GROWTH OF ECR-CVD CARBON NITRIDE FILMS, WITH A HIGH NITROGEN CONTENT, FROM $CH_4/N_2/Ar$ MIXTURES

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1. INTRODUCTION

Great efforts for increasing nitrogen content in carbon nitride films are being made in order to improve their properties. This aim may be achieved by deepening in the knowledge of the deposition mechanism of the process (1,2). In this work, different activation mechanisms for methane molecules, depending on gas mixture composition, during ECR-CVD carbon nitride formation process are proposed.

2. EXPERIMENTAL

Carbon-nitrogen films were deposited by ECR-CVD from $Ar/N_2/CH_4$ gas mixtures. CH_4 was supplied downstream the discharge zone. CH_4 partial pressure was kept always constant, varying either nitrogen (in series 1) or argon (in series 2) pressure. Profilometry (Dektak 3030) and Energy Dispersive X-ray Analysis (EDAX) (Rontec 501) have been used for thickness and composition measurements and Optical Emission Spectroscopy (OES) for plasma analysis (EG&G Princeton).

3. RESULTS AND DISCUSSION

In figure 1, the increase of the growth rate with the $[CH_4]/([N_2]+[Ar])$ ratio, for the studied series, is shown. For low ratios ($[CH_4]/([N_2]+[Ar])<0.095$), the detected low growth rate, likely due to etching processes by nitrogen atoms (1,2), varies similarly for both series. Thus, in this range it may be considered that the activation agent of methane molecules does not affect appreciably the deposition process. On the contrary, for higher $[CH_4]/([N_2]+[Ar])$ ratios (>0.095), the variation of the deposition rate is clearly different, depending on the $[N_2]/[Ar]$ ratio in the gas mixture. In mixtures with $[N_2]/[Ar]>3$, the deposition rate sharply increases with the $[CH_4]/([N_2]+[Ar])$ ratio, likely because methane molecules are predominantly activated by the, in majority, nitrogenated species. However, for $[N_2]/[Ar]<3$, the deposition rate reaches a saturation value ($[Ar]/CH_4]=3$ argon species being the main activation agent). It is important to point out that the decrease in the growth rate coincides with the nitrogen enrichment of the films, as measured by EDAX.

In OES spectra, the peaks at 359 nm (N_2) (3) and 811.8 nm (Ar(I)) (4) correspond to the main species being able to activate methane molecules. Figure 2a presents the variation of the (I_N/I_{Ar}) ratio with the methane content in the gas mixture for both series of experiments and a rough evaluation of the main methane activation agent can be made. As observed in the figure, the (I_N/I_{Ar}) ratio increases (series 2) or decreases (series 1) for increasing $[CH_4]/([N_2]+[Ar])$ ratios. Therefore, for low nitrogen or high argon contents in the gas mixture, methane molecules are mainly activated by argon species, however in the opposite (i.e. high nitrogen or low argon contents) the principal activation agent is nitrogen. Also from OES spectra, in figure 2b it can be seen that the emission signal of atomic nitrogen (868 nm) becomes higher with the increase of nitrogen as well as argon content in the gas mixture. The enhancement of surface etching processes by atomic nitrogen accounts for the low deposition rates detected.

4. CONCLUSIONS

High nitrogen content carbon nitride films have been deposited by ECR-CVD from $Ar/N_2/CH_4$ gas mixtures. From the results about the deposition rate and composition of the films as well as OES analysis for different gas mixtures, we find that, at the conditions of this work, :i) Methane molecules, introduced downstream the discharge zone, may be activated by nitrogenated and/or argon species, previously excited, depending on the N_2/Ar ratio ii) Two processes should be considered during the deposition of carbon nitride films: The formation process, mainly regulated by methane molecules activation, and the etching process controlled by the atomic nitrogen present in the plasma during the process.

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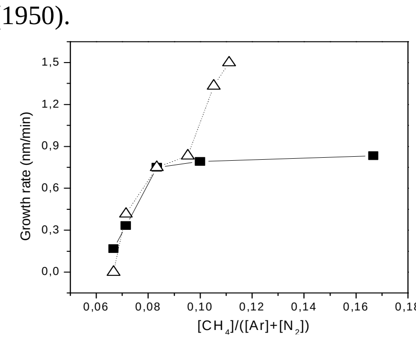

Figure 1.- (a) Growth rate of CN_x films for different $[CH_4]/([N_2]+[Ar])$ ratios: series (■)1 and (⇆)2.

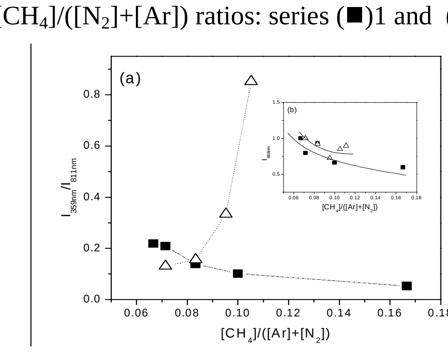

Figure 2.- (a) OES intensity ratio (I_{N2}/I_{Ar}) and (b) Normalized 868 nm peak for different $[CH_4]/([N_2]+[Ar])$ ratios: series (■)1 and (⇆)2.