Gas phase studies during roll-to-roll processing of polymers in air-like atmospheric pressure DBDs

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The effluent of an industrial roll-to-roll reactor for synthesising silica-like barrier layers using atmospheric pressure glow discharges has been studied by means of ex-situ FT-IR spectroscopy. The focus of this study was on etching conditions in air-like gas mixtures without precursor admixture. Main stable etch components, e.g. CO, CO₂ and HCOOH have been detected. Particularly, HCOOH was found to be a good indicator for etching conditions present during foil treatment. Additionally, a modified N₂O₃ chemistry will be discussed.

1. Motivation

Diffusive dielectric barrier discharges (DBDs) at atmospheric pressure (AP) have been shown to be a promising tool in large-area plasma-enhanced chemical vapour deposition (PE-CVD). A key aspect to sustain, particularly oxygen containing, atmospheric pressure DBDs in a diffusive mode is the application of an electronic stabilisation circuit [1]. Excellent SiO₂-like barrier layers on polymeric substrates such as PEN (Polyethylen-Naphtalate) have been obtained through PE-CVD in a roll-to-roll mode [2]. It should be mentioned that the film properties among them the self-similarity to the polymeric substrate have been achieved in cost-efficient air-like gas mixtures of Ar/N₂/O₂ in conjunction with organo-silicon precursors (fig. 1). Extensive studies on the deposition process have been carried out using surface analytical techniques. In this way, distinct regimes of plasma-polymer interaction along the electrodes were identified (fig. 1) which are mainly characterised by a competition between deposition and etching processes [3]. In this contribution complementary gas-phase studies using infrared (IR) absorption spectroscopy are reported. The focus was thereby on precursor-free gas mixtures to mimic an etching regime of the polymer (fig. 2).

Fig. 1: Schematic diagram of the roll-to-roll AP PE-CVD setup used for synthesising SiO₂ barrier layers on polymeric substrates. Three different film-formation regimes along the electrodes (and the gas flow) are indicated.

Fig. 2: Overview of plasma-surface interactions in PE-CVD processes. In the present approach the precursor is omitted to study gas-phase products under etching conditions.
2. Experimental

Given the challenging optical access to small gap (0.5 mm) DBDs in general and to the industrial roll-to-roll configuration in particular (fig. 1) an ex-situ approach was chosen to study the gas phase composition. A gas sampling system was implemented which collected continuously a fraction of the effluent into a multi-pass absorption cell (White type). A high-resolution Fourier-Transform IR (FT-IR) spectrometer (Bruker IFS66/s) was aligned to the sampling cell to yield 7 m total absorption path at reduced pressure. The discharge was operated in diffusive mode in gas mixtures of air/Ar (15/1 slm) and O₂/Ar (0...2/1 slm), respectively. To distinguish gas phase species produced from etching of the PEN substrate several experiments were carried out with a polymeric substrate pre-deposited with an SiO₂ protecting layer.

3. Results and Discussion

A (differential) survey spectrum (fig. 3) reveals the main (stable) gas phase components: apart from NO, NO₂ and N₂O carbon containing species such as CO, CO₂ and formic acid (HCOOH) are detected. It should be noted that HONO is usually present whereas other typical components in air-like DBDs such as N₂O₅, HNO₃ and O₃ are usually not identified in the spectra.

From the analysis of the gas phase composition it can be concluded that under present discharge conditions a chemistry similar to de-NOₓ processes, i.e. NₓOᵧ chemistry in the presence of trace amounts of hydrocarbons, is observed. This leads to quenching of reaction channels which would form N₂O₅ or HNO₃. On the other hand, HCOOH is produced and turns out to be a good indicator for dominant etching conditions in the discharge (fig. 4). Additionally, the ozone generation is usually hampered due to the poisoning of the process [4].

Fig. 3: Typical FT-IR survey spectrum from the effluent of an air-like DBD. Carbon containing species such CO, CO₂ and HCOOH are clearly visible and confirm the etching environment for the polymer.

Fig. 4: Sample spectrum under etching conditions in air/Ar (solid black, dashed) and O₂/Ar (solid grey). Etch products, e.g. HCOOH (dashed), are not detected when the polymer is protected with a SiO₂ cover layer (black). O₃ is only observed in absence of N₂.

References