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A method for the deposition of controllable chemical gradients†

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A new methodology for creating surface chemical gradients is reported. By way of a demonstration of the technique, gradients of amine/carboxyl and of hydrocarbon/carboxyl functionality are deposited over a distance of 11 mm. The gradient chemistries are examined by X-ray photoelectron spectroscopy (XPS) and chemical derivatisation of acid functional groups by TFE labelling.

Chemical gradients are regions of change in surface chemistry between two points on a surface. These may be useful in a number of experimental situations, where it is desirable to probe the effect of differing surface chemistries in a single experiment.[1]

In the literature the terms 'chemical gradient' and 'wettability gradient' are used interchangeably, when in reality these are two very different types of surface.

There are a number of strategies available for the formation of gradients. Among the earliest work in this area was that of Elwing *et al.*,[2] who used a chlorosilane self-assembled monolayer (SAM) on a silicon dioxide surface to produce a gradient running from hydroxyl groups, through to methyl groups.

The most widely used methods for producing gradients have been reviewed by Ruardy.[3] In general, there are two major subdivisions in these techniques. Firstly, there are those methods that rely on the diffusion of active species to form the gradient. This is most commonly seen in conjunction with thiol or silane molecules to form gradient SAMs, but has also been applied to a plasma-treatment based method.[4] The second group of methods are characterised by using different exposure times to form gradients (for example, a wet-chemical derivatisation, or exposure to a radio frequency argon discharge).

Several of the methods described utilise a plasma treatment to form a gradient, but these methods are entirely limited to the production of wettability gradients. By its very nature, a plasma treatment relies on modification of an existing material by the action of excited plasma species. The limitations of this approach are well known, and include surface roughening and poor control over chemical group incorporation.

In this paper, we describe a method of forming chemical gradients that does not fall into either of the above categories, since it is neither based on controlling exposure time, nor does it rely on a particular geometry to take advantage of diffusional effects. In addition, it is a method capable of introducing specific chemical functional groups, and it is scalable in a spatial sense so that gradients of varying lengths may be deposited.

This method utilises plasma polymerisation to form surfaces that contain specific functional groups. In plasma polymerisation, an organic precursor is allowed to flow into a reaction chamber under vacuum (around 10^{-2} mbar) at a controlled rate. A radio-frequency glow discharge is then excited from the precursor gas. Deposition occurs on any surface exposed to the plasma, and by careful choice of precursors and plasma conditions (flow rate, power, pulse duty-cycle, pressure, *etc.*) significant and controllable amounts of chemical functional groups can be retained in the polymeric deposit.[5,6]

The plasma reactor used for this work is based upon one already described adequately in the literature.[7] Instead of a cylindrical reactor, a T-shaped reactor was used, with a sample drawer (Fig. 1) mounted on the side arm and projecting into the centre of the major axis. The sample drawer has a screw thread which allows the substrate placed within it to be incrementally shielded from the plasma during polymerisation.

The substrate for deposition (13 mm glass cover slip) was placed in the drawer and immersed in the plasma. The drawer was mounted *via* an insulating connector and hence was not earthed. Initially, the drawer was fully extended and a plasma was excited using an allylamine monomer at a continuous wave power of 10 W. This plasma was allowed to deposit for a period of 10 minutes, providing an underlayer for the gradient that had good adhesion to the glass substrate. The power was then reduced to 5 W and the drawer was then retracted at a uniform rate (1 mm min^{-1}) whilst the composition of the plasma was altered in a controlled manner. Hence at each point during the deposition, a different chemical composition of the plasma was used. In effect the gradient is a continuous spectrum of plasma copolymers.

This was achieved by introducing a second monomer (acrylic acid) into the chamber while simultaneously reducing the flow of allylamine in such a way that that a constant flow rate (of 4 cm$^3_{\text{stp}}$ min^{-1}) and pressure (2×10^{-2} mbar) were maintained. For the deposition of the acid-octadiene gradient, the same method was used, but with octa-1,7-diene being substituted for the allylamine monomer.

The gradient surfaces were analysed by XPS using a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) which utilizes a monochromated AlKα source, axial charge neutralization, and a magnetic immersion lens. Each sample was analysed at a take-off angle normal to the surface, using the oval X-ray spot of ~0.5 mm (along the axis of the gradient) by 1 mm. Survey and core-level spectra were acquired from a rectangle of 0.3 mm (along the axis of the gradient) × 0.7 mm within the X-ray spot at 0.5 mm intervals across the width of the sample using an analysis time of around 12 min per position. Prior to running this analysis, the degradation of the samples under X-ray flux was measured and found to be negligible within this time period.

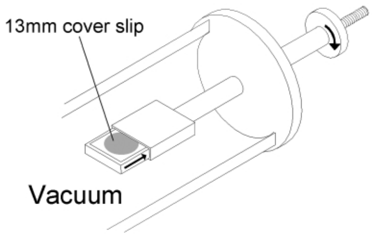

Fig. 1 Apparatus used for the deposition of the chemical gradient. The drawer mechanism is immersed in a plasma system similar to those described elsewhere.[7]

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The data were analysed using CasaXPS software (Neal Fairley, UK). Acrylic acid plasma polymers have been well described in the literature, and the C1s regions from all the points along the gradient were curve fitted using chemical shifts previously well documented.[8,9]

Figure 2 shows the O/C and N/C ratios of the allylamine/acrylic acid gradient surface at 0.5 mm intervals across the surface. The C 1s region of this surface (Figure 3) shows how the high-energy component peak associated with the COOR/H functional group ($\Delta B.E. = +4.2$ eV) is well defined and increases steadily in intensity across the length of the chemical gradient.

Figure 4 shows the results of a chemical derivatisation of an octadiene/acrylic acid chemical gradient using trifluoroethanol (TFE). This process has been shown to label carboxyl groups and has previously been applied to plasma polymerised surfaces deposited from acrylic acid plasmas.[9]

Figure 4 demonstrates the retention of a particular chemical functional group (acid) from the monomer structure, and the derivatisation illustrates that by changing the concentration of this group across the surface, we have been able to vary the reactivity of the surface in a spatially controlled fashion. It can be seen that this may be easily extended to other functional groups, and alternative chemical reactions.

The gradient shown in Figs. 2 and 3 is potentially even more versatile. The changing surface concentration of amine and acid chemistry across the surface (in opposite directions) means that the use of different derivatisation chemistries would allow a wide range of possible entities to be coupled to the surfaces in a spatially controlled fashion in terms of surface concentration.

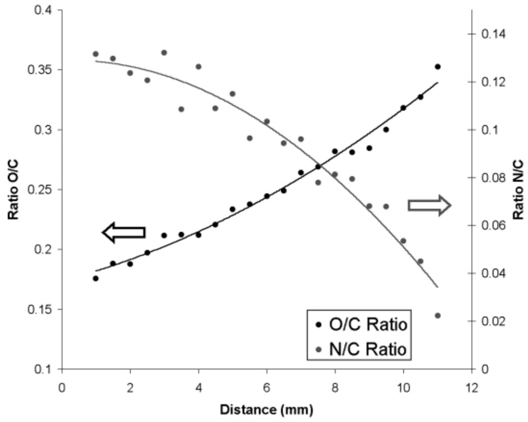

Fig. 2 O/C and N/C ratios as a function of position along an amine-acid chemical gradient.

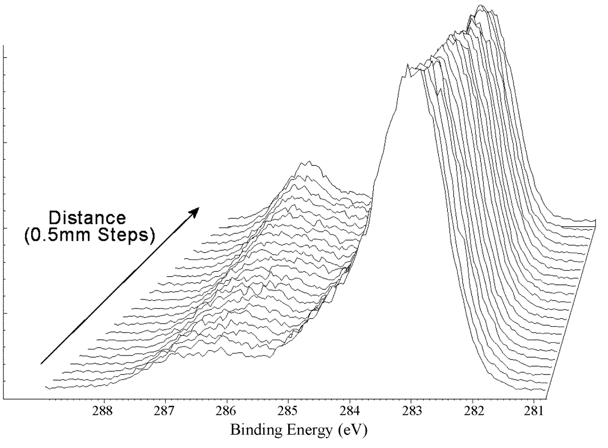

Fig. 3 C1s Region of an amine-acid gradient as a function of position across the sample (0.5 mm steps).

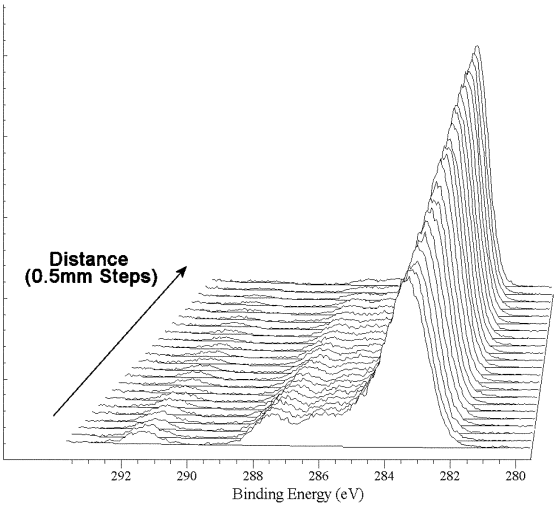

Fig. 4 C1s region of a trifluoroethanol derivatised octadiene-acrylic acid chemical gradient as a function of position (0.5 mm steps). The CF_3 signal at ~292 eV originates from the TFE labelled carboxyl group.

We have demonstrated a versatile and straightforward method of depositing chemical gradient surfaces, which does not rely on any substrate chemistry, or time-dependent behaviour. Moreover, our method is totally general in that the form of the gradient, and its endpoints are defined by the changes in the plasma composition and the movement of the substrate relative to it. In principle this means that the dimensions over which gradient surfaces are produced can be readily scaled up or down to match the required application. In addition, the shape of the gradient can be altered by manipulation of the rate of movement of the substrate. A continuous gradient, such as that described in this report, may be deposited between any pair of different chemistries deposited by plasma polymerisation. Alternatively, novel functional groups can be introduced by derivatisation of the deposited chemical groups. Furthermore a bi-directional gradient of two different derivatisable groups has been demonstrated. This may be applied as a tool to immobilise biomolecules or other entities by chemical means as a route to investigating the effect of their surface concentration.

The method described in this report potentially allows the deposition of robust, multifunctional chemical gradients with controlled profile, length and endpoints, without limitations on substrate materials. These gradients may be applied as a research tool in many areas of chemistry, biochemistry and biomaterials science.

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