of great interest for many applications in optical, tribological and chemical areas. Indeed, the films are IR transparent, they have low friction coefficient and high chemical inertness. Amorphous carbon films can be prepared by various techniques, namely physical vapour deposition (sputtering, ion beam processes) and chemical vapour deposition in microwave, radio-frequency or direct current (DC) discharges [1].

However the most widely used technique for amorphous carbon deposition is RF PECVD. The plasma is created between two electrodes and the substrates receive high energy ion flux. In the case of microwave discharges [2], the electronic density is largely higher than for RF discharges. The ionisation degree being over 10%, the deposition rates are relatively high. Furthermore, there is no need of electrodes so the pollution of the films is reduced.

Raveh *et al.* [3] used an original method, called "dual-frequency" microwave-radio-frequency plasma deposition technique where the substrate is immersed into the microwave and is RF biased. In comparison with "conventional" RF plasma deposition, they showed that film properties (density, microhardness, internal stresses) were improved. In this method [3,4], the discharge is characterised by a plasma sheath region near the RF powered electrode, having a pronounced negative DC self bias. This leads to bombardment by positive ions which is beneficial for deposition of amorphous carbon films. The energy flux delivered by the incident charged species to the growing film surface has been proposed as the main parameter controlling the final film characteristics.

In this study, amorphous carbon films are deposited in the afterglow of a microwave plasma device offering the possibility of applying a RF bias voltage on the substrate. This microwave remote (indirect, afterglow or downstream) PECVD method successfully used for silica deposition [5,6] has not yet been applied to these films.

In remote PECVD [7], only some of the process gases are subjected to direct plasma excitation. The active species created in the plasma are extracted via high gas flow rates and mixed with the second gas reactant injected in the afterglow. Hence the substrate is outside the plasma glow region *i.e.* in the afterglow where many active species have decayed sufficiently. Remote PECVD can separate production from bombardment in contrast to direct PECVD illustrated by RFPECVD as an example.

The aim of the present work is to study the respective role of RF and microwave (MW) excitation for amorphous carbon deposition, through *in situ* optical emission spectroscopic characterisation of the afterglow, for different configurations. Furthermore, deposition rates are compared and amorphous carbon films obtained by "dual-frequency" remote MWRF PECVD are characterised. Finally, the influence of hydrogen addition in the microwave plasma is discussed.

2. EXPERIMENTAL

2.1 Apparatus

The equipment (Fig.1) used for this study is derived from a reactor developed at the LETI (microelectronic division of the "Commissariat à l'Energie Atomique" in Grenoble, France) for microelectronic wafers. It has been described in more details elsewhere [8].

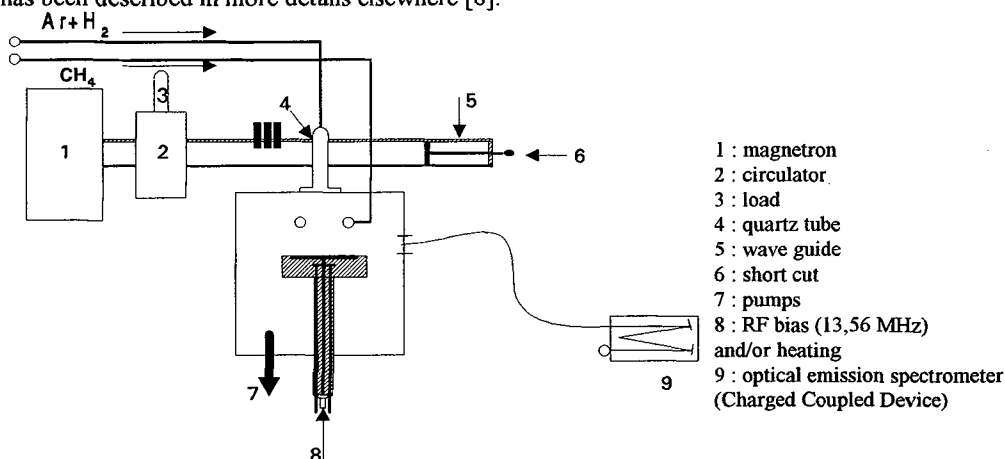


Fig. 1 : Experimental set-up

Before the deposition, the reactor is evacuated with a turbomolecular pump to a pressure of 10^{-4} Pa. During deposition, the pressure is around 10-80 Pa. The available gases are H_2 , Ar, N_2 , O_2 , and CH_4 .

The microwave power (2.45 GHz) is coupled to the plasma gas (Ar or $Ar+H_2$), sustained by a surface wave. The plasma gas flows through a fused quartz tube crossing the rectangular wave guide and expands in the afterglow region. A mobile short cut provides the impedance matching that minimises the reflected power. The reactive gas (CH_4) is directly fed into the deposition chamber through an injector which is located under the glow plasma region and a few centimetres above the substrate.

The substrate-holder is RF biasable and can be heated up to $600^\circ C$.

2.2 In-situ diagnostic

A Jobin-Yvon optical emission spectroscopic (OES) system including a THR 1000 monochromator with a 1200 *gr/mm* grating and a liquid nitrogen cooled charged coupled device (CCD) is connected by means of a quartz optical fibre to the plasma reactor. The CCD allows the afterglow analysis.

During OES measurements, the RF bias voltage is kept constant at 100 V, the microwave power at 400 W and the pressure at 81 Pa. Ar and $Ar-H_2$ mixtures are introduced into the quartz tube. The percentage of H_2 mentioned in all this paper corresponds to the relative flowrate (D) of H_2 in the microwave plasma, *i.e.* $D_{H_2}/(D_{H_2}+D_{Ar})$. The proportion of CH_4 is kept constant at 30% of the total gas flowrate, *i.e.* $30\% = D_{CH_4}/(D_{CH_4}+D_{H_2}+D_{Ar})$. Mixtures are introduced into the reactor at a total flow rate of

760 sccm (standard cubic centimetre per min.). The fibre allows to analyse the area between the substrate and the injector (3 cm above the substrate) in the afterglow. The emission spectral line intensities of CH(387.1 nm), CH(431.4 nm), C₂(473.7 nm), C₂(516.5 nm), H β (486.1 nm), H α (656.3 nm), and Ar(727.3 nm) were normalised to the emission of Ar(425.9 nm).

2.3 Film characterisation

Amorphous carbon films are deposited onto single crystal silicon wafers. The film thickness, ranging from 2000 Å to 3 μ m, is measured using a DektakIIA profilometer. IR transmission spectra are obtained with a Bomem Fourier transform IR spectrometer. ERDA allows to determine the content of hydrogen in the films. Stresses are deduced from measurements of the substrate (4.15 mm²) curvature, before and after deposition. Compressive stresses will have negative values.

3. RESULTS AND DISCUSSION

3.1 Comparison of RF, MW and MWRF plasma deposition techniques

3.1.1 Optical emission spectroscopy from Ar-CH₄ discharges

In the case of pure argon injected in the quartz tube, the highest intensities are obtained in the MW configuration, whatever the lines (Fig.2(a)). The important spectral emission of C₂ points out a higher population of energetic electrons [9]. The RF configuration produces the lowest intensities and no emission of C₂. The MWRF discharge appears as intermediate. As noted by Martinu *et al.* [9], MWRF coupling enhances the emission of H lines and new fragments as C₂ are created. We have also observed the enhancement of CH spectral lines.

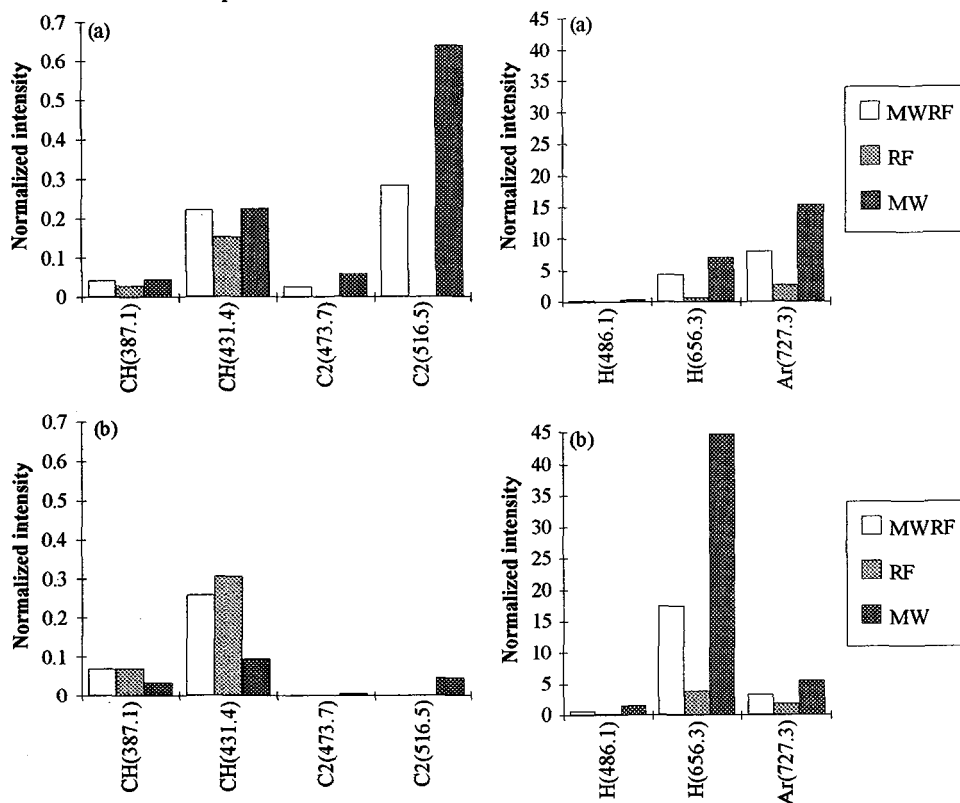


Fig.2 : Emission line intensities for (a) Ar-CH₄, *i.e.* with 0% H₂; (b) Ar-H₂-CH₄, *i.e.* with 44% H₂ mixtures.

3.1.2 Optical emission spectroscopy from Ar-H₂-CH₄ discharges

In the case of an Ar-44%H₂ mixture, injected into the quartz tube, the OES results are different. The emission intensity of CH line is high in the RF discharge, relatively low in the MW afterglow and intermediate in the MWRF mode (Fig.2(b)). The C₂ (516.5 nm) and C₂ (473.7 nm) lines appear only in the case of a MW discharge, but very weakly for the last one.

The intensities of H α , H β and Ar lines are increasing going from the RF to the MW mode. Furthermore, in the "dual" MWRF mode, RF bias voltage increases (Fig.3). This results in an increase of the ionization degree and of the H α , H β and Ar line intensities.

According to Tsuji *et al.* [10], in a DC glow discharge of CH₄-Ar, carbon deposition is closely related to the presence of excited CH and C₂ species in the plasma. In the present study, carbon deposition occurs even when there is no C₂ emission (RF). Conversely, in the case of the Ar-CH₄ mixture, carbon deposition is negligible, although there is a strong emission of C₂ line (MW). On the other hand, carbon deposition is always associated to the presence of CH excited species.

3.1.3 Deposition rates

The results of Table I show that the deposition rates are far lower for remote MW deposition than for RF and MWRF deposition. But, the MWRF configuration appears to be the fastest, independently of the gas phase composition, the pressure, and the total flow rate. Such a tendency was also observed by Martinu *et al.* [9], who obtained higher deposition rates of about 1-3 $\mu\text{m/h}$.

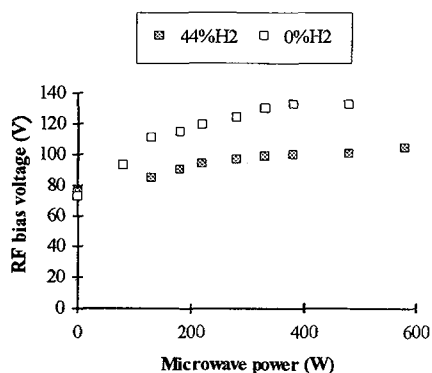


Fig.3 : Dependence of RF voltage on microwave power.

	RF	MW	MWRF
30%CH ₄ -44%H ₂ 0.8 mbar 760 sccm	$9.2 \cdot 10^{-2}$ (0.76 $\mu\text{m/h}$)	#0	$1.22 \cdot 10^{-1}$ (0.92 $\mu\text{m/h}$)
5%CH ₄ -0%H ₂ 0.2 mbar 379 sccm	$2.69 \cdot 10^{-2}$	$2.78 \cdot 10^{-3}$ (0.08 $\mu\text{m/h}$)	$3.49 \cdot 10^{-2}$ (0.22 $\mu\text{m/h}$)
5%CH ₄ -44%H ₂ 0.8 mbar 379 sccm	$1.01 \cdot 10^{-4}$	-	$1.21 \cdot 10^{-1}$

Table I : Deposition rates (mg/cm²) in the different configurations.

3.1.4 Conclusions

When the substrate is placed in the afterglow, the MW excitation is less efficient than the RF one and the corresponding deposition rates are lower, while the mixed MWRF mode leads to the highest deposition rates.

The detection of C₂ emission is not significant of carbon deposition. On the other hand, the presence of CH emissive species seems to be necessary for deposition.

3.2 Hydrogen role

3.2.1 Effect of hydrogen addition on emission intensities

MW configuration : The presence of hydrogen causes a decrease in the Ar, CH, and C₂ optical emission intensities and of course an increase in H emission (Fig.2).

RF configuration : The Ar emission decreases, while the H and CH emission intensities increase when hydrogen is added (Fig.2).

MWRF configuration : As in RF configuration, the CH emission intensity increases while the C_2 emission disappears (Fig.2).

Ricard *et al.* [11] have shown that the carbon atom density in Ar- CH_4 and Ar- H_2 - CH_4 post-discharges is higher when no hydrogen is introduced into the plasma. By comparing the emission intensities of hydrocarbon fragments and by admitting that line intensities are related to carbon atom densities, our results exhibit a similar tendency in both MW configurations. Furthermore, Thomas, [12] working in similar conditions, has deduced that the emission intensity of the $H\alpha$ line is significant of hydrogen atom density. Adding hydrogen results in a decrease in the electronic density. In addition (Fig.5), when the hydrogen content increases, the RF bias voltage decreases and tends to a limit value suggesting that the ion number decreases.

C_2 being not detected in the RF discharge, we can conclude that plasma dissociation mechanisms strongly depend on the excitation mode. This absence is in accordance with the results of Martinu *et al.* [9] who have only noted the apparition of C_2 when argon is added and/or when microwave is superimposed. Meanwhile, in the RF mode, with CH_4 -Ar mixture no C_2 emission is observed in our case.

3.2.2. Effect of hydrogen on deposition

After a parametric study, the following deposition conditions have been chosen : 100 V RF voltage, 30% CH_4 of the total gas flowrate introduced in the afterglow and 44% H_2 -Ar in the quartz tube. Films obtained in this configuration (MWRF) have been characterised.

The value of 18 at.% H obtained by ERDA is lower than those reported by Tang *et al.* (27-37 at.%) [13] and Martinu *et al.* (25-30 at.%) [9].

Stresses in the films are compressive going from -0.7 to -0.3 GPa. Martinu, [9] who showed that MW superimposition results in a decrease in stresses, obtained similar values.

For a thickness of 9000 Å stress is -0.95 GPa without hydrogen and -0.61 GPa with 44% hydrogen in the plasma. This result suggests that an increase of hydrogen proportion in the plasma leads to more incorporation of hydrogen in the films [13]. The slight decrease of the film density when the hydrogen proportion increases tends to confirm this hypothesis (Fig.5). Moreover, the IR spectrum of Fig.6 shows the presence of different bands corresponding to carbon hydrogen bonds.

The addition of hydrogen results in a decrease in the deposition rate. This decrease could be explained by the etching role of hydrogen [14]. Indeed, an increase in hydrogen proportion results in an increase of H and CH lines (Fig.7). So, if CH are strongly related to film deposition as we have supposed, the only explanation is hydrogen etching.

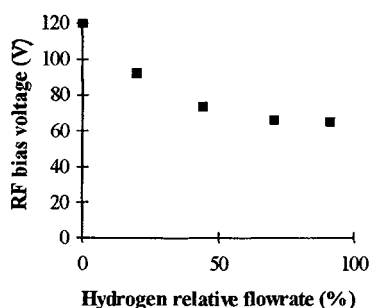


Fig.4 : Dependence of RF voltage on hydrogen proportion.

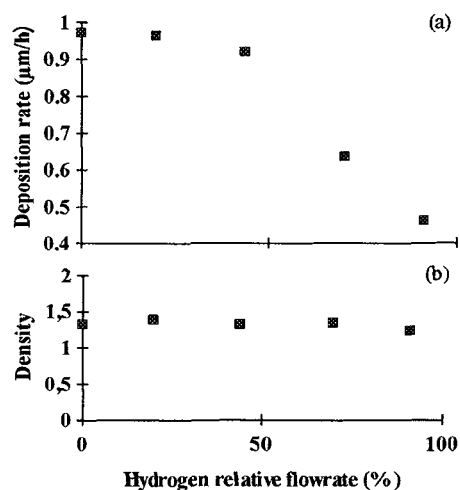


Fig.5 : Hydrogen proportion influence on deposition rate (a) and film density (b).

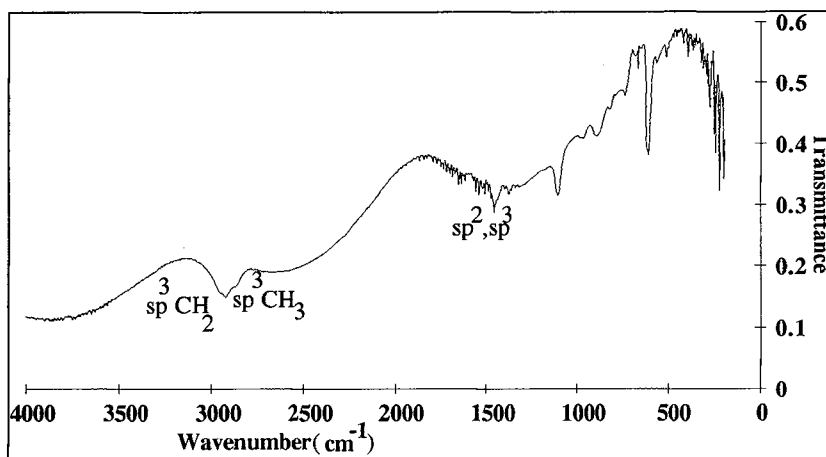


Fig. 6 : IR spectrum of amorphous carbon.

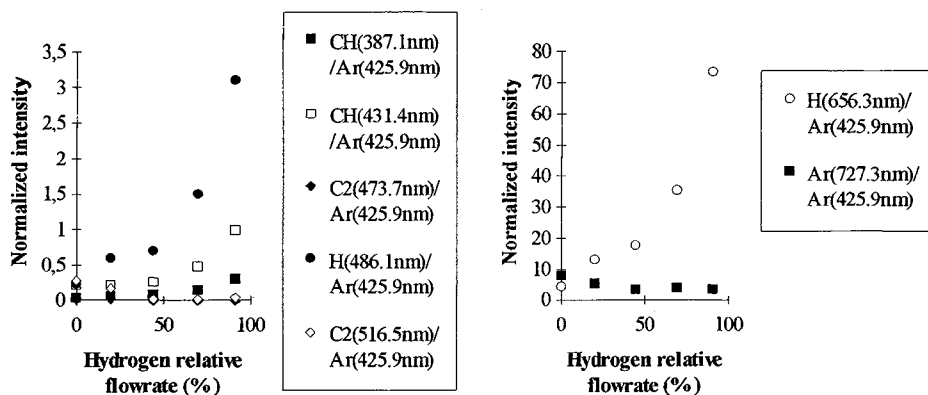


Fig. 7 : Emission intensities evolution versus hydrogen proportion.

3.2.3. Conclusion

Concerning the H content and stress values, films obtained by MWRP PECVD have properties similar as those obtained by the other methods.

Hydrogen addition in the plasma decreases the deposition rate. This can be related to the increase in H α and H β line intensities which confirms the etching role of hydrogen.

3.3 Microwave power influence

The influence of microwave power on the film properties has been studied for a phase composition of 30%CH₄ in Ar-44%H₂ mixture.

The deposition rate weakly increases with MW power (Fig.8(a)). At the same time, H α and H β line intensities increase and the CH line intensity remains relatively constant (Fig.9). An increase of reactive species could be balanced by the etching effect of hydrogen.

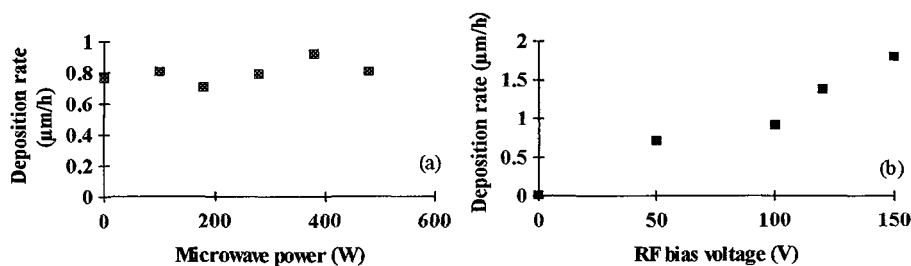


Fig.8 : Deposition rate versus (a) MW power, (b) RF bias voltage.

3.4 RF bias voltage influence

An increase of the RF bias voltage results in an important augmentation of the deposition rate (Fig.8(b)). While the $\text{H}\beta$ line intensity is minimum at 100 V, the $\text{H}\alpha$ line intensity decreases as CH line intensity increases. At the same time, C_2 line intensity decreases. These results confirm the importance of CH line intensity as a control parameter for deposition.

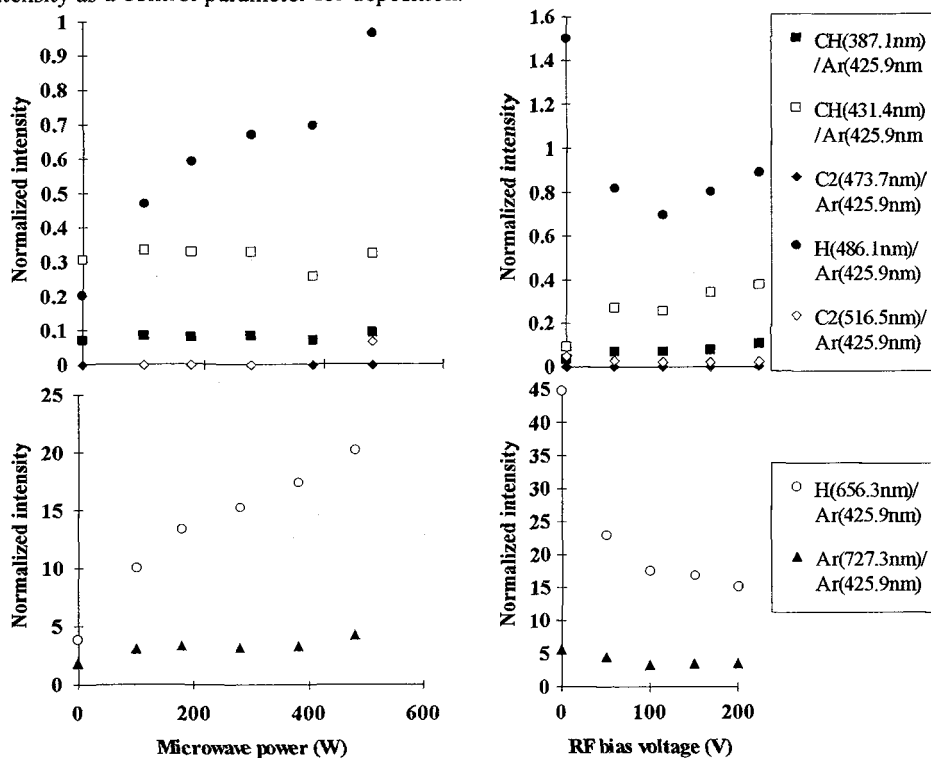


Fig.9 : Emission intensities evolution versus microwave power and RF bias voltage.

4. CONCLUSION

This study reveals the complexity of the reactive processes within remote PECVD reactor having the mixed MWRP configuration.

RF bias voltage appears to be a key parameter having a greater influence both on deposition rates and on emission intensity of the afterglow than in direct MWRP PECVD [15].

Microwave excitation results in a different distribution of emission intensities. It has a weak influence on deposition rates, but it would be interesting to have more information on the film composition to precise its role.

Hydrogen is acting as an etching reactant which decreases deposition rates.

The MWRF mode allows one to obtain amorphous films with suitable properties and deposition rates, close to those achieved by the other PECVD techniques.

Emission spectroscopy gives very interesting information on the influence of process parameters, but the results have to be analysed carefully. Indeed this method allows detection of emissive species, but the determination of densities is achieved only in particular conditions.

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