Insight into plasma polymerization with the significant contribution of ions towards deposition and etching balance

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Low pressure radio-frequency (RF) discharges in CO_2/C_2H_4 can be used for the deposition of organic coatings with carboxyl and other oxygen functional groups that provide permanent hydrophilic surfaces [1] required in many applications. Moreover, carboxylated surfaces can be platforms for immobilizing biomolecules, *i. e.* creating biointerfaces for biosensors and artificial tissues [2, 3, 4]. The CO_2/C_2H_4 plasmas are processing environments in which etching and deposition are competing processes, especially in CO_2-rich mixtures. The etching effect is further enhanced in low pressure discharges that can provide significant ion energy flux toward the growing film. We studied neutral and ionic species in CO_2/C_2H_4 RF capacitively coupled plasma (13.56 MHz) with Hiden EQP 500 mass and energy analyzer placed between the powered and grounded electrodes. To obtain information about plasma chemistry for gas mixtures that were used previously for the deposition of carboxyl plasma polymers [5, 6], we carried out the measurements for different CO_2:C_2H_4 ratios (1:1, 2:1, and 6:1), with and without admixed Ar. The mass spectra of neutrals from plasma contained a small amount of oligomers. The compounds with four carbon atoms were still clearly detected. Larger ionic species were observed when extracting the positive ions directly from the discharge (Fig. 1). In the case of $Ar/CO_2/C_2H_4$ discharge, Ar ions were not at all the most abundant ionic species because ArH^+ (41 a.u.) and hydrocarbons combined with CO_2 and CO, *e. g.*, $C_2H_2{}^+$ (26 a.u.), $C_2H_3{}^+$ (27 a.u.), $C_2H_4{}^+/CO^+$ (28 a.u.), $C_2H_5{}^+/COH^+$ (29 a.u.), $C_3H_3{}^+$ (39 a.u.) and $CO_2{}^+$ (44 a.u.), had much stronger signals.

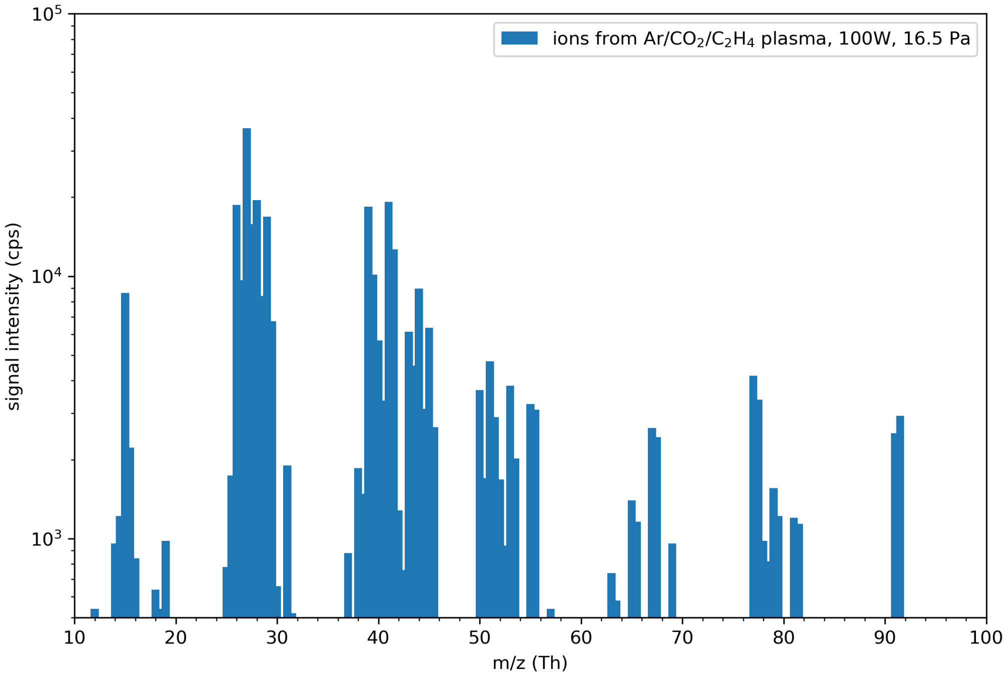

Fig. 1: ions from $Ar/CO_2/C_2H_4$ plasma, 100W, 16.5 Pa

In CCP discharges, the energy flux brought by ions towards the growing film can be substantial. In the asymmetric discharge, the substrate is often placed on the RF electrode, which acquires negative DC self-bias added to the plasma potential to create a high-voltage plasma sheath. In the symmetric discharge, the substrate is usually at the grounded electrode, but the plasma potential is high, i.e., resulting in a high-voltage sheath adjacent to the substrate. The effect of ions on the growing film depends on the deposited energy, the kinetic energy delivered at the surface per condensing atom (or molecule) [6]:

$$\varepsilon = \frac{E_{\mathrm{mean}}\Gamma_i}{R},$$

where R is the film deposition rate, Γ_i is the ion flux, and E_{mean} is the mean ion energy, which depends on the sheath voltage and collision processes governed by the pressure.

Understanding how the ions contribute to the overall deposition process requires complex plasma diagnostics combined with thin film characterization. A dedicated experiment involving the deposition into cavities partially shielding the incoming ions offers an easier way to gain insight into the process without detailed plasma diagnostics. Using the cavity with a slit opening [7], we studied the film deposition rate and chemistry in the CCP discharges of 2:1 and 6:1 CO_2/C_2H_4 mixtures at 10 Pa. In the 6:1 mixture characterized by the high contribution of etching, besides the deposition, the deposition rate inside the cavity below the slit opening (0.5, 1 and 2 mm) was about $2.5\times$ higher than on the flat surface exposed directly to the plasma. In the 2:1 mixture, the deposition rate inside the cavity was higher than on the flat surface only for the largest cavity, 2 mm.

We performed a simple Monte Carlo simulation of the film deposition to find what effects will be able to explain the film thickness profiles at two different gas mixtures and three types of slits, 0.5, 1 and 2 mm. The observed higher deposition rate in the cavity required a small probability of etching species being deactivated at the collision. However, this probability had to be low because the explanation of narrow thickness profiles inside the cavity required the presence of the directional etching species that etch sideways diffusion-caused deposition. Thus, to obtain the observed narrow profiles, the angular distribution of the sputtering yield with the maximum at around 35 ° angle of incidence was taken from the work of Hamaguchi *et al.* [8].

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