Ion flux and deposition rate measurements in the RF continuous wave plasma polymerisation of acrylic acid

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Ion flux and deposition rate measurements made in plasmas of acrylic acid support the view that at low plasma power ions are primarily responsible for deposit growth.

In general, the mechanisms that lead to the deposition of plasma polymers are poorly understood. Yasuda[1] has described plasma polymerisation as proceeding through a rapid step-growth polymerisation (RSGP) mechanism. The RSGP mechanism is very general and was probably not intended to cover the entire range of conditions under which plasma polymer deposits form. However, in the absence of other schemes, it is widely quoted.[2] The nature of the reactive species in the RSGP mechanism is not made clear, but the orthodox view is that they are radicals.

This paper is concerned with the plasma polymerisation of acrylic (propenoic) acid in RF sustained glow-discharges of low input powers, P. Previously, functional group retention has been reported in the deposits from plasmas of carboxylic acids[3,4] and unsaturated alcohols.[5] Based on plasma-phase mass spectral measurements of ions and neutrals, we have proposed that functional group retention arises from oligomerisation (ion–molecule) reactions in the plasma.[3–5] At low P, dimeric[3–5] and trimeric[3,4] cations have been detected by mass spectrometry and under these same conditions functional group retention was highest.[3–5] The degree of dimer and trimer formation and functional group retention decreased with increased P. Deposition of polymer has been attributed to the ion flux arriving at a surface, but this has not been proven.[6]

Ion flux measurements are particularly difficult to make in plasmas used for the deposition of polymers. The problem arises from the build-up of an insulating layer on the active area of the probe used to measure the ion flux. Braithwaite *et al.*[7] have described a novel electrostatic probe that allows ion flux measurements to be made even when the surface of the probe is coated with an insulating material. The principles of operation are described in ref. 7.

To the best of our knowledge, ion flux measurements have not been made before in plasmas of C-, H- and O-containing monomers. The plasma polymerisation of these compounds has received considerable attention, as deposits from these compounds are used to control processes that depend upon surface chemistry. The effect of P on ion flux and deposition rate has been investigated. XPS analysis of the solid-phase plasma polymers is undertaken. We correlate changes in ion flux, deposition rate and surface chemistry with those previously reported in the plasma-phase.[4]

The apparatus (described more fully in ref. 8) consisted of a tubular glass reactor which was pumped by means of a rotary pump. The plasma was sustained by an RF generator (13.56 MHz) and amplifier inductively coupled to the plasma reactor. The P used was in the range 0.5–15 W and flow rate (ϕ) was fixed at 0.8 cm^3 (STP) min^{-1}. Acrylic acid (Aldrich $>$ 99% purity) was pumped through a needle valve at a pressure of 2.5 $\times$ 10^{-2} mbar. Deposition rate measurements were made using a quartz crystal microbalance (Leybold, Manchester, UK), which was inserted into the plasma region, using a solid support to ensure consistent positioning of the crystal. In a separate series of experiments, the ion flux probe was placed in the plasma, close to where the quartz crystal had been, to determine the relationship between RF power and ion flux to this region. The presence of this probe is no more perturbing than the crystal balance, merely providing a loss surface for ions. The probe is biased negatively by RF pulses and the transient current used to determine ion flux. Changes in the probe voltage are limited to ensure the sheath potential changes at a much slower rate compared to the transit time of the ions crossing the sheath, this having a square-root dependence on ion mass and plasma density. This ensures the measured current is due to the particle fluxes only and not a redistribution of charge in the sheath.[7] This mode of operation makes the probe insensitive to ion mass.

Fig. 1 shows how the deposition rate varies with P. It clearly show two regimes: at P of $<$ 4 W, the deposition rate increased with P; the deposition rate increased three-fold from $P = 0.5 \rightarrow 3$ W. Above $P = 4$ W, the deposition rate remained essentially constant. These regimes are consistent with those previously described in the plasma-phase mass spectrometry of acrylic acid.[4] Over the range $P = 1$–4 W, the ion signal from the dimer of acrylic acid, expressed as the ratio of the intensity of the dimer signal to monomer signal, decreased smoothly by over 90% with P. By $P = 5$ W, the dimer signal had effectively fallen to zero.

Fig. 2 shows that the ion flux increased at a constant rate between $P = 1$–3 W ($0.1 \pm 0.1 \times 10^{18}$ ions m^{-2} s^{-1}). Just above $P = 4$ W there was a marked jump in ion flux. Ion flux then continued to rise steadily with P, up to $P = 14$ W ($1 \pm 0.1 \times 10^{18}$ ions m^{-2} s^{-1}).

It is between $P = 0.5$–4 W that the most significant change in the retention of carboxylic acid from the acrylic acid occurred. At $P = 0.5$ W, 80.5% retention of carboxylic acid was achieved, but at $P = 1$ W this was down to 58% retention. Retention continued to decline further with increased P, and a wider range of oxygen–carbon functional groups were incorporated into the plasma deposit.

The correlation between ion flux and deposition rate is not a simple one. In the plasma there is both deposition and ablation

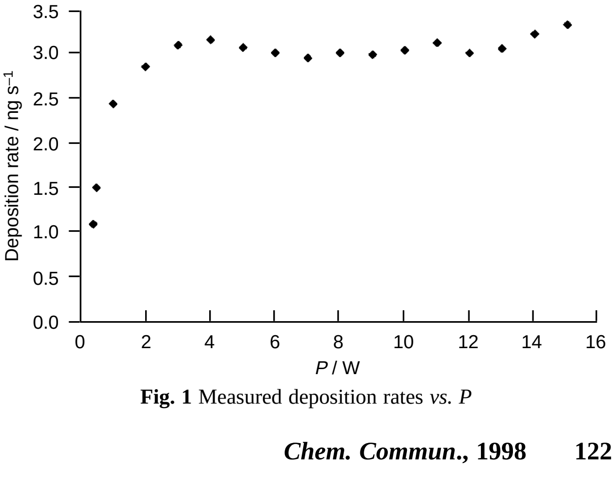

Fig. 1 Measured deposition rates *vs.* P

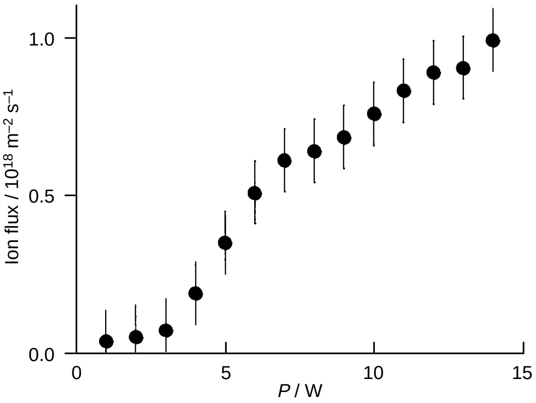

Fig. 2 Measured ion flux *vs.* *P*

of material. Ablation becomes more important at higher *P*. When this is taken into account, the different trends in ion flux and deposition rate data can be accommodated and fit with our understanding of plasma polymerisation.

In the acrylic acid system, at low *P* (0.5 W) there is extensive oligomerisation in the plasma-gas phase and these oligomers deposit to give a highly functionalised, low molecular weight film. These oligomers make up the bulk of the ion flux, which was too low to measure, with confidence, below $P = 1$ W. The deposition rate was correspondingly low.

The ion flux and deposition rate increased steadily with *P*, but at $P = 4$ W, their behaviour diverges. The deposition rate did not increase further with *P*. The constant deposition rate above $P = 4$ W represents a balance between deposition and ablation, with the increased ion flux being responsible for ablation.

Increased *P* had a dramatic effect on the extent of gas-phase oligomerisation. Above $P = 4$ W, oligomeric species from the plasma do not appreciably contribute to the deposit growth, which may now be explained by the flux of smaller ionic fragments and possibly radical grafting. Incorporation of carboxylic acid functional groups may have occurred by reaction of the surface with ‘intact’ monomer in the plasma, or other fragments containing carboxylic acid. Oxidation of the surface by the plasma can not be ruled out. At high *P*, the surface chemistry becomes closer to that of a plasma oxidised polymer surface.

This interpretation challenges the more orthodox view that neutral and free radical chemistry are solely responsible for deposit growth. The ability to make ion flux measurements in depositing plasmas is an important advance. The measurements themselves further point to the importance of the ionic component of these plasmas. Ion flux measurements help explain the effect *P* has upon surface chemistry and deposition rates.

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Notes and References

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