

# Gas phase IR studies on the dissociation of organo-silicon precursors in high-current dielectric barrier discharges

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The gas phase of an atmospheric pressure dielectric barrier discharge in roll-to-roll configuration for synthesising SiO<sub>2</sub>-like barrier layers was studied by infrared absorption spectroscopy. The aim of this contributions is threefold, (i) to identify main dissociation products of organo-silicon precursors (HMDSO and TEOS), (ii) study their dependence on the (average) power density in pulsed plasmas, and (iii) to establish links to earlier model assumptions on the film formation and precursor consumption. At high average power densities a gas phase composition similar to pure etching conditions (i.e. no precursor present) was observed.

## 1. Motivation

Recently it has been shown that silica-like layers formed during large-area plasma-enhanced (PE) roll-to-roll processing of polymeric substrates such as PEN (Polyethylen-Naphtalate) in diffusive dielectric barrier discharges (DBDs) yields high-quality barrier layers [1]. This has been achieved through chemical vapour deposition (CVD) at atmospheric pressure using organo-silicon precursors (e.g. HMDSO (hexamethyldisiloxane) or TEOS tetraethyl-orthosilicate)) and air-like gas mixtures (N<sub>2</sub>/O<sub>2</sub>/Ar) (fig. 1). An essential requirement to establish a diffusive mode is an electronic stabilisation circuit [2] along with pulsed operation to avoid dust formation [3]. In this way, high discharge currents of a few A can be obtained. Extensive studies on the deposition process have been carried out using surface analytical techniques. A competition between deposition and etching processes was established in conjunction with a model for the precursor consumption along the active plasma zone (fig. 1) [4]. This contribution is concerned with complementary gas-phase studies using infrared (IR) absorption spectroscopy. The aim was threefold, (i) to identify main dissociation products, (ii) study their dependence on the (average) power density in the pulsed DBDs, and (iii) to establish links to earlier model assumptions [4].

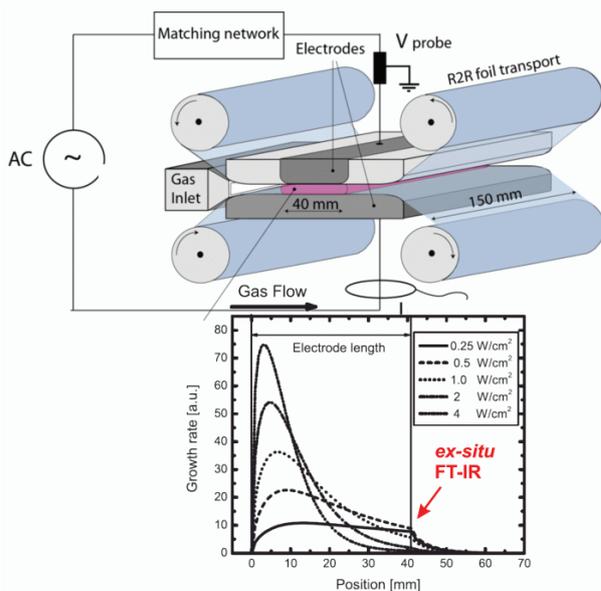


Fig. 1: Schematic diagram of the roll-to-roll AP PE-CVD setup used for synthesising SiO<sub>2</sub> barrier layers on polymeric substrates. A model for the precursor dissociation and thus the growth rate based on surface analytical methods [4] is indicated.

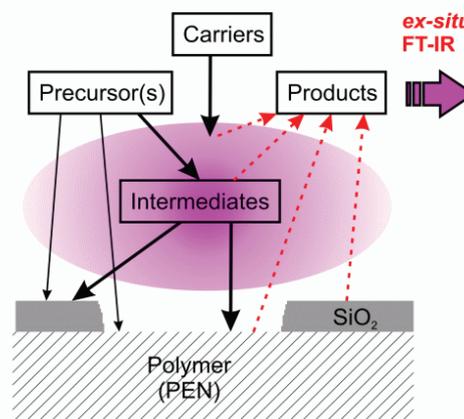


Fig. 2: Overview of plasma-surface interactions in PE-CVD processes. Gas phase products were sampled *ex-situ* at the effluent of the active plasma zone.

## 2. Experimental

The experimental AP PE-CVD setup used was an industrial roll-to-roll configuration (fig. 1) which makes the direct optical access to the gap (0.5 mm) even more challenging. Therefore, a Fourier-Transform IR (FT-IR) spectrometer (Bruker IFS66/s) was used for *ex-situ* measurements. A small fraction of the effluent of the discharge was sampled under flowing conditions into a multi-pass absorption cell. The White cell was aligned to 7 m total absorption path and was used at reduced pressure ( $\sim 50$  mbar) to increase the selectivity for different absorption features.

The discharge was driven by an AC power supply (185 kHz) and operated in pulsed mode with duty cycle between 10 - 75 %, i.e. plasma-on periods of 0.16 to 1.20 ms. In this way, the precursor dissociation could be studied, even through sampling at the end of the active plasma zone (c.f. bottom fig. 1), as at low power densities precursor fragments might be still present.

## 3. Results and Discussion

Figure 3 shows two (differential) survey spectra for discharges using HMDSO and TEOS respectively. At high (average) power densities the gas phase composition is comparable to situations where no precursor is present [5]. This result is in good agreement with earlier model assumptions about the precursor dissociation (fig. 1). Main (stable) species are NO, NO<sub>2</sub>, N<sub>2</sub>O and HONO as well as carbon containing species such as CO, CO<sub>2</sub>.

On the other, even under similar discharge conditions, distinct difference in the product distribution between the two precursors can be seen. Additionally, at low power densities, precursor fragments can be detected. Similar to etching conditions (i.e. without precursors admixed [5]), HCOOH transpires to be a good marker molecule to distinguish different discharge and film formation regimes. Quantitative aspects of selected gas phase species will be discussed along with the influence of oxygen admixtures and analysis of the injected energy.

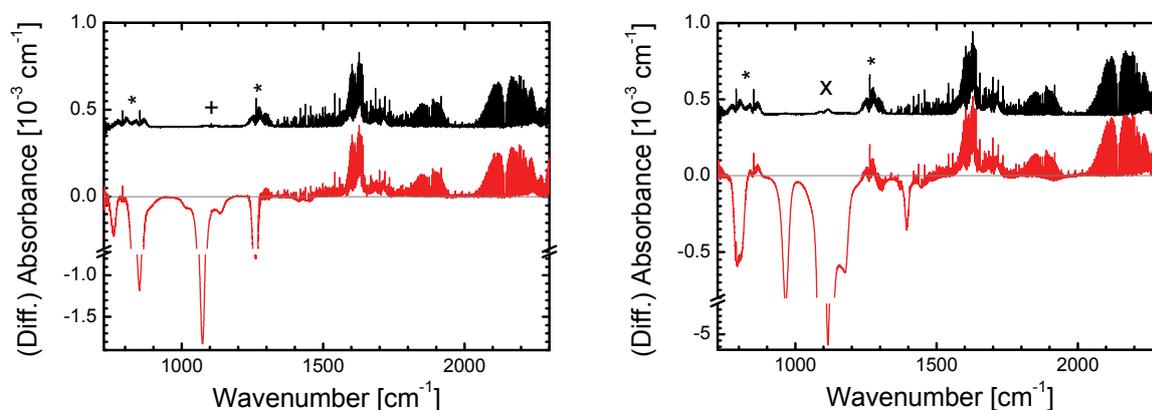


Fig. 3: Survey FT-IR spectra (identical scale) recorded in discharges containing HMDSO (left) and TEOS (right). The lower traces show a differential spectrum (plasma on - off) with an almost complete precursor dissociation at 50 % duty cycle. The upper traces (stacked for clarity) are added to highlight the formation of intermediate species, e.g. HONO (\*), HCOOH (+), precursor traces (x). Although the spectra were recorded under similar discharge conditions ( $N_2/O_2/Ar = 15/1.8/1.0$  slm + 2 g/hr HMDSO or 5 g/hr TEOS) distinct differences in the  $N_xO_y$  chemistry and precursor oxidation are visible (e.g. NO<sub>2</sub> and CO features around 1600 cm<sup>-1</sup> and 2100 cm<sup>-1</sup>)

## References

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