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CN radical excitation during CNx thin film deposition by RF generated plasma beam

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CN RADICAL EXCITATION DURING CN_x THIN FILM DEPOSITION BY RF GENERATED PLASMA BEAM

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Introduction

Different techniques have been investigated in the last period having in view the synthesis of β-C_3N_4 material supposed to be harder than diamond (laser ablation combined with ionic exposure [1], magnetron sputtering of carbon targets in nitrogen [2], filament assisted chemical vapour deposition [3], etc.)

In our approach an RF generated expanded plasma [4] has been used. The discharge (P= 40-60 watt) is generated in a narrow gap (1-2 mm) plan - parallel discharge at a pressure around 10-20 torr between a plane electrode and a nozzle. The plasma expands from this discharge into a vacuumed vessel, carrying out the excited species.

For CN_x deposition the discharge electrodes have been made from graphite, the working gas being nitrogen. The carbon atoms are produced by RF sputtering of electrodes in the gap region and are transported through the nozzle by the plasma flow.

Little is known about the deposition mechanisms of CN_x materials. In the present work a spectroscopic study of plasma beam during deposition is presented.

Experimental results

The spectra were recorded at different positions, like:
a-spectra recorded directly from the discharge, *b*-spectra recorded in the early expansion, just downstream the nozzle, *c*-spectra recorded at the level of substrate (few centimetres downstream the nozzle), in three situations:
A) the RF electrode is selfbiased (U_{self} = -90 V); *B*) the RF electrode is negatively biased (U_{bias} = - 180 V); *C*) the RF electrode is positively biased (U_{bias} = + 160 V)

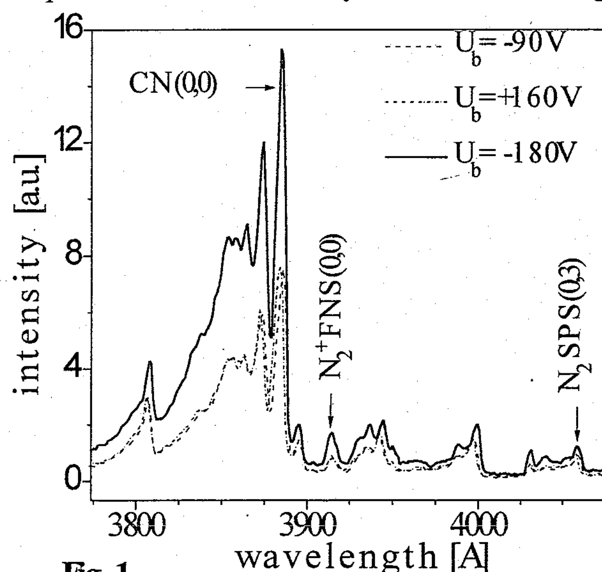

Fig. 1.

The spectra reveal the emission of SPS, N1N spectral systems of nitrogen and the violet spectral system of CN. In Fig. 1 is presented a part of the spectra, where the CN radical emission is exhibited at the level of substrate for the different bias conditions. A strong enhancement of CN violet emission is observed for negative biasing (case Cc).

In order to compare the spectra the bands intensity have been normalised to the height of (0,3) peak of SPS spectral system of nitrogen.

Discussion

In a frame of an excitation model based on direct electronic collisions the intensity of an emitted band is dependent on the electronic temperature, the position of the excitation threshold (ε_{th}), the magnitude of the excitation cross-section and the transition probability. From measurements of the bands N1N(0,0) at 3914 A, SPS (0,3) at 4059 A, CN (0,0) at 3883 A it is possible to evaluate the actual presence of CN radical in the plasma beam. The ratio of the peaks intensities could be calculated, using the processes rates given in [5] as:

$$\frac{I_{3914}}{I_{4059}} \propto \exp(-(\varepsilon_{th,FNS} - \varepsilon_{th,SPS}) / kT_e) * \cdot (1 + k_{col} \cdot [N_2(X)])^{-1}$$

$$\frac{I_{3884}}{I_{4059}} \propto \exp-(\varepsilon_{th,CN} - \varepsilon_{th,SPS} / kT_e) * \frac{[CN(X)]}{[N_2(X)]}$$

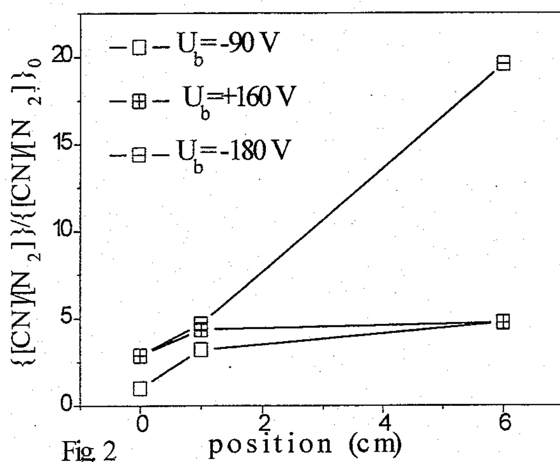

Fig 2

(where k_{col} is the collisional quenching rate of $N_2^+(B)$).

The electronic temperature has been calculated using first equation. Also using these relations it was possible to calculate (excepting a multiplying constant), the concentration of CN radical particles relative to the N_2 molecules. Its dependence on position (normalised to the value obtained in case Aa) is presented in Fig. 2. The strong increase of the CN concentration in the expansion (case Cc) is related to the behaviour of the electronic temperatures, showing the persistence of the electric field in expansion in the last case.

Conclusions

In an RF discharge expanding plasma with carbon electrodes the CN radical is strongly excited. By applying a supplementary negative bias to the RF electrode it appears that the CN radical concentration is efficiently produced in expansion proving this system as very appropriate for CN_x material deposition.

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