

Energy Conversion Efficiency in Low- and Atmospheric-Pressure Plasma Polymerization

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Abstract: Energy conversion efficiency (ECE), i.e. a representative energy-related output parameter per energy input into the plasma is used to compare plasma polymerization processes at low- and atmospheric pressure. The study of different starting molecules (monomers) indicates that gas phase processes are governed by the energy uptake per monomer molecule and are thus independent of pressure.

Keywords: plasma polymerization mechanism, energy per molecule, reaction pathway

1. Introduction

In the plasma polymerization literature, there has been an interest since at least the 1970s to correlate the structure of plasma polymer films (PPF) with plasma parameters during deposition, most particularly with the energy input per monomer molecule, E_m . In our two laboratories, we have developed methods for measuring E_m (or somewhat equivalent, E_a) in low- (LP) and atmospheric-pressure (AP) discharge plasmas [1,2]. In this work we propose a new parameter, the so-called energy conversion efficiency, ECE, which permits direct comparison of LP and AP experiments. This is done for the case of different model monomer compounds, including acrylic acid (AAc) and hexamethyldisiloxane (HMDSO) [3,4]. “Critical” energy values that demarcate ECE regimes separating different fragmentation/reaction mechanisms agree remarkably well for the monomers examined – independent of pressure. The resulting E_m (or E_a) values are now correlated with specific mechanisms yielding the plasma chemical reaction pathway to deposit PPFs.

2. Formalism

The energy conversion efficiency (ECE) relates an energy-related output parameter to energy input into the plasma, the latter expressed as power input per monomer flow rate, W/F_m . If energy uptake by the monomer molecules (and fragments thereof), E_m , can be directly measured – as for Ar-based AP DBD plasmas by comparing with pure Ar discharges – ECE becomes:

$$ECE = \frac{E_m}{W/F_m} \quad (1)$$

In the case that the energy-related output parameter is measured indirectly, e.g. by measurement of normalized deposition rates (which are proportional to the flux of film-forming species as generated in the gas phase), ECE gives:

$$ECE = \frac{R \cdot A_{dep} / F_m}{W / F_m} \quad (2)$$

with the deposition rate, R , and the respective deposition area, A_{dep} .

3. Experimental

Experiments discussed here were carried out with acrylic acid, $\text{CH}_2=\text{CH}-\text{COOH}$, or with hexamethyldisiloxane, $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$. At low pressure conditions (7-10 Pa) pure monomer gases were used, whereas Ar served as carrier gas for the atmospheric pressure experiments. For LP, RF-driven (13.56 MHz) capacitively-coupled reactors were taken, while AP experiments were carried out in a DBD reactor with audio frequency (20 kHz) [1,4]. Deposition rates were measured by determining the deposited film thickness (ellipsometry and profilometry) and deposited mass (microbalance).

4. Results and Discussion

The measurement of the energy uptake by the monomer molecules (and fragments thereof), E_m , is a function of energy input and of the available number of species in the gas phase. Dissociation yields a higher number of fragments, while deposition (or recombination) reduces the number of monomeric gas phase species, i.e. their partial pressure is changed. Hence, transitions of the plasma chemical reaction pathway can be followed by changing the energy input. For AP conditions, power input, W , was fixed and monomer flow rate, F_m , was varied over a broad parameter range. For LP, W/F was varied and related deposition rates measured. Furthermore, W/F was related to the energy uptake per (intact) monomer for LP conditions regarding absorbed power and plasma geometry to obtain the energy delivered per monomer molecule, ϵ_{pl} [5].

At first, plasma polymerization with acrylic acid had been examined. Energy conversion efficiency was calculated for AP and LP following equation (1) and (2), respectively. Such values were plotted with respect to energy per monomer molecule, E_m and ϵ_{pl} , respectively. As can be seen from Fig. 1, two regimes occurred (separated by transitions) starting at apparent activation energies of around 8 and 22 eV both for LP and AP conditions. The data within those regimes follow an

Arrhenius-like behaviour, i.e. activation reactions yield a corresponding plasma chemical reaction pathway.

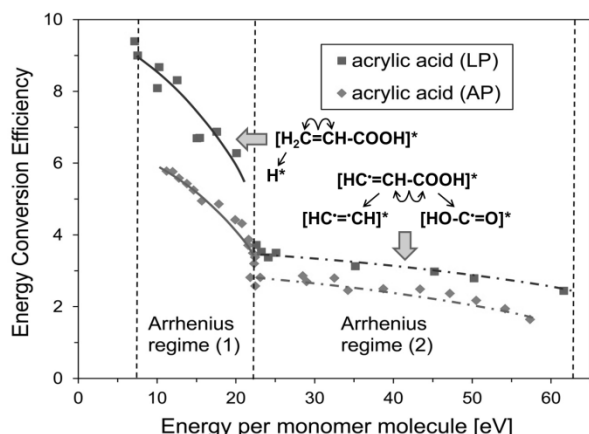


Fig. 1. ECE vs. energy uptake by the monomer gas, acrylic acid, in LP and AP discharges. The corresponding plasma chemical reaction pathways are indicated for the two Arrhenius regimes.

Investigation of film chemistry supports the view that the reaction pathway at lower energy uptake corresponds to the activation of the monomer molecule with retention of the carboxylic group, while higher energy input results in dissociation and a different reaction pathway yielding a-C:H:O films [3]. Moreover, it can be inferred that all activated species contribute to film growth, since gas phase activation processes (AP) are in agreement with deposition processes (LP).

Next, plasma polymerization regarding HMDSO discharges was studied. This time, energy uptake per monomer molecules, E_m , and deposition rate, R , were measured for AP conditions, while only deposition rates were utilized for LP. ECE values were again calculated according to equations (1) and (2).

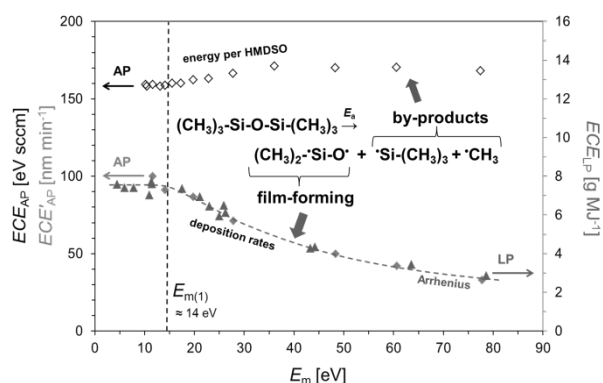


Fig. 2. ECE vs. energy uptake by the monomer gas, hexamethyldisiloxane, in LP and AP discharges. The plasma chemical reaction pathway is indicated.

Fig. 2 reveals an excellent agreement of ECE as determined from deposition rates between LP and AP conditions. Again, an apparent activation energy (at 14 eV) indicates an Arrhenius-like regime based on the film-forming species, $(CH_3)_n^*Si-O^*$, resulting in hydrophobic plasma polymer films with PDMS-like properties [4]. Different to the case of acrylic acid, the ECE curve based on E_m shows an increase starting at $E_{m(1)} \approx 14$ eV. This increase indicates dissociation of the HMDSO monomer yielding rather stable fragments (by-products) that do not contribute to film deposition besides the production of the film-forming species. Increasing partial pressure can thus result in an increase of energy uptake per energy input, since more species take up energy.

In any case, plasma polymerization was found to proceed in the same way at LP and AP conditions, i.e. its gas phase processes are controlled by the energy input per monomer molecule and are independent of pressure. Surface processes, on the other hand, rest on the actual energetic conditions during film growth which are dependent on pressure.

5. References

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