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

S. Welzel [(*)1], S.A. Starostin [2], H. de Vries [2], M.C.M. van de Sanden [1,3], R. Engeln [1]

[1] *Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[2] *FUJIFILM Manufacturing Europe B.V., P.O. Box 90156, 5000 LJ Tilburg, The Netherlands*
[3] *Dutch Inst. for Fundam. Energy Research (DIFFER), P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands*
[(*)] s.welzel@tue.nl

The effluent of an industrial roll-to-roll reactor for synthesising silica-like barrier layer 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, CO_2 and HCOOH have been detected. Particularly, HCOOH was found to be a good indicator for etching conditions present during foil treatment. Additionally, a modified N_xO_y 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 SiO_2-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 $Ar/N_2/O_2$ 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).

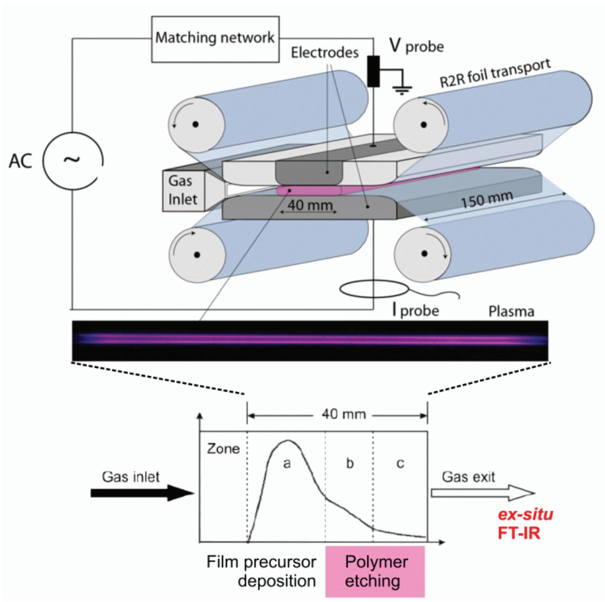

Fig. 1: Schematic diagram of the roll-to-roll AP PE-CVD setup used for synthesising SiO_2 barrier layers on polymeric substrates. Three different film-formation regimes along the electrodes (and the gas flow) are indicated.

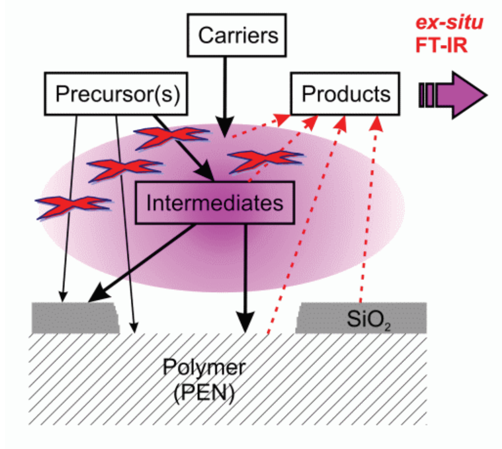

Fig. 2: Overview of plasma-surface interactions in PE-CVD processes. In the present approach the precursor is omitted to study gas-phase products under etching conditions.

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 O_2/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 SiO_2 protecting layer.

3. Results and Discussion

A (differential) survey spectrum (fig. 3) reveals the main (stable) gas phase components: apart from NO, NO_2 and N_2O carbon containing species such as CO, CO_2 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 N_2O_5, HNO_3 and O_3 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-NO_x processes, i.e. N_xO_y chemistry in the presence of trace amounts of hydrocarbons, is observed. This leads to quenching of reaction channels which would form N_2O_5 or HNO_3. 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].

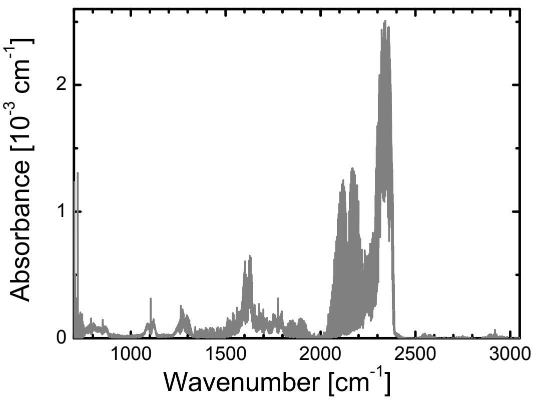

Fig. 3: Typical FT-IR survey spectrum from the effluent of an air-like DBD. Carbon containing species such CO, CO_2 and HCOOH are clearly visible and confirm the etching environment for the polymer.

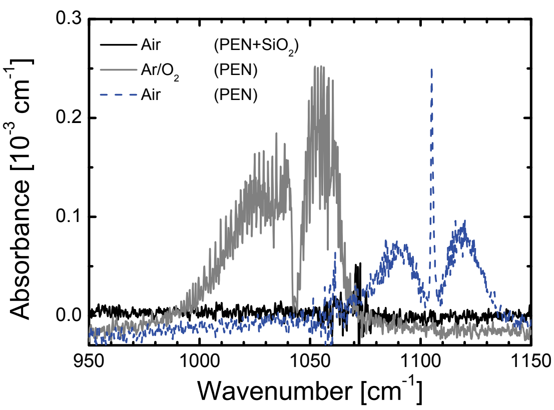

Fig. 4: Sample spectrum under etching conditions in air/Ar (solid black, dashed) and O_2/Ar (solid grey). Etch products, e.g. HCOOH (dashed), are not detected when the polymer is protected with a SiO_2 cover layer (black). O_3 is only observed in absence of N_2.

References

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