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The effect of ion energy upon plasma polymerization deposition rate for acrylic acid

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A novel technique, which allows the importance of ion energy in plasma polymer film growth to be investigated, without perturbation of any other plasma parameter (particle densities or temperatures) or, in principle, perturbation of particle (neutral or ion) fluxes is applied in the plasma polymerisation of acrylic acid and new insight into polymer formation is gleaned.

Plasma polymerisation under various plasma conditions such as pulsed or continuous wave is the subject of much current work[1,2] as films produced using this technique often display unique properties, for example carboxylic acid group containing monomers, including acrylic acid, are currently studied because of their affinity for cell attachment. Whilst film properties and potential applications receive attention, the fundamental processes occurring in the plasma that lead to the formation of these films are not well understood. Ions are potentially important in the formation of polymerised films as they transport both mass and energy to the substrate and are therefore, in principle, able to contribute in more than one way to deposition. For example, it has previously been estimated that the ion mass flux in an allylamine plasma[2] could account for a significant amount of the total deposition rate. Conversely, the energy transported to the surface by ions is capable of both the removal or addition of film material, through etching, or the creation of radical sites, which are then available for graft polymerisation.

The basic plasma reactor and outline of the technique used have been described in reference 3. However, in the current configuration, the RF biased grid previously used is enlarged to cover the entire cross section of the vessel. This forms a substrate onto which it is possible to adjust the ion energy independently of other plasma parameters. It is important to recognise that this technique controls only the ion energy to the substrate. All other plasma parameters such as electron temperature and plasma density and hence ion flux remain unaffected. For this experiment, the substrate also incorporated an ion flux probe and an XPS stub.

Briefly, the technique relies upon applying an RF signal onto the substrate which is matched in phase and amplitude to the RF potentials in the plasma.[4] This applied potential nulls the RF potential drop across the sheath region, and thereby reduces the ion energy at the substrate by removal of the time average self bias potential.[5]

A monomer pressure of 5×10^{-2} mbar and generator power of 5 W, were chosen on the grounds that these values produced COOH retention in a similar reactor.[1] Under these conditions, the observed ion energy distributions range between a broad, twin peaked structure which is typical of those found in RF plasmas,[6,7] to a narrow single peaked structure which is more typical of DC plasmas.[6] The two extreme ion energy distribution functions (IEDF's) are shown in Fig. 1. The profiles of these energy spectra are important as they demonstrate that control over the IEDF's has been achieved.

Fig. 1 also shows the difficulty in assigning a mean energy to the ions, since when there is an RF potential drop across the sheath, the energy spectrum is broad and non-Gaussian. For convenience, we calculate the ion energy from the difference between the time average plasma and substrate bias potentials, V_p and V_b respectively. The plasma potential is taken from the ion energy spectra and the bias potential measured directly from the grid, through an RF blocking filter. These potentials were measured to be −3.0 V and 54.2 V without and with the applied bias respectively, giving measured ion energies of 64.5 eV, and 21.0 eV respectively.

Fig. 2 shows RGA spectra taken when the ion energies were at these two energy values. There is remarkably little difference between the two, which confirms that applying the bias potential does not deposit any power into the plasma since

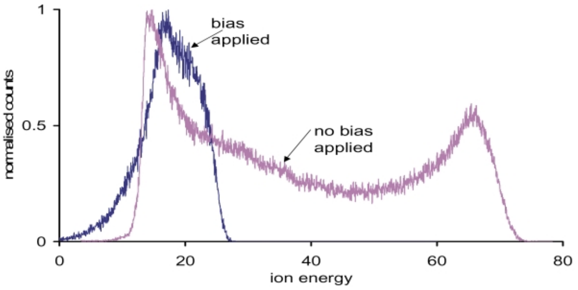

Fig. 1 Ion energy distribution functions at the substrate with and without the applied RF bias signal.

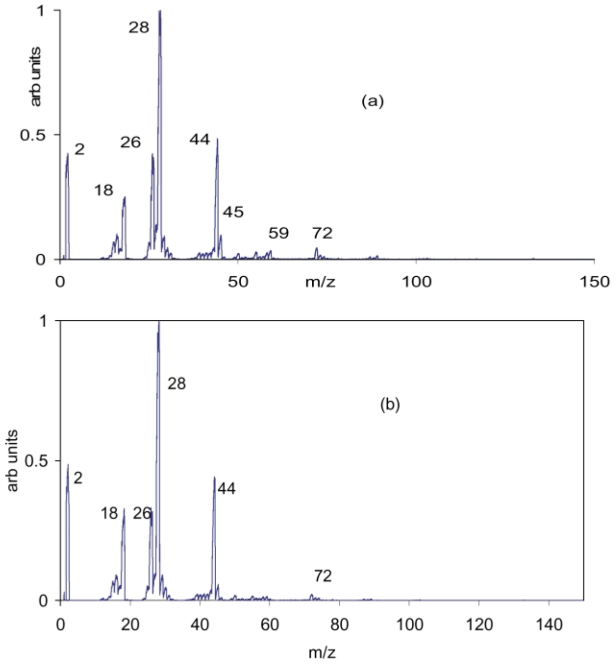

Fig. 2 (a) Electron impact (neutral species) spectrum of 5 W plasma, without applied RF substrate bias. *m/z* 26 = $C_2H_2^{\cdot+}$, 28 = $C_2H_4^{+}$; $OC^{\cdot+}$; $N_2^{\cdot+}$, 44 = $C_2OH_4^{\cdot+}$; $CO_2^{\cdot+}$, 72 = $C_3H_4O_2^{\cdot+}$. (b) Electron impact mass spectrum of 5 W plasma with applied RF substrate bias. This spectrum is virtually identical to that obtained without the application of the bias potential, indicating that this technique does not deposit a significant amount of power into the plasma.

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increasing the input power is known to increase the fragmentation of the monomer.[1,2,8] Another interesting and important point arising from the neutral spectra is that raising the ion energy does not increase the level of sputtered or etched material that is backscattered into the spectrometer. If increasing the ion energy were changing the sputter or etch rate, it would be anticipated that some of the sputtered material would be backscattered into the spectrometer and detected.

Conversely, the positive ion spectra (Fig. 3) show that reducing the ion energy results in the emergence of higher mass ions ($m/z > 45$). This is an interesting observation because this technique does not perturb the bulk plasma, so any difference in ion chemistry must be the direct result of sheath processes. Although the change is modest, it is noteworthy as previously this change has been seen with plasma power, but always with a concomitant change in the chemistry of the plasma-phase neutrals.[8]

By calculating a mean mass from the ion spectra,[2] it is possible to estimate the (positive ion) mass flow rate to the substrate. This may then be compared to the measured deposition rate provided the total ion flux is known. The average mass and ion fluxes were 46 Da and 3.51×10^{17} ions m^{-2} s^{-1}, and 59 Da and 3.65×10^{17} ions m^{-2} s^{-1} for maximum and minimum ion energy conditions respectively. These values give ionic mass flow rates of 27 μg m^{-2} s^{-1} and 36 μg m^{-2} s^{-1} respectively. These compare to the measured deposition rates of 54 μg m^{-2} s^{-1} and 33 μg m^{-2} s^{-1} for the high and low energy conditions respectively. These figures clearly demonstrate that, in principle, there is a sufficient mass flow of ions to the surface to account for between 50 to 100%, of the deposited mass.

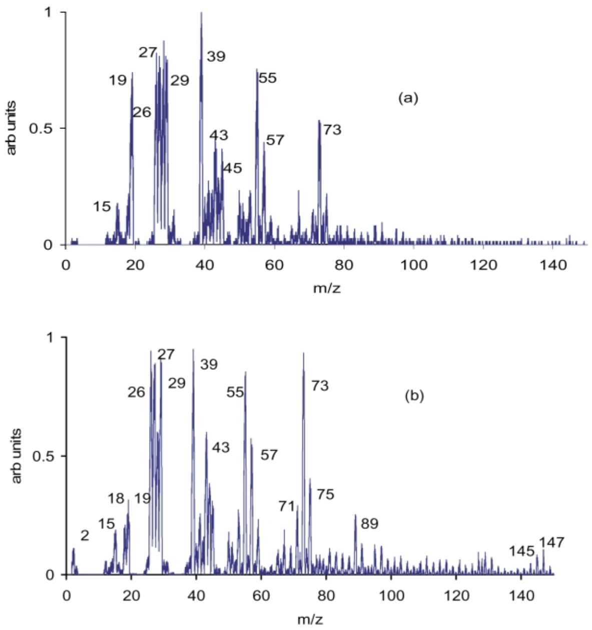

Fig. 3 (a) Positive ion mass scan at 5 W without applied RF bias. This corresponds to the maximum ion energy at the substrate. We assign the masses to the following; 15 = CH_3^+, 19 = OH_3^+, 26 = $C_2H_2^+$, 27 = $C_2H_3^+$ 29 = $C_2H_5^+$; COH^+, 43 = $C_2OH_3^+$, 45 = $C_2OH_5^+$, 59 = $C_3OH_7^+$, 73 = $C_3O_2H_5^+$. (b) Positive ion mass scan at 5 W with applied RF bias. Note the predominance of higher masses compared with (a).

However, whilst the ion mass flow rate to the substrate increases as the ion energy is reduced (because the ions are present in larger fragments, increasing the average mass) the measured deposition rate falls. This demonstrates the importance of energy carried by ions in the deposition process, as the deposition rate increases by a factor of greater than 2 with ion energy.

The influence of ion energy on the chemistry of deposits was measured using XPS. Manipulation of the ion energy produced no appreciable change in surface chemistry; the surface oxygen level, expressed as the ratio O : C, changed from 0.392 to 0.395. Peak fitting of the C 1s core line again showed no significant difference between the chemistry of films produced at the two ion energies.

The results show that in the plasma polymerisation of acrylic acid, reducing the ion energy results in a modest change in the ion chemistry in the sheath region, with negligible effect on ion flux, but reduces the deposition rate by a factor of greater than 2.

This may arise from an increased ion sticking probability with energy or the creation of more radical sites, and a greater degree of neutral grafting. Ion energy does not notably alter film chemistry. For this monomer, and under these particular plasma conditions, we show ion energy is a significant parameter in the plasma polymerisation mechanism. Moreover, it is shown how ion energy may be decoupled from the rest of the plasma and investigated as an independent variable. The power of doing this is made clear by the relationship that is established between ion energy and the polymer deposition rate.

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