

# On the suitability of high vacuum electrospray deposition for the fabrication of molecular electronic devices

Robert H. Temperton<sup>a</sup>, James N. O'Shea<sup>a</sup>, David J. Scurr<sup>b</sup>

<sup>a</sup>*School of Physics, University of Nottingham, Nottingham NG7 2RD, UK*

<sup>b</sup>*School of Pharmacy, University of Nottingham, Nottingham NG7 2RD, UK*

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## Abstract

We present a series of three studies investigating the potential application of high vacuum electrospray deposition to construct molecular electronic devices. Through the use of time of flight secondary ion mass spectrometry we explore the use of this novel deposition technique to fabricating multilayer structures using materials that are compatible with the same solvents and films containing a mixture of molecules from orthogonal solvents. Using x-ray photoelectron spectroscopy we study the deposition of a polymer blend using electrospray and find evidence of preferential deposition of one of the components.

*Keywords:* Electrospray Deposition, ToF-SIMS, XPS, Molecular Electronics, Polymers

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## 1. Introduction

Vacuum electrospray deposition (ESD) is an emerging technique that has allowed researchers to study complex molecules on surfaces, *in-situ*, using a vast array of analytical techniques requiring high vacuum including various photoemission[1, 2, 3] and scanning probe techniques[4, 5]. Early examples of work using high vacuum ESD studied the bonding of molecules used in dye sensitised solar cells such as the benchmark N3 sensitiser dye on the titanium dioxide surface[1]. The technique has also been applied beyond

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*Email addresses:* [robert.temperton@nottingham.ac.uk](mailto:robert.temperton@nottingham.ac.uk) (Robert H. Temperton),  
[J.Oshea@nottingham.ac.uk](mailto:J.Oshea@nottingham.ac.uk) (James N. O'Shea)

9 traditional surface science experiments and used with biological systems[6,  
10 7]. In recent years molecular photovoltaics, such as organic solar cells, are  
11 increasingly reliant on the construction of multilayer and bulk heterojunction  
12 structures[8, 9]. Ambient electrospray deposition has been used as a tool  
13 to construct such structures[10] providing a pathway to use high vacuum  
14 electrospray to study critical parts of such devices *in-situ*.

15 Electrospray deposition relies on the formation of a beam of molecular  
16 ions via the electrospray ionisation process. This has been thoroughly dis-  
17 cussed elsewhere[11, 12, 13], but in summary, a fluid is passed through a  
18 small capillary tube with a large voltage ( $\sim$  kV) applied to it. The voltage  
19 causes the liquid emerging from the capillary to be drawn into a well-defined  
20 shape known as a Taylor cone - at the tip of which the charge on the liquid  
21 is so high a jet of liquid is expelled. Due to the charge on the liquid's sur-  
22 face, the jet pinches off into a stream of droplets which in turn repeatedly  
23 fission into ever smaller drops. This plume of ionised droplets can be fired  
24 into a differentially pumped vacuum system where a series of apertures al-  
25 low the pressure to be reduced to high vacuum conditions whilst skimming  
26 the ionised droplets, from which solvent is evaporating, into a narrowly di-  
27 verging beam of molecular ions. Placing a surface in the path of this beam  
28 allows a film of the solute to be grown on the surface with minimal solvent  
29 contamination.

## 30 2. Instrumentation

31 The ESD system used was a Molecularspray UHV4 (a schematic is shown  
32 in Figure 1a). This portable deposition source consisted of a 250  $\mu$ m inlet  
33 capillary, 0.4 mm and 0.6 mm skimmer cones separating the first two vac-  
34 uum stages (pumped using roughing pumps) from the 3rd vacuum stage  
35 pumped using a turbomolecular pump. The exit from the instrument was  
36 a 1 mm aperture. The deposition chamber, pumped using a turbomolecular  
37 pump, had a base pressure of  $1 \times 10^{-7}$  mbar and a deposition pressure of  
38  $1 \times 10^{-6}$  mbar. The depositions were monitored by observing fluctuations in  
39 the pressure and the inlet capillary was flushed regularly (with the valve to  
40 the deposition chamber closed) to avoid clogging/blockages from the sprayed  
41 molecules.

42 The solutions were fed into the emitter capillary (New Objective Stainless  
43 Steel TaperTip) by a syringe pump delivering a flow rate of  $0.3 \text{ ml h}^{-1}$ . Before  
44 each deposition the emitter, syringe and tubing were thoroughly flushed with

45 solvent. A bias of  $\sim 2$  kV was applied to the emitter with respect to the  
46 grounded entrance capillary.

47 Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used as  
48 an imaging technique. ToF-SIMS utilises ion sputtering to lift fragments off  
49 the surface whilst a time of flight mass spectrometer measures mass spectra of  
50 the fragments. These spectra can be collected as a function of time and/or  
51 space in the x,y plane of the sample. This allows chemical maps of the  
52 sample to be constructed, in which each pixel represents a full mass spectrum,  
53 making it the ideal technique for imaging sub millimetre structures with  
54 chemical contrast. The instrument used was an ToF-SIMS IV instrument  
55 (IONTOF GmbH) with a 25 keV Bi primary ion source (with a  $\text{Bi}_3^+$  cluster  
56 beam applied). The primary ion dose was kept below the static limit and an  
57 electron flood gun ( $< 20$  eV) was used to prevent charging.

58 X-ray photoelectron spectroscopy (XPS) was used to provide chemical  
59 analysis of thin films and bulk samples. By irradiating a sample with x-  
60 ray photons, electrons are emitted from the sample into the vacuum (the  
61 photoelectric effect). By measuring the kinetic energy of these emitted pho-  
62 toelectrons, the original binding energy of the electrons can be determined  
63 meaning XPS is sensitive to the chemical environment of electrons. XPS  
64 therefore allows quantitative measurements of blends of molecules that may  
65 contain the same elements existing in different chemical states, and due to its  
66 high surface sensitivity (limited to the nanometre range by the escape depth  
67 of the photoelectrons), XPS is ideal for studying the chemistry of thin films.  
68 In this study, a Kratos Axis Ultra instrument was used with a monochromat-  
69 ised aluminium  $K\alpha$  x-ray source. Charge neutralisation was provided using  
70 an electron flood gun. The analyser was set to measure in hybrid mode with  
71 a pass energy of 20 eV.

72 The molecules and solutions used for each of the three experiments are  
73 detailed in their respective sections. All were purchased from Sigma Aldrich.

### 74 **3. Methods, results and discussion**

#### 75 *3.1. Layered deposits of molecules from the same solvent*

76 Multilayer structures of different organic materials are critical in the con-  
77 struction of a range of devices including Bragg reflectors[14], photovoltaic  
78 devices such as organic solar cells[8], and drug delivery systems[15]. Tech-  
79 niques like spin casting provide the capability to build high quality multilayer

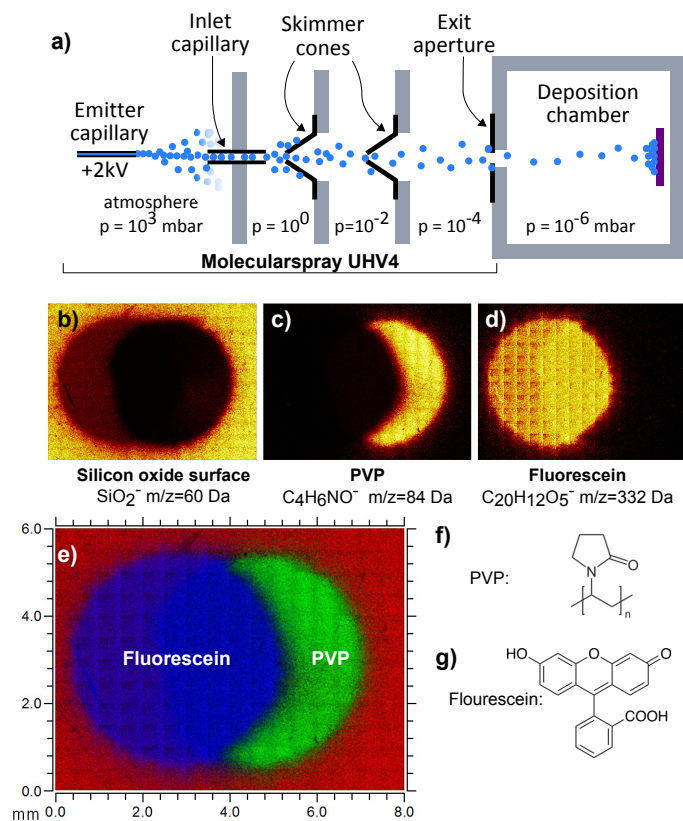


Figure 1: a) Schematic of the Molecularspray UHV4 system used to fabricate bi-layer structures. b-d) ToF-SIMS images built using markers for SiO<sub>2</sub>, PVP and fluorescein respectively. e) Composite image using the above 3 markers shown in red, green and blue respectively. f-g) chemical structure of PVP and fluorescein.

80 structures from molecules that are compatible with different solvents: Bai-  
 81 ley et al have shown, using ToF-SIMS, that alternate spin cast layers of  
 82 polystyrene (PS) and polyvinylpyrrolidone (PVP) dissolved in toluene and  
 83 water respectively, can produce multilayer structures that have highly re-  
 84 peatable layer thickness and sharp interfaces[16]. However, these traditional  
 85 wet chemistry preparation methods are limited to the use of materials dis-  
 86 solved in orthogonal solvents (solvents that will dissolve one species but not  
 87 another). Solvent free techniques, such as electrospray deposition, provide a  
 88 potential solution to overcoming this experimental limitation.

89 A silicon wafer substrate was cleaned via ultrasonication in acetone,  
 90 methanol and isopropanol. Thin films of polyvinylpyrrolidone (PVP), with

91 an average molecular weight 360 kDa, followed by fluorescein dye were de-  
92 posited at room temperature using electrospray onto the native oxide surface.  
93 Both molecules were dissolved in methanol to a concentration of 0.1 % (w.t)  
94 and further diluted to 0.05 % (w.t) for deposition. Each deposition lasted an  
95 hour and the sample, which was held on a transfer arm 0.5 m away from the  
96 exit aperture of the UHV4, was moved slightly between depositions; both  
97 depositions were therefore visible but with an overlapping area.

98 ToF-SIMS was used to image this fluorescein/PVP bi-layer on the silicon  
99 oxide surface. Figure 1b-d shows secondary ion images constructed from  
100 the intensity of individual peaks in the mass spectra selected as markers  
101 for the surface and each molecule. The spectral values used as markers for  
102 the oxide surface, PVP and fluorescein were 60 Da, 332 Da and 84 Da.  
103 A composite image showing the intensity of the different markers is also  
104 included in Figure 1e. These images show there is minimal mixing between  
105 the layers where the fluorescein film appears on top of the PVP deposit  
106 eclipsing the image of the PVP (Figure 1c) with little signal attributed to  
107 the PVP in the overlapping region. Although, the depositions were very  
108 thin, some preliminary depth profiling experiments illustrated the presence  
109 of underlying PVP in the overlapping region (data not shown).

### 110 *3.2. Deposition of immiscible polymer blends*

111 Producing a film containing a blend of molecules from orthogonal solvents  
112 can be an experimentally challenging problem. Electrospray deposition pro-  
113 vides a potential solution; as there should be minimal amounts of solvent,  
114 simultaneous depositions of the two molecules from different electrospray  
115 sources should allow the mixing of the molecules at the surface. This was  
116 attempted using the setup shown in Figure 2a. Two electrospray sources,  
117 of the type used in section 3.1, were placed at 90° to each other with the  
118 sample at 45°. The sources were 8 cm from the surface. It was not possible  
119 to monitor the pressure in the chamber during deposition but the system was  
120 allowed to pump down sufficiently that the ultimate deposition pressure of  
121  $\sim 1 \times 10^{-6}$  mbar was achieved.

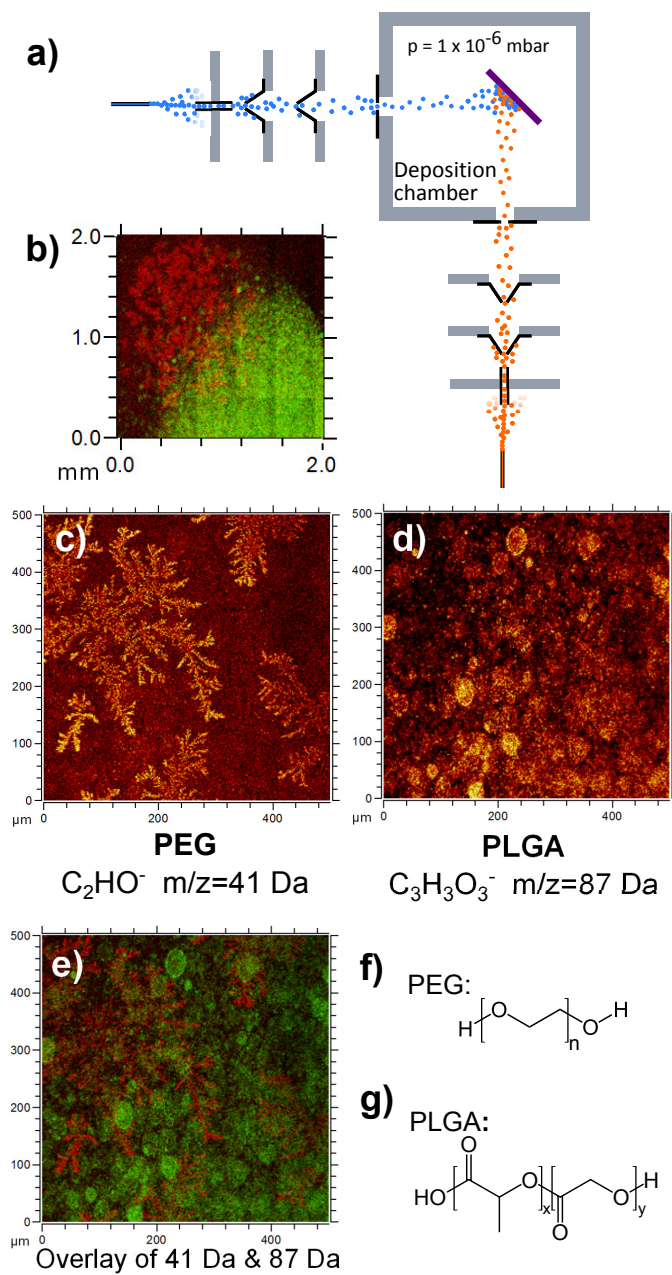


Figure 2: a) Geometry used to co-deposit molecules from two solutions using two Molecularspray UHV4 systems. b) ToF-SIMS composite image showing the markers for PEG (red) and PLGA (green). c-e) high resolution images of the overlap region for each of the two markers a composite respectively. f-g) show the chemical structure of PEG and PLGA.

122 The two polymers used were poly(lactic-co-glycolic acid) (PLGA) and  
123 Polyethylene glycol (PEG) dissolved in acetone and methanol respectively  
124 to a concentration of 0.1% (w.t.). The PLGA, a co-polymer with average  
125 molecular weight between 40 kDa and 75 kDa, had a ratio of 65:35 for the  
126 lactide:glycolide monomer components. The PEG had a molecular weight  
127 of 3.35 kDa. PLGA and PEG were co-deposited at room temperature for  
128 around 1 hour onto a clean silicon wafer (ultrasonicated in acetone, methanol  
129 and isopropanol) and the resulting deposition was imaged using ToF-SIMS.  
130 A sample of the images collected are shown in Figure 2. The two diagnos-  
131 tic secondary ions used are  $m/z = 41$  ( $C_2HO^-$ ) for PEG and  $m/z = 87$   
132 ( $C_3H_3O_3^-$ ) for PLGA. A 2 mm area overlay image is shown in Figure 2b il-  
133 lustrating the overlapping deposits. A 500  $\mu m$  area within the overlap region  
134 is shown for the PEG and PLGA markers and as an overlay in Figures 2c  
135 2d and 2e respectively. Secondary ion images were also measured away from  
136 the overlapping region in areas containing each individual species. The mor-  
137 phologies of which showed comparable structure to that of the overlapping  
138 region.

139 Firstly it is clear that in the overlapping region there has been some  
140 mixing of the two components. The PEG has also formed a large scale fractal  
141 structure on the surface. This behaviour implies the molecule is mobile on the  
142 surface, which, considering the size of the PEG polymer chains, implies there  
143 is likely a small amount of solvent on the surface allowing such structures to  
144 form. The same argument could also be made for the “blob” like structure  
145 of the PLGA. Despite this, an immiscible polymer blend has been achieved  
146 on the surface with domain sizes on the micron length scale.

147 Although acetone and methanol are miscible, when the two solutions  
148 were mixed, the mixture turned cloudy as the molecules partially drop out  
149 of solution. The same experiment does however have the potential to be  
150 applied to completely immiscible polymer solutions, for example those soluble  
151 exclusively in water and toluene.

### 152 3.3. Miscible polymer blends for organic photovoltaics

153 The polymer blend PEDOT:PSS is used in organic photovoltaic devices as  
154 a hole conducting layer. It contains a mixture of poly(3,4-ethylenedioxythiophene)  
155 and polystyrene sulfonate as shown in Figure 3d and 3e. Here we use XPS to  
156 compare films of PEDOT:PSS deposited using electrospray deposition and  
157 the more traditional spin casting directly from solution.

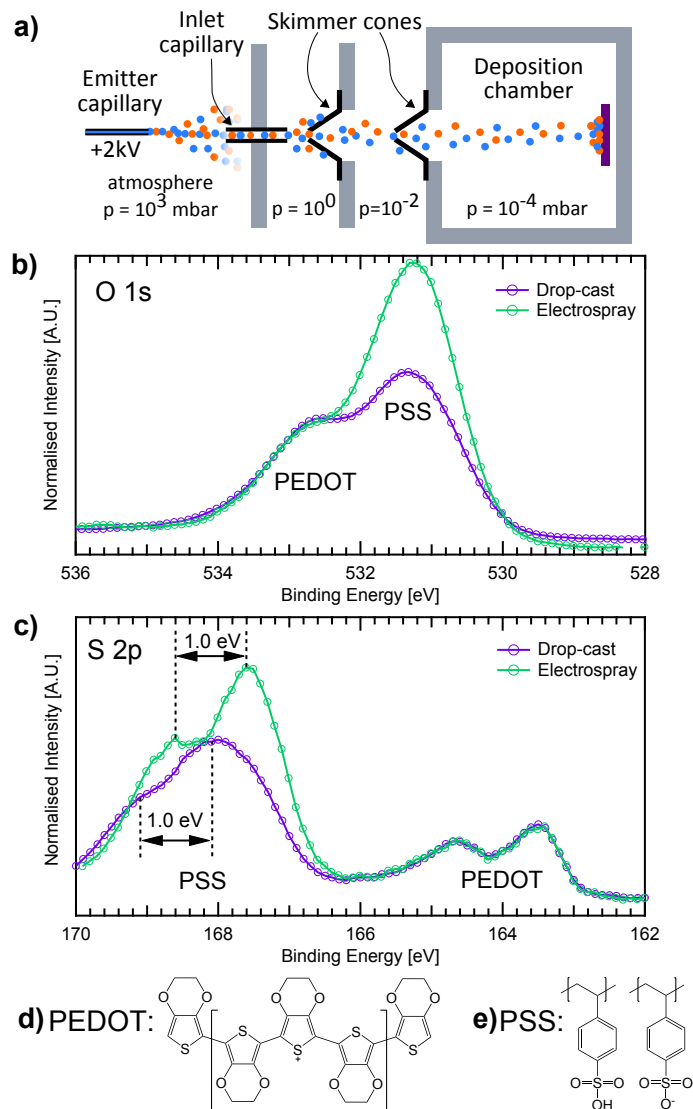


Figure 3: a) The electro spray deposition source used to deposit PEDOT:PSS consisted of one less pumping stage than the UHV4 source used in the previous sections. b-c) show O 1s and S 2p XPS measurements for an electro spray deposited sample and a drop cast sample of the same solution. d-e) show the two components of the PEDOT:PSS polymer blend. PSS is a co-polymer of the two groups shown.



158 Gold substrates were made by thermally evaporating 10 nm of titanium  
159 and 100 nm gold onto silicon wafer. The titanium was used to improve co-  
160hesion between the gold film and the silicon oxide surface. The silicon wafer  
161was cleaned by ultrasonication in acetone, methanol and isopropanol prior to  
162evaporation. PEDOT:PSS (Orgacon dry re-dispersible pellets by Agfa) was  
163dissolved in deionised water and drop cast onto one substrate. This solution  
164was diluted to 0.01 % (w.t.) and electrosprayed onto another substrate using  
165the apparatus shown in Figure 3a. Both experiments were carried out with  
166the substrates at room temperature. This apparatus contained one fewer  
167pumping stage than the Molecularspray UHV4 (as used in Sections 3.1 and  
1683.2) to maximise deposition flux as low pressures and desolvation were less  
169critical. 10 % methanol added to the solution to improve the quality of the  
170spray.

171 Figures 3b shows XPS measurements of the O 1s region for both the  
172drop cast and electrospray deposition samples (both were prepared *ex-situ*).  
173The O 1s spectra contains two overlapping peaks with binding energies of  
174532.8 eV and 531.3 eV. We have attributed the higher binding energy peak  
175to the ethylenedioxy attachment to the thiophene ring of the PEDOT and  
176the lower binding energy peak to the sulfonate side group of the PSS. Both  
177spectra have been normalised to the PEDOT/thiophene shoulder. There  
178is a clear increase of the PSS/sulfonate contribution for the electrosprayed  
179sample.

180 Figure 3c shows XPS spectra of the S 2p region (measured at the same  
181position on both samples as the O 1s data). There are two doublets in the  
182spectra resulting from the spin orbit splitting of the 2p states of sulphur in  
183the PEDOT and PSS molecules. We have attributed the lower binding en-  
184ergy doublet, centred at approximately 164 eV, to the PEDOT's thiophene  
185ring and the much broader feature at higher binding energy, centred at ap-  
186proximately 168 eV, to the sulfonate group of the PSS. Again, both spectra  
187are normalised to the PEDOT contribution and there is a clear increase in  
188PSS signal for the electrosprayed sample.

189 The broadening and binding energy shift of the sulfonate peaks of the  
190drop cast relative to the ESD sample is attributed to charging effects due to  
191the thickness of the drop cast deposit. We suspect that this is only present in  
192the PSS and not the PEDOT as the PEDOT is a fully conjugated conductive  
193polymer. Measurement at different sample positions shows the same feature  
194shapes and there was no sign of beam damage between the start and end  
195measurements at a single position.

196 It is worth noting that the two polymers in the PEDOT:PSS blend are  
197 individually charged. As shown in Figures 3d 3e, PEDOT has positive  
198 charges on the thiophene backbone whilst PSS has negatively charged sul-  
199 fonate groups. It is possible this could explain why the electrospray technique  
200 would preferentially deposit one species over the other - however in this case  
201 the experiment was carried out in the positive bias mode and we are see-  
202 ing potential preferential ionisation of the negative species which is counter  
203 intuitive.

204 Analysis of the C 1s was hindered by atmospheric carbon contamination  
205 (during transport of the samples from the deposition apparatus to the XPS  
206 instrument) so is not included here. Carbon spectra were used to provide  
207 relative calibration between the two samples where the low binding energy  
208 edge of the C 1s region implies a 0.9 eV shift between the two samples. This  
209 offset was applied to all the included spectra.

#### 210 4. Summary and conclusions

211 Three experiments have been presented highlighting the capabilities and  
212 potential challenges of using electrospray to produce multi-layered structures  
213 and blends of materials. Firstly we have shown that the solvent contamina-  
214 tion on the surface is low enough to build up thin layers of molecules that are  
215 compatible with the same solvents without substantial mixing of the films.  
216 However, ultra high vacuum compatible electrospray deposition is not well  
217 suited to building up thick deposits and although SIMS is surface sensitive  
218 enough to measure surface coverage, conventional sputtering does not allow  
219 depth profiling of such thin films (when probed with XPS we find similar  
220 deposits are several monolayers thick). With the co-deposition experiment  
221 we have shown there is almost certainly a small solvent contribution to the  
222 deposit allowing structure to form on the surface. More sophisticated electro-  
223 spray instruments have applied techniques such as mass selection and heated  
224 inlet capillaries to attempt to combat these issues.

225 The XPS analysis of the PEDOT:PSS blend is of importance and certainly  
226 needs further study. It appears as though the electrospray deposition process  
227 preferentially ends up with one species over another being ionised, entering  
228 the vacuum system and landing on the surface. Although we have shown with  
229 SIMS that a simple vacuum compatible electrospray source can be utilised  
230 to build the sort of films used in molecular devices, care should be taken if  
231 simultaneously depositing multiple species.

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