



Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Modelling of the gas flow and plasma co-polymerization of two monomers in an atmospheric-pressure dielectric barrier discharge

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ARTICLE INFO

Article history:

Received 30 June 2016

Revised 22 October 2016

Accepted in revised form 24 October 2016

Available online xxxx

Keywords:

Plasma polymerization

Atmospheric pressure

Dielectric barrier discharge

Deposition model

Gas flow model

ABSTRACT

We present a combined experimental and numerical study of plasma co-polymerization of maleic anhydride and acetylene in an atmospheric-pressure dielectric-barrier discharge. It combines a three-dimensional model of the gas dynamics in close-to-real geometry with a semi-analytical model of the deposition which reduces the unknown plasma chemistry into several averaged species. The unknown coefficients of the model are found by correlating it with measurements of film thickness at various deposition conditions. Even though the model is calibrated only based on spatially-resolved thickness, it is proven using FT-IR that it also makes valid predictions regarding the film composition. The predictive capabilities of the model are also tested on independent experiments, illustrating that the model retains its predictive capabilities even outside of the calibration region. The work aims not only to provide more insight into the specific deposition process but it also illustrates efficient use of numerical modelling in process control and design.

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1. Introduction

Plasma polymerization at the atmospheric-pressure is a more recent alternative to low-pressure plasma polymerization that has been studied since 1970s [1,2]. Atmospheric-pressure (AP) plasma polymerization processes are potentially more cost-efficient as they require less sophisticated or no vacuum equipment, are energy-efficient and also offer comparatively higher deposition rates [3]. Successful atmospheric-pressure plasma polymerization from a range of monomers has been reported by several teams in the past few years [4–8]. The class of plasma sources most frequently used for AP plasma polymerization is the so-called DBDs (dielectric-barrier discharges), in which one or both of the electrodes are separated by a dielectric layer in order to limit the plasma current and prevent arcing.

There are several challenges that have to be tackled when designing a plasma polymerization process at the atmospheric pressure. Firstly, the plasma at the atmospheric pressure, even in the DBD configuration, tends to be filamentary which might cause disintegration of the desired functional groups, damage of substrates or disruption of flow patterns [9]. However, AP-DBD plasmas can also be operated in homogeneous mode suitable for plasma polymerization. The homogeneous mode

can be achieved either by changing the dielectric covering the electrodes [10], by finding the optimum frequency [11,12] or by introducing a small amount of an appropriate molecular gas [13]. It has recently been shown that the homogeneous mode in argon plasma can also be achieved by adding a small amount of acetylene [14], which is advantageous since this molecule can promote the growth of the polymer chain and its cross-linking.

A characteristic feature of atmospheric-pressure plasmas is the high collision frequencies of particles, several orders of magnitude higher compared to low pressure. This implies that the delivery of active species to the substrate is much more advection-driven than diffusion-driven [15], as opposed to low-pressure sources. High electron-neutral collision frequency results in fast conversion of the monomers in plasma and if the process is not designed properly, the majority of the monomer is consumed before reaching the edge of the plasma, leading to non-uniform deposition [16]. Consequently, it is imperative that the monomer delivery is uniform in space, which is achieved by optimizing the gas flow patterns in the DBD reactors, as discussed for example in [15–17].

For the reasons described above, designing and optimizing an AP plasma polymerization process is a rather challenging task, in which numerical simulations of the relevant processes can be instrumental. A full kinetic model of the plasma chemistry and sustainment is feasible when the plasma is ignited in a mixture of relatively common gases, for which the reaction rate coefficients and cross sections are known [18]. Quite recently, advanced two- and three-dimensional models of AP-DBD plasma formation have been published [12,19], which provide valuable

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insight into the mechanism of discharge formation and regime transition. However, similar models are not appropriate for simulating the polymer growth from organic monomers, as the collision cross sections and reaction rate coefficients for these molecules are, in most cases, not known.

A reasonable middle ground is not to model the detailed plasma chemistry of the monomer but to take into account only a few averaged states of the monomer and then find or estimate rate coefficients leading to population or depopulation of these states. Consistently with the Yasuda theory [2], these averaged species are the original monomer, activated monomer (either ionized or a radical), which leads to the deposition of the film, and stable species, which are not deposited and leave the reactor volume. This approach dramatically reduces the number of balance equations that have to be solved and the number of unknown coefficients to only a few. Consequently, such models can even be analytical or semi-analytical, as demonstrated in [20], where deposition of SiO_x polymers by an AP plasma jet was modelled. In a DBD discharge, a similar model has been published in [21], demonstrating its capability to describe plasma polymerization from one monomer.

In this work, we employ an approach similar in principle to [20,21] in order to model plasma co-polymerization process from two monomers in an AP-DBD discharge. We combine a three-dimensional numerical model of the gas flow with a semi-analytical model of monomer activation and deposition on the substrate. The gas dynamics model is also utilized for the design of the gas inlet so that the gas delivery is uniform along one direction while along the other direction, film uniformity is achieved by periodic movement of the driven electrode and the gas inlet. The velocity above the substrate obtained from the gas flow model also serves as an input to a semi-analytical model of activation and deposition of the two monomers.

As already mentioned, the unknown coefficients of the model are the rate coefficients of monomer activation and conversion to stable species as well as the sticking probabilities of the activated monomers. Their values are obtained by fitting the model to experimental data so that the calculated fluxes of the activated species to the substrate match the spatially-resolved thickness of the film measured by ellipsometry, as discussed in Section 4.2. Despite the fact that the unknown model coefficients are obtained only based on thickness measurements, it is shown in Section 4.3 that the model also provides insight into the composition of the film as it predicts a spatial non-uniformity in composition at certain conditions. This was verified by Fourier-transform infrared spectroscopy. Finally, it is illustrated in Section 4.4 that the model is capable of predicting the film thickness and composition at new conditions, different from the calibration conditions.

With the help of this model, we obtain deeper insight into the mechanisms of the co-polymerization of the two monomers. By calibrating the model and comparing it with measurements, we illustrate that even such a relatively simple model has good predictive capabilities, both regarding the thickness of the resulting film and also, to some extent, its composition.

2. Experimental

2.1. Atmospheric-pressure DBD plasma

The plasma polymers were deposited in an atmospheric-pressure dielectric barrier discharge (AP-DBD) reactor, the geometry of which is shown in Fig. 1. The plasma is ignited in a 1.6 mm gap between two ceramic plates separating bottom and top copper electrodes. The top, high-voltage, electrode is divided into two segments, allowing to feed gas mixtures in the middle. The gas is supplied through an inlet slit with the surface area of $2 \times 48 \text{ mm}^2$ connected to a 4 cm long rectangular duct. The duct is connected to a cylindrical pipe and pre-mixed gases are supplied from two sides of the tube. The plasma is localized only underneath the two segments of the high-voltage electrode. In the region between these segments – i.e. directly underneath the inlet slit – no plasma is visible and also no deposition occurs.

The plasma is ignited in argon with a small admixture of two gaseous monomers – maleic anhydride (MA) vapors (Sigma-Aldrich, briquettes, purity 99%) and acetylene C_2H_2 (Messer, technical acetylene, purity >98%) which are co-polymerized in the plasma. The schematic view of the gas supply and pumping system is shown in Fig. 2. The typical flow rate of argon as the main carrier gas was 2500–7000 sccm and additionally, there was 60–700 sccm of argon flowing through a bubbler with maleic anhydride pellets. The bubbler was heated to a constant temperature of 35 °C using a thermostatic bath which results in constant partial pressure of MA vapors. Consequently, changing the flow rate of argon through the bubbler allows to vary MA flow rate between 0.008 and 0.4 sccm (corresponding to 7–300 nmol/s). In the Results section, the quantity “argon flow rate” denotes the total flow of argon (main branch and MA branch) and the “MA flow rate” denotes the mass flow of maleic anhydride without the argon carrier gas. The flow of acetylene is controlled independently and varies typically between 1 and 3 sccm (corresponding to 700–2000 nmol/s).

Acetylene helps to suppress formation of filaments due to Penning ionization as already shown in [14] with a slightly different electrode configuration. Even though the volume concentration of acetylene was always below 0.1% in the deposition gas mixture, the measured IV characteristics did not contain large amount of separated current peaks and one broad current peak confirmed the homogeneous mode of DBD.

The plasma is sustained by a 4 kHz AC power supply with typical peak-to-peak voltage of 4 kV. In all the experiments presented, the power in the high-voltage circuit was maintained at $3.3 \pm 0.2 \text{ W}$. This value should be considered the upper bound to the power deposited in the plasma since it is difficult to accurately assess the losses in the high-voltage circuit at kHz frequencies.

As already mentioned, the monomers are consumed very fast in the atmospheric pressure plasma, which makes it challenging to achieve uniform thickness and composition of the deposited layer. To ensure that the deposition is uniform in the direction perpendicular to the

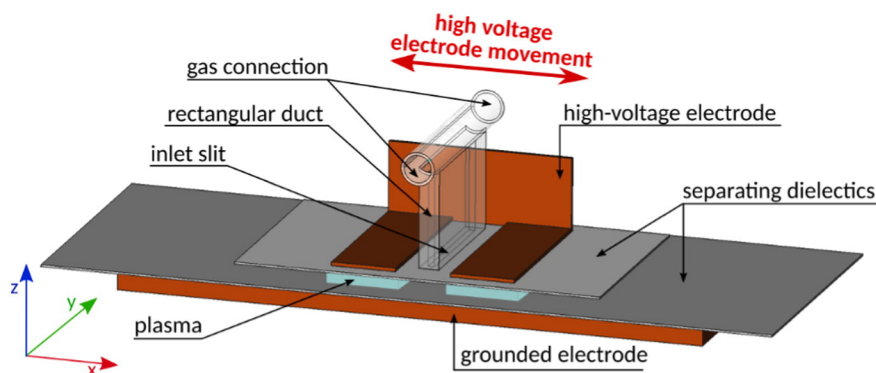


Fig. 1. The geometry of the DBD used for the depositions.

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