Infrared gas phase studies on plasma-polymer interaction in high-current dielectric barrier discharges

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1. Introduction

Atmospheric-pressure plasma enhanced chemical vapour deposition (AP-PECVD) has been applied to obtain $SiO₂$ -like barrier layers on polymeric substrates in air-like dielectric barrier discharges (DBDs) in conjunction with organosilicon precursors [1, 2]. A competition between deposition and etching was concluded from previous studies [3]. In this contribution quantitative *ex-situ* infrared studies of the plasma exhaust were carried out using a high-resolution Fourier-transform infrared (FTIR) spectrometer. The gas phase composition, the production rates of stable molecules and the plasmapolymer interaction were analysed.

2. Experimental set-up

The discharge was ignited between two cylindrical copper electrodes with a radius of 120 mm, both covered by a polymer substrate PEN (Polyethylene Naphthalate) of 100 μm thickness. The smallest gap between the two electrodes was 0.5 mm. The gas mixture was injected via a controlled mixing unit while the electrodes were rotating in the direction of the gas flow. The exhaust from the plasma was sampled by 12 pipettes into a high-resolution FTIR spectrometer $($ \sim 0.15 cm⁻¹ resolution) equipped with a multi-pass absorption cell adjusted to 7 m absorption pass. The frequency of the applied voltage was 185 kHz. The injected power was modulated at 625 Hz with a duty cycle of 50%.

3. Results

From the infrared spectrum of the atmospheric pressure air-like plasma, both N-related species $(NO, NO₂, N₂O, HNO₂)$ and C-related species $(CO,$ $CO₂$, HCOOH) were identified. The variations of the molecule production rates, X , in $N_2/Ar/O_2$ $(15/1.0/0.5~2.0~\text{slm})$ mixture with substrate of PEN are presented in Fig. 1. The production rates of NO, $NO₂$, $N₂O$ and HCOOH clearly increase with the $O₂$ content in the gas flow while the CO production remains relatively stable at about 10 times higher level than the N-related species (about 4×10^{19} s⁻¹). The latter species are all in the order of 10^{18} s⁻¹ and are characterised by $X(NO) > X(NO₂) > X(N₂O)$. Similar

results were also observed in [4] for a plasma jet using Ar as carrier gas and 0.1% admixture of air.

Fig. 1: *Molecule production rates in* $N_2/Ar/O_2$ *(15/1.0/0.5~2.0 slm) plasmas in contact with (unprotected) substrate of PEN*

When the polymeric substrate is protected by a thin $SiO₂$ film, the production rate of CO reduces significantly while HCOOH cannot be observed. This behaviour indicates that HCOOH as well as CO are mainly formed as etch products of the polymer. Among all components in the gas mixture, the oxygen content plays the main role in PEN etching as HCOOH increases with $O₂$ flow (Fig. 1). Three potential sources of CO have been identified: (1) the etching of the polymer substrate which is the dominant source, (2) the impurities from the gas injection system such as precursor pollution from previous deposition experiments ($\sim 10^{18}$ s⁻¹), and (3) the basic C-impurities in the entire discharge and measurement system $(<10^{18} s^{-1})$.

References

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