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Influence of gas phase and surface reactions on plasma polymerization

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ABSTRACT

The formation of plasma polymers is based on multistep reactions that are taking place both in the gas phase and on the surface of the growing film. In order to gain more insights and to control plasma polymerization processes, some assumptions can be made that allow a macroscopic description. Following this idea, a concept was developed based on the energy input both into the gas phase (plasma) and during film growth (surface) that helps in up-scaling plasma polymerization processes. In order to test this concept, various a-C:H:N thin films were deposited under different NH_3/C_2H_4 gas ratios, power inputs W, and gas flow rates F. Thereby, the energy consumed in the gas phase is controlled by W/F yielding a flux of film-forming species. The comparison of two comparable plasma reactors of different sizes indicate that while the reaction parameter W/F plays a major role for the transfer of plasma polymerization processes, the energy input into the film by ion bombardment during film growth should also be taken into account.

1. Introduction

The deposition of functional plasma polymer thin films enables the adjustment of surface properties for different applications such as hydrophilic textiles with improved sweat management or cytocompatible materials for tissue engineering [1–3]. Industrial applications require reliable and manageable processes, which can be transferred to production-scale reactors [4]. This often has a strong influence on the choice of process gasses and reactor geometry, for instance. Moreover, plasma polymers optimized with respect to functionality and stability in aqueous environments are often required [5]. Due to the enormous difficulties lying in the microscopic description of plasma polymerization processes, we are considering a macroscopic approach which is based on the energy input into the plasma process [6–8]. Since plasma polymerization processes involve both gas phase reactions and surface reactions, it is important to consider the energy input into the plasma zone as well as the energy input into the film itself. While the former gives the energy invested per particle within the active plasma zone, the latter is mostly related to ion bombardment at the growing film surface. Both reaction parameters are mainly determined by the external parameters power input W and unit of gas flow F when some internal parameters such as power absorption, direction of gas flow, plasma expansion, plasma density, and sheath potential are known.

Assuming that the film growth is limited by the activation of the monomer in the gas phase (reaction kinetics limited regime), i.e. it is not determined by diffusive transport or high overall conversion, a quasi-Arrhenius relation can be used to describe the mass deposition rate per unit of gas (monomer) flow R_m/F as a function of the specific energy input W/F as reaction parameter:

$$\frac{R_m}{F} = G\,exp\left(-\frac{E_a}{W\,/\,F}\right), \tag{1}$$

where E_a represents an apparent activation energy (activation barrier) and G is a reactor and process dependent factor related to the maximum monomer conversion into film growth [9–12].

The energy dissipated in the film during growth, on the other hand, is approximated by the energy density ε (in [eV nm^{-3}]):

$$\varepsilon = \frac{\Gamma_i E_{mean}}{R}, \tag{2}$$

which represents ion bombardment (ion flux times mean ion energy) per film growth rate R (in [nm s^{-1}]) [13]. The ion flux Γ_i incident on the substrate (in [nm^{-2} s^{-1}]) can be estimated using a model proposed by Lieberman et al. [14]:

$$\Gamma_i = n_0 v_B\,cos\,\theta \tag{3}$$

with n_0 being the plasma density in the plasma bulk (which equals the electron density n_e for electropositive gasses) and v_B, the Bohm velocity of the ions entering the plasma sheath. The reduction of the number of ions fulfilling the Bohm criteria due to collisions is considered by the factor cos θ which in turn depends on the plasma length and the ion mean free path — it is roughly 0.2 for the plasma conditions considered here (pressure of 10 Pa). The mean energy

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E_{mean} of the ions impinging on the substrate (in [eV]) can be estimated from the sheath potential V_s according to a study by Manenschijn and Goedher [15]:

$$E_{mean} = eV_s \cos\varphi, \tag{4}$$

where the factor cos φ regards collisions in the plasma sheath and depends on the sheath length, the ion mean free path and the type of collisions (elastic or charge-exchange). For the considered plasma conditions (pressure of 10 Pa) it is roughly 0.15. The sheath voltage is proportional to the excitation voltage with $V_s = 0.39\ V_0$ for symmetric RF discharges [14]. Hence, measuring the electron density and the excitation voltage (which both depend on power input W, but not on flow rate F) as well as the deposition rate enables the calculation of the energy density according to Eqs. (2)–(4).

A macroscopic approach has thus been used in this work to investigate plasma polymerization processes for the deposition of amine-functional a-C:H:N coatings that can also be transferred to industrial reactors [8,16].

2. Experimental

Two different reactors were used to investigate the transfer of plasma polymerization processes: a lab-scale batch reactor and a pilot-scale web coater (Fig. 1). The (symmetric) batch reactor is composed of two plane parallel electrodes of the same size (30 cm in diameter) separated by a glass cylinder [16]. The distance between the upper showerhead electrode and the lower RF-driven (13.56 MHz) electrode was 5 cm. The pressure was fixed at 10 Pa, while the power input was varied between 7 and 150 W. The monomer flow rate of ethylene (C_2H_4) was held constant at 8 sccm. Beside pure C_2H_4 discharges, ammonia (NH_3) was added with 8 and 16 sccm to obtain gas ratios of NH_3/C_2H_4 of 1:1 and 2:1. The web coater consisted of a RF-driven (13.56 MHz) drum electrode (with a diameter of 59 cm and a length of 65 cm) enclosed in a larger cylindrical vessel [17,18]. The substrates were fixed on the drum which was rotated during plasma deposition. The gas inlet was distributed at four positions (showerhead) around the drum to obtain a homogeneous gas flow. The power input was varied between 300 and 1000 W at a pressure of 10 Pa. The following gas flow rates were used: 100 sccm C_2H_4 (pure C_2H_4 discharge), 250 sccm C_2H_4 with 250 sccm NH_3 ($NH_3/C_2H_4 = 1{:}1$), and 100 sccm C_2H_4 with 250 sccm NH_3 ($NH_3/C_2H_4 = 2.5{:}1$). Due to the (nearly) symmetric set-up of the electrodes in both reactors, the bias voltage remained small and the discharge homogeneously occupied the whole inter-electrode space allowing for the comparison of both reactors.

The deposited mass was measured by weighing thin glass slide substrates right before and after deposition, while profilometry was used to determine the film thickness. The film density was simply calculated from both values. A V/I probe (ENI Model 1065) was used to measure excitation voltage V_0 and absorbed power W (the latter had a value around 80% of the generator's nominal power). Electron densities were measured within the batch reactor using microwave interferometry (JE PlasmaConsult MWI 2650) by integrating over the line of sight with a plasma length of 28 cm (see Fig. 1). The method is based on the phase shift of 26.5 GHz microwave radiation transmitted through the plasma [19]. Fig. 2 displays the obtained electron densities, which show a linear dependence over a broad range of power input, thus showing reliable plasma conditions. Since the electron density could not easily be measured for the web coater (due to technical reasons), we did a comparison based on the power input per plasma volume, the latter being roughly 66,000 cm^3 for the web coater and 1850 cm^3 for the batch reactor. XPS surface analysis was performed in a PHI 5600 LS system, using a non-monochromatized MgKα source and an electron take-off angle of 45°. All samples were analyzed within one day following their deposition. The surface concentration of primary amines, [—NH_2], was determined by XPS after derivatization with 4-(trifluoromethyl)benzaldehyde (TFBA) vapor [20].

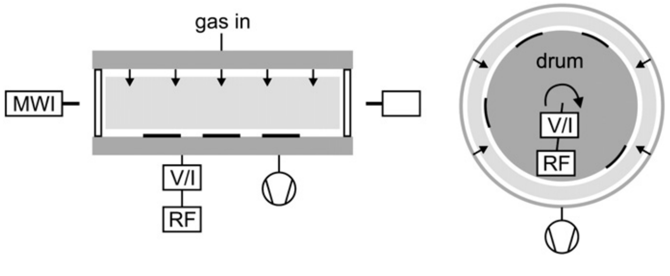

Fig. 1. Scheme of the batch reactor (left) and the web coater (right) experimental set-ups. Substrates were placed on the driven electrode in both cases.

3. Results and discussion

We have recently investigated the plasma polymer growth from CO_2/C_2H_4 discharges with varying gas ratio and flow rates [7,11]. We found that the evolution of the deposition rate as a function of the reaction parameter W/F follows an Arrhenius-like behavior according to Eq. (1) over a broad parameter range. This range was named regime II (reaction kinetics limited range), while regime I shows deviations from the Arrhenius-like behavior at low energy input and regime III is indicated by deviations at the high energy side [7]. Similar results were obtained for NH_3/C_2H_4 discharges as shown in Fig. 3 and as already reported in the literature [21–23]. While examining a broad range of W/F within the batch reactor, the three regimes including the linear Arrhenius-like regime can clearly be seen for the NH_3/C_2H_4 gas ratio of 1:1. With increasing gas ratio, the deposition rates were found to be reduced compared to pure C_2H_4 discharges, which is ascribed to formation of CN and HCN species in the gas phase yielding incorporation of nitrogen as well as chemical etching during film growth. Nevertheless, the deposition of the a-C:H:N coatings is mainly described by an Arrhenius-like behavior (regime II). Therefore, we assume a similar reaction pathway over a broad range of energy input, where mainly the number of film-forming species is increased. The chemical reaction pathway might proceed via film-forming species which show a high sticking coefficient, but a low to moderate reactivity in the gas phase [24]. Thus, specific reaction channels might be promoted despite of unselective plasma-chemical processes in the gas phase. Moreover, the surface elemental composition of the a-C:H:N plasma polymers was found to be approximately constant within this regime, e.g. $N/C = 0.24 \pm 0.02$ for $NH_3/C_2H_4 = 1$ (agreeing well with data obtained by others [25]), while the N content is reduced for regime III.

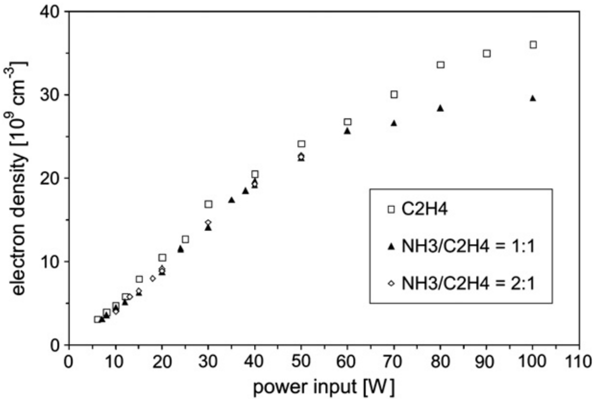

Fig. 2. Electron density measured as a function of power input for the batch reactor.