

Discussion session summary: MD2, Organic Thin Films^{†‡}

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Programme pressures at many major conferences generally result in very limited opportunity for extended public discussion of the papers. Materials Chemistry Discussions provide a valuable forum for debate of this type, and will play an important role in the future development of the subject. Such discussion has three valuable functions: it provides authors with balanced feedback and the opportunity for this to be questioned, supported or refuted by additional comments; it provides a forum for experts in the field to develop the themes of papers on a wider scale, presenting additional material from their own research and broadening perspectives; and for younger scientists it sets standards, inspires enthusiasm and even offers opportunities for the bold to challenge the views of established figures. The discussions at MD2 fulfilled all of these functions. The purpose of the following summaries is to make available on a wider scale the principal content and flavours of these discussions.

Each discussion session was planned around a themed group of papers, and each section of the summary is prefaced by the titles and authors (the name underlined in each case is that of the presenting author) of the papers in the session, in the order in which they were covered in the discussion. Readers may find it helpful to read the papers from each session first, followed by the discussion summary for that session.

Session I—Chairman: Professor A. R. West

Organic materials for electronic and optoelectronic devices, Y. Shirota (p. 1)

The discussion of Professor Shirota's paper centred on the charge transport in the amorphous glasses (Taylor). Time of flight mobility data showed a well-defined arrival time, and the dependence of $\log(\text{mobility})$ on $(\text{field})^{1/2}$ suggested a simple Poole–Frenkel trap lowering mechanism, with a single trap, rather than the Bässler disordered material model discussed in the presentation. Shirota said no thermally stimulated current or DLTS work had been done yet to determine the trap distribution, and although the good transient curve shapes were perhaps surprising for an amorphous material, X-ray studies confirmed that the materials were indeed amorphous. No information was yet available on the detailed structure or possible local ordering within these glasses, which were stable in the glassy state for very long periods at room temperature, particularly when bulky groups were incorporated. A comment was made (Willis) that the hole mobilities of $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were impressive, being close to those observed for some single crystals, and this led to a question on whether electron mobilities had been measured and whether the materials were considered intrinsic or extrinsic. Shirota commented that the amorphous materials had been studied with hole transporting materials. If electron transporting materials had been studied, perhaps electron transport could also have been measured, but this had not been done. He also pointed out that any impurity effects would reduce the observed mobility and imply a true

value even higher than the reported one. Another question (Cook) referred to the change from a photostationary state of 85:15 *cis:trans* in the azabenzene system in solution to 26:74 when doped in *m*-MTDATA (1 mol%), which had been explained in terms of differences in the free volume available in the solid material. Could another factor be that the 450 nm light used might be filtered out by absorption by the host matrix? Shirota confirmed that although the main absorption of the host was at below 450 nm it was possible that this factor was a minor contributor. Other discussion points included the complex electrochemistry (Bryce), where a CV showing 9 electrons transferred for a dendrimer may reflect shielding of the inner regions by the outer regions, and the mechanism of the very high resolution electron beam resist material which had been shown in the lecture (Wright). The latter was a positive resist developed by an aqueous alkaline reagent, and involved incorporation of onium salts which were involved in proton transfer reactions affecting the solubility.

Session II—Chairman: Dr. J. D. Wright

Preparation of highly ordered quinquethiophene thin films on TiO_2 substrates, E. Müller and C. Ziegler (p. 47)

Molecular beam deposition of crystalline layers of polar perhydrotriphenylene inclusion compounds characterised by second harmonic generation microscopy, A. Quintel, F. Budde, P. Rechsteiner, K. Thoma, A. Zayats and J. Hulliger (p. 27)

Formation and spectroscopic characterisation of self-assembled phthalocyanine monolayers, D. J. Revell, I. Chambrier, M. J. Cook and D. A. Russell (p. 31)

The control of molecular self-association in spin-coated films of substituted phthalocyanines, B. M. Hassan, H. Li and N. B. McKeown (p. 39)

Discussion in this session centred on the influences of substrate interactions, intermolecular attractive forces and steric factors in determining the structures of films of various organic materials. The four papers covered a variety of

[†]Based on the presentations given at Materials Chemistry Discussion No. 2, 13–15 September 1999, University of Nottingham, UK.

[‡]In preparing the summaries, tape recordings of the sessions (made with the full agreement of participants) were used to ensure accuracy. Some re-organisation of material has been made, to provide a more logical flow in cases where discussion diverged and then returned to an earlier point, and some minor clarifications of misunderstandings have been omitted. Although every effort has been made to give an accurate and balanced summary, it is the author's individual overview, and he accepts full responsibility for any errors or omissions.

substrate types and deposition methods, which led to a wide-ranging discussion.

Ziegler had said the layers described in her paper were liquid crystalline, and was asked if this had any meaning for monolayers. She said the films always had at least 2 layers of molecules, standing upright, and 24 Å layers corresponding to the molecular length could be removed one at a time by scratching with the AFM tip, even for films as thick as 100 nm. This could not be done with crystalline layers. IR studies showed that films evaporated onto RT substrates give splittings into 2 components and on heating the peak splits into 4 components, in line with a smectic layer structure. It was pointed out that two ways in which the molecules could interact with the substrate would be *via* the S atoms or the π clouds, neither of which would give the upright orientation. The implication is that the interaction with the surface is relatively weak, in which case it is surprising that changing the surface gives a different picture. Ziegler said most of the work was done on completely amorphous substrates, which gave the same structures as on TiO₂, but much more easily. Layers are formed only because of intermolecular interactions, not because of substrate–molecule interactions. TiO₂ substrates which have been polished have surface scratches, but the molecular layers simply cover these regardless. Calculation of the interactions shows an energy gain as soon as a cluster of vertical molecules forms. IR, UV and X-ray absorption measurements always show dichroic absorption. On SiO₂ the molecules lie 15° from perpendicular to the surface whereas with TiO₂ it is 30°, and this angle is roughly what is obtained by just putting the single crystal structure on top of the TiO₂.

Metzger asked Quintel to elaborate on the molecular rectification properties of her materials. She said that measurements, made in field gradients of $8 \times 10^5 \text{ V m}^{-1}$, on bulk crystals up to 1 mm long contacted with silver carbon or gallium electrodes, showed conductivities around $10^{-14} \text{ S cm}^{-1}$. The conductivity was $100 \times$ larger for measurement parallel to the molecular chains than perpendicular to them, suggesting intrinsic conductivity. Rectification was very small, but did not depend on the electrode material. Non-polar guest molecules in the same set up gave symmetric current–voltage curves. Wright asked if the reported angle of incidence of 45° used in the evaporation of the films could be varied. Quintel said such work was planned. Ideally the channels in the film should be aligned perpendicular to the substrate plane to permit use of AFM to examine the inclusion, but so far this had not been achieved.

In discussion of Russell's paper, Willis recalled his own work with Maruyama on epitaxial growth of phthalocyanine films on alkali halide crystals, which was an attempt to obtain stacking perpendicular to the substrate. He asked whether the use of two or four thiol bridging molecules to link each molecule to the surface would lead to a higher chance of such an orientation. Russell said he had used this successfully with proteins, although the alignment was somewhat disordered. Cook pointed out that another problem with this approach was dimerisation *via* disulfide bridging. Ziegler suggested using space-filling layers of linker chains to improve ordering, but pointed out that close packed layers of alkanethiol substituents would be electrically insulating. Leggett said he would expect the sulfur to be oxidised over the periods of up to 24 months for which the films had been reported to be stable, and asked whether any spectroscopic studies had been done to establish the oxidation state of the sulfur. Russell replied that although alkane thiol layers do oxidise over 9 months, the thiol side chain phthalocyanines do not, and that possibly the phthalocyanine groups prevent the oxidising species (ozone) from diffusing to reach the thiol groups. Metzger pointed out the difficulty of obtaining spectroscopic evidence for sulfoxide formation, since all the S–O bonds were likely to lie in the film plane. Russell reported that they believed they could see the SO

vibration, so the bonds may not lie in the film plane. Sulfoxide head groups could be washed off the surface easily with water. Bryce asked what happened to the SH hydrogen during SAM formation. Leggett said the SH IR bands could be seen disappearing, and Russell said that it was thought that molecular hydrogen was evolved, albeit in very small quantities. Taylor asked why the short chain substituted phthalocyanines lay parallel to the surface but the long chain derivatives lay perpendicular, whereas he would have expected the parallel orientation to be more difficult to achieve when only a short relatively inflexible chain was used. Russell explained that gold was hydrophobic, so interacted with the aromatic group when it was held close to the surface by a short chain, whereas van der Waals interactions between longer chains gave a well-packed side chain layer which prevented the parallel orientation. Ryder asked whether dilution of the surface interaction of substituted phthalocyanines by addition of another alkane thiol might change the orientation in a controlled way. Russell replied that frequently phase separation into separate domains occurred when thiol mixtures were used. Nabok said that it was surprising that the UV/visible spectra (Fig. 6 of the paper) were very similar despite the different orientations. Russell replied that the different intensities could be explained by the different areas occupied by a molecule in the different orientations. The curve shapes could not be interpreted with any certainty due to the very low absorbances involved. Nabok suggested that the spectra might be influenced by interactions between the phthalocyanine and the gold surface, and said he had often observed that the spectrum of the first single layer of an LB film was different from that of thicker films. Wright pointed out that the glass substrate surfaces used were far from flat on a molecular scale, so that it was perhaps surprising that the IR evidence for different orientations was so clear. Could differences in surface coverages arise from longer side chains being more able to penetrate into crevices in the gold film, and had any measurements been made of the actual amounts absorbed (*e.g.* using QCM) or of surface enhancements of vibrational spectra due to surface roughness effects? Russell agreed that for rough surfaces intuitively the observed IR spectral differences would not have been expected, but doubted whether QCM could detect the very small differences in amounts adsorbed in the different monolayers. Surface enhanced IR studies were planned, although the ideal gold thickness of 4 nm for this was rather thin for good SAM formation. Finally, Ashwell asked whether other techniques such as SPR had been explored for measurement of film thicknesses. Russell replied that he believed the resolution of SPR would be good enough to see the difference in thickness of C3 and C11 films, but possibly not to distinguish between these and C8.

Discussion of McKeown's paper began with Willis asking if there was any information on the orientation and size of domains of order in spin coated films. Although this deposition process was very rapid ($\approx 200 \text{ ms}$), spin-coated films often showed the best Davydov splittings (better than LB films), contrary to the expectation that time was required for weakly interacting organic molecules to find their equilibrium stable orientations. His group's high-speed photography had shown that the drop rapidly becomes an annulus of increasing diameter, suggesting that radial forces might lead to radial organisation. McKeown replied that nothing was visible under the polarising microscope, possibly because of small domain size. Cook stated they had seen UV/visible dichroism at different points in such films spun at 2000 rpm. Hillman commented that if the rotation speed was changed, hydrodynamic calculations showed that fluid flow was established in 4% of a revolution. The discussion then turned to the origin of the intermolecular interactions responsible for organisation in spun films. Bryce commented that the paper reported cofacial stacking was observed even when bulky substituents were used,

and asked whether this phthalocyanine stacking could be used as a template to generate order in peripheral groups—an approach which he was exploring with TTF substituents. It was noted that liquid crystal side chain structures could be achieved in this way, and that Nolte's group had formed a helical chiral column of phthalocyanines substituted with chiral side chains. Shirota enquired what was the main driving force for phthalocyanine stacking. Cook suggested π - π interactions, but asked at what point the cofacially aligned molecules in solution 'dimers' started to tilt when forming a film. McKeown said it depended on the space around the phthalocyanine core. Alkyl substituents had steric requirements which led to tilted structures, while there was less steric demand around the oxygen of alkoxy groups, which led to columnar structures. Wright enquired about electronic effects, and McKeown used the example of non-peripherally substituted phthalocyanines, where steric effects are identical for alkoxy, alkyl and alkoxymethyl substituents. Electron donating alkoxy groups weaken π - π interactions and give edge-to-edge interactions rather than cofacial stacks; alkyl groups which are less electron donating give some cofacial interaction with tilted stacks; electron withdrawing alkoxymethyl groups promote strong cofacial interaction. Wright pointed out that Desiraju had highlighted the importance of collective $\text{CH}\cdots\text{C}$ interactions, and McKeown agreed that there were many peripheral substituent contacts around 3 Å which could reflect such interactions. Sato asked about the orientation around the columnar axis, and McKeown answered that this was probably random, with dynamic reorientation. Ziegler suggested that it might be possible to promote columnar ordering by growing crystallites in the linear electric field between an AFM tip and the surface.

The session concluded with a brief discussion of the device potential of such films. Wright commented that although we seem to understand their structures increasingly well, we have not made much progress in commercial applications. Ziegler emphasised that organic materials were already being used in electronic devices, but only as polymer films in cheap relatively unsophisticated applications, where structural ordering and ultra-purity were not an issue. Even though we understand how to make highly ordered organic films, McKeown agreed it would be difficult to attain 'electronic' purity levels with chromatographic methods, and Ziegler concluded that no company had current plans to develop applications demanding highly ordered ultra-pure organic films.

Session III—Chairman: Professor D. M. Taylor

Diode-like electron transfer across nanostructured films containing a redox ligand, D. I. Gittins, D. Bethell, R. J. Nichols and D. J. Schiffrin (p. 79)

All about (*N*-hexadecylquinolin-4-ium-1-yl)methylidetricyanoquinodimethanide, a unimolecular rectifier of electrical current, R. M. Metzger (p. 55)

Second-harmonic generation from alternate-layer and Z-type Langmuir-Blodgett films: optimisation of the transparency/efficiency trade-off, G. J. Ashwell, R. Ranjan, A. J. Whittam and D. S. Gandolfo (p. 63)

Structure and conductivity in LB films of low-dimensional polymer electrolytes, Y. Zheng, A. Gibaud, N. Cowlam, T. H. Richardson, G. Ungar and P. V. Wright (p. 69)

The papers in this session concerned organised films with functional electrical, electrochemical or NLO properties, and the discussion naturally centred around the relationship between film structure and properties, beginning with comments on the paper by Gittins *et al.*

Ryder commented that viologens in polymers often give a second redox process which is less intense than the first, and this has been attributed to slow electron self-exchange between the forms of the viologen. He asked if the second redox step could be seen for the present systems. Gittins said that if the scan was taken far enough the second reduction could be seen but since it is only quasi reversible it had not been studied in this work. Similarly, asked if the gold-thiolate bond might be oxidised, he replied that this would not occur until +0.8 V whereas all the reported measurements only scanned down from +0.4 V. Russell expressed surprise that the dithiols did not loop over and self-assemble to the gold surface by both ends. In reply, Gittins pointed out that by integrating the current it was possible to deduce the number of surface molecules and hence, knowing the molecular footprint, the area covered. This only matched the observed area available if single-site binding was assumed, with 100% surface coverage. It would not match if the molecules looped over to occupy two sites.

Fig. 3 of the paper attracted several discussion points. Explaining the saturation of current density as thickness increased, in Fig. 3a, Gittins said that the idea that the internal layers may sinter was disproved by the fact that the absorbance (Fig. 3b) increased linearly with the number of layers. Current limitation was explained by the need for the anion to leave in order to maintain electroneutrality during reduction, which occurs in cyclic voltammetry in a few seconds. As more layers build up, only the outer 6 layers reduce and allow the anion to diffuse out. Those in the inside cannot lose the bromine, so no reduction is seen. Bartlett pointed out that this implied the inner layers must be metallic. The other possibility would be that it is the inner 6 layers in contact with the electrode which are involved each time, with the outer layers inactive. Roser asked if any structural measurements had been done, for example using grazing incidence X-rays. Were the inner layers perhaps collapsing as more layers were added, leaving the gold nanoparticles touching? Gittins replied that this was unlikely since, if they were touching, the plasmon absorption would not increase linearly with the number of layers, but no structural studies had yet been done.

Wright suggested that the surface offered preformed viologen pair structures with potential for molecular recognition. There was a possibility that other organic molecules could interact *via* charge-transfer interactions with pairs of neighbouring viologen cation acceptors, and was there any spectroscopic evidence for this? Gittins replied that he had used bromide and phosphate as soft anions which would not lead to charge transfer, but there was a possibility that small donor molecules such as phenol might interact in this way.

Willis made a general comment about self assembly. People who use these thiols almost invariably attached them to a long alkyl chain but, as Dr Ziegler had pointed out in session II, this is highly undesirable electrically. Ideally it should be a conducting pathway. Is there any good reason why the thiol cannot be on the end of either an aromatic or a conjugated polyene system? Gittins answered that there was no reason at all why this should not be done. Thiolated β -carotene chains had been used by other workers and had shown self-assembly without any problems.

Questioned about the size of the measured resistance of the molecular devices, Metzger pointed out that most of the resistance arose from the electrode contacts (oxide on both sides of the aluminium, and contact resistance from the gallium eutectic). He had tried to deposit gold electrodes, using a modified evaporator with a distance of 20 cm between the source and the film, with the film cooled to 77 K, but the gold vapour was still too hot and damaged the film. Nabok said that aluminium has a 2 nm oxide layer, and asked if Metzger had seen electron tunnelling effects. Could the observed temperature independence be a consequence of tunnelling? Metzger

said that measured currents amount to about $0.33 \text{ e molecule}^{-1} \text{ s}^{-1}$ whereas STM currents are about a million times larger. This suggested that about one molecule in a million happens to be at a point on the surface where there is no oxide. There is an insulating effect of the oxide elsewhere, otherwise much higher currents would be seen. In relation to the observed degradation of rectification after switching many times, Ziegler asked if the degradation decreased on cooling the samples. Metzger replied that he believed the degradation was due to a molecule flip. The molecule has a fat mid section and a thin tail and there is room for flipping within the LB film plane, but it was not possible to obtain images with sufficient resolution to prove this. Taylor reported that he had seen a similar effect many years ago in monolayers and trilayers of phospholipids. He saw rectification and rapid erosion, and had interpreted it as something happening in the oxide layer. Different results were obtained in air and vacuum. For fresh samples placed in a vacuum, the current decreased as moisture was lost from the aluminium oxide bottom layer. He asked how Metzger's samples were dried. Metzger replied that his layers were dried for 2 days in a vacuum desiccator under P_2O_5 to ensure all the water was out. Bartlett asked if it was possible to avoid these electrode problems by using molecular metals. He showed STM images of TMTSF/ PF_6 crystals with no evidence for reorganisation in air. Exposing these surfaces to naphthalene vapour or solution or with electrochemically controlled deposition gave ordered monolayers which were stable for days in air. Metzger said that this approach would be excellent—but the problem was still what to do for the other electrode.

It was pointed out that surface potential measurements on layers of Metzger's molecules gave a dipole which did not agree with that expected from the value for the individual molecules. Ashwell commented that he had looked at a variety of chain lengths from C8 to C22 on the same molecule. Going from C8 to C14 the films are blue, while from C16 to C22 they are purple. The SHG is zero up to C14 but strong for C16 and above. It is very likely that molecules go antiparallel at the air/water interface, the crossover point being between C14 and C16, and this type of interfacial alignment might explain the odd surface potential data.

Nabok asked Ashwell about the orientation of the molecules in his films. Ashwell replied that at low surface pressures the chromophore lay on the surface with the chains (C18 and dibutylamino) in a U-shape up out of the water. On compression they come together and the dibutylamino group then points downward. In another series of molecules, a C22 chain at one end and C12 at the other had been shown to be the optimum combination. The longer chain points upwards and surprisingly a hydrophobic chain is adjacent to the water interface. Thickness studies on the deposited films show the molecules are stretched and in vertical alignment. Neutron reflection at the air/water interface also shows the expected film thickness. Bryce said that LB films are criticised for being frail, and asked if it was possible to modify the syntheses to put thiols on the chain ends to permit self assembly? Ashwell replied that he was trying that, although his existing LB films (kept at room temperature) gave the same SHG now as they did when first made 4 years ago. He pointed out that the SHG intensity could in principle be increased significantly if the optically passive long chains could be eliminated so that a higher proportion of the layer material was composed of the SHG-active parts of the molecule. He mentioned that a Japanese group had demonstrated this 4 years ago.

In discussion of Peter Wright's paper, Latham said that the suggestion of Li ions moving down holes formed by polymer helices was at odds with normal ideas for a bulk PEO system. Wright said the amorphous phase was identified as the main pathway in bulk materials, but the problem was that ion aggregation could occur. What he had tried to do was to split

the system into surfaces, eliminating coulombic interactions. This pushed the stability to the limit, by limiting the thickness of the ionic material to get interactions more like surface 2-D than bulk 3-D. Another problem is that on heating bulk materials, free volume is generated but this collapses again on cooling. In the new systems described in the paper he had put in a 'pit prop' so that structure could not collapse. In the LB films there is a metastable open structure. Bartlett asked how much water there was in the LB films. Could there be a lyotropic liquid phase with thin 2-D layers of water in which the ions move? Wright replied he hoped his films were water free—they were studied under vacuum. He saw no evidence in X-ray d -spacings to suggest that water is present—they correlated with anion sizes. Ashwell asked if there could be a phase change due to solvent. Could transitions at around 100°C be trapped water bursting out on boiling? Perhaps the transition temperature might change if a different subphase than water was used. Wright commented that these temperatures were also around the transition point to isotropic phases (T_i) and this was their more likely origin. Lösche asked about the lateral homogeneity of the films. He thought the X-ray reflectivity looked rather odd below about 5 degrees and doubted if any structural information could be obtained from the low angle regime. How was the reflectivity curve related to the electron density profile? Wright said he obtained different results for lateral ordering depending on whether the salt was derived from the subphase or from the top at the beginning. In the latter case—*i.e.* making the complex first and spreading that on the surface—a rather hard film was obtained, suggesting rather more rod-like molecules. If there were no ions in the film, the rods were very soft and flexible. In conclusion, Shiota summarised by asking: In the bulk sample the ionic dissociation takes place by the coordination of the polymer to the inorganic salt, and ion transport is assisted by the motions of the polymer, but for in-plane processes in the LB film both carrier generation and transport may be different from those of the bulk sample—is that right?

Wright replied: We think that what one has to do in these systems is to maximise the surfaces. We believe that what we are doing in the bulk is to make a system of micelles, where the ions are moving along the surfaces of the micelle while the hydrophobic material is inside the micelle. This is where the organisational problem comes in—we must not allow ion traps to form by having reverse emulsions. We maximise the surface area of the micelles by stabilising them by other polymers, and have these conducting pathways along the surfaces of the micelle. Then we have a kind of pseudo 3-D system—we still have the benefits of the two-dimensional order but we have a pseudo three-dimensional system where we get round the problem of having a single crystal all the way between the electrodes. By allowing only two surfaces to come together we are not allowing large coulombic lattices to form. At the transition point in the LB film, when the system reorganises as one raises the temperature, ideally it would be best if the system just flopped over and we put the conducting phase in between the electrodes, but I guess in fact the system breaks into some kind of micellar structure and it is on the decorated surfaces of these micelles that we are seeing the conductivity.

Session IV—Chairman: Dr. M. R. Willis

Nanometric electrostatic interfacial phenomena in organic semiconducting thin films, M. Iwamoto (p. 99)

Unoccupied electronic structure in organic thin films studied by inverse photoemission spectroscopy, N. Sato, H. Yoshida and K. Tsutsumi (p. 85)

The electrical characteristics of a heterojunction diode formed from an aniline oligomer LB-deposited onto poly(3-methylthiophene), A. Riul Jr., C. A. Mills and D. M. Taylor (p. 91)

The three papers in this session, presented by Iwamoto, Sato and Taylor, were all concerned with electronic structure and electrical characteristics, and discussion mainly focussed on clarifying the chemical and physical state of the samples.

Iwamoto said about 1% of the molecules accept excess charge at the interface, but no explanation in terms of the chemistry and physics of the films was yet available. Asked by Cook if he had any information on the homogeneity of the layers in the films, Iwamoto said he had no direct surface images, but had established a linear relationship between reciprocal capacitance and the number of layers which suggested that they were uniform. Willis commented that perhaps it is more appropriate to discuss the phenomena in terms of charge transfer than in terms of a band model when using monolayer structures. Ziegler agreed that it was better to think of the surface as being heterogeneous with a number of different sites of slightly different energies, *i.e.* a small number of electrons localised on some of the molecules, giving a shift of the HOMO or LUMO. Iwamoto confirmed that in experiments with the same metal on both sides of the film no voltage was observed, as the electron transfer processes between metal and organic molecules were equal and opposite at the two electrodes.

Ziegler continued this theme in a comment on Sato's paper. She believed the material became n-conductive because of the presence of fragmented molecules produced by thermal decomposition during sublimation. From her group's work, she would expect that if the perylene derivatives were absolutely pure, with no fragmented molecules, the Fermi level should be in between the HOMO and LUMO. They had purified PTCDA for more than a week using very low temperature sublimation (more than 150 °C lower than reported by other workers) and obtained materials which were not conductive at all. She asked what sublimation temperatures had been used in Sato's work. Sato replied that he had not measured the sublimation temperature, but had used as low a temperature as possible to avoid decomposition. Willis commented that in his view a bilayer photovoltaic device fabricated using a compound similar to PTCDA was a heterojunction with a large internal bias to separate the charges. This view was unpopular as it implied extrinsic materials, with Fermi levels right at the top or bottom of the band gap. These could be produced by degradation during film deposition as one of the possible causes. In this concern, Sato mentioned that in general there might be some extrinsic phenomena or, in the case of organic materials, an intrinsic asymmetry of electronic structure around the energy gap. Metzger asked if it was possible to measure electron affinities from the onset of electron capture with this technique. Sato said that estimates of solid state electron affinities and polarisation energies for unoccupied states (typically 1.8 eV) had been obtained. Such information should be very important in many problems in organic solid state chemistry, *e.g.* the photoconduction mechanism.

Willis opened the discussion of Taylor's paper by referring to the AC frequency dependence data of Fig. 3. He said such dependences were very common for organic materials, and enquired about their possible origin in this case. Taylor replied that there were two broad dispersions—one related to the depletion region and one to the bulk. The low frequency dispersion was believed to be due to interfacial states from a series of traps at the interface that could be populated by the carriers as a result of the AC signal. Hillman commented that device properties should be strongly influenced by the interfacial structure between the two materials, as illustrated by the work of Royce Murray in the early 1980s, and asked if

Taylor had characterised the polymer/polymer interface. Taylor replied that they had no means of measuring any interdiffusion, but that they had shown the depletion region was very thin—only about 10 Å—at zero bias. He believed there was a step in the valence band at the interface, leading to a potential barrier which prevented hole transport and led to hole accumulation, while in reverse bias the holes were driven away. He believed the LB method would give a sharp interface, or at least one which followed the contours of the substrate surface. Hillman said he believed this was unlikely since the surfaces of conducting polymer films were extremely rough. Taylor said that although this appeared to be so at low magnification (micron scale), they look smoother under very high magnification. These images were obtained under dry conditions, but images pre- and post-dipping were similar. Nabok asked why gold and aluminium in Fig. 2 gave very different characteristics. Taylor said gold does penetrate LB films, but that for a series of samples deposited on the same polymer substrate the data correlated well with the thickness of those layers. This would probably not have been the case if the gold was causing problems. Films from 5–41 layers gave superimposed Schottky plots. The poly(3-methylthiophene) is a hole transporter so one would expect in forward bias that the holes would accumulate at the hetero junction, building up the field in the LB layer. As that field builds up either counter electrons are thermally emitted from the metal or holes are thermally emitted over the barrier of the hetero junction. He did not have a means of deciding which. Therefore Al was tried because, having a lower work function, it should give a smaller barrier and one would therefore have expected a rather higher current in forward bias, because there would be easier electron emission across the LB layer. This had not been observed, possibly because of the effects of oxide formation. Ziegler remarked that one advantage of gold on thiophene layers is the high interaction of gold and sulfur, which minimises diffusion problems.

Bartlett said he would expect the polyaniline measurements to be very sensitive to humidity, and asked what was the humidity during the measurements in air. Taylor replied that there was a small humidity dependence. If the poly(3-methylthiophene) was controlling things, oxygen dopant would have been removed *in vacuo*, reducing the conductivity of the polymer. That did not happen, so measurements had been made on pure oligomer, pure stearic acid and the mixed LB film to determine which component of the LB layer might be controlling things. There were small dependences on the ambient conditions that might be due to moisture or the oxygen, but he suspected it was probably the moisture. Finally, Hillman asked about the dopant level and protonation state of the polyaniline, which could also influence the effects of humidity. Taylor and Riul replied that the films had very low doping levels, and that experiments using DC fields applied for periods of time had shown no ionic polarisation, suggesting electronic rather than ionic conductivity.

Session V—Chairman: Professor M. J. Cook

Manipulation of electroactive polymer film viscoelasticity: the roles of applied potential and frequency, M. J. Brown, A. R. Hillman, S. J. Martin, R. W. Cernosek and H. L. Bandey (p. 115)

Neutron reflectivity studies of the structure of polymer/polymer and polymer/substrate interfaces at the nanometer level, M. Sferazza, R. A. L. Jones, J. Penfold, D. B. Bucknall and J. R. P. Webster (p. 127)

Strategies towards functionalised electronically conducting organic copolymers, L. F. Schweiger, K. S. Ryder, D. G. Morris, A. Glidle and J. M. Cooper (p. 107)

The three papers in this session covered polymer synthesis (Ryder *et al.*) and characterisation by the electrochemical quartz crystal microbalance (Hillman *et al.*) and by neutron reflectivity (Jones *et al.*). Discussion was dominated by lengthy and at times highly technical discussions of the complications of Hillman's paper, of which only the main outlines are presented here.

Latham began discussion of Hillman's paper by referring to the 'scheme of squares' (Fig. 17) which depicts rapid electron transfer and slow solvent transfer processes. He asked whether more detailed schemes such as Bruckenstein's 'scheme of cubes' had been considered, and whether the reported experiments had been repeated with a variety of solvents to explore solvent effects more completely. Hillman replied that in the circumstances of the reported experiments the viscoelastic characteristics were controlled not by the redox state but by solvent transfer. Although they had initially hoped to achieve equilibrium by moving to a new potential and waiting a few minutes, in fact equilibrium was only achieved for charge transfer processes and the viscoelastic properties proved much slower to equilibrate. Electron transfer was driven electrochemically, but solvent transfer was not driven by the field in any way. The square was a representation of this situation. It was a two-dimensional projection on a time scale too slow for polymer reconfigurational changes. If one waited for a much longer time still, those would be seen as well and that would give a cube. If higher electrolyte concentrations were used, where counter-ion and salt permeation needed to be included, it would become even more complicated, with a hyper-cube *etc.* He added that if he gave everybody in the room a sample of a monomer and sent them away to make the polymer and the measurements, he guessed he would get as many different sets of results as there were people, and they would all be right, because everybody would use different conditions. The number of possible mechanistic routes as a function of time scale was very large.

Bartlett said that while the idea of the cube or the scheme of squares was very attractive, there was a danger in using it. The original scheme of squares was for things like protonation and electron transfer on quinones, where events were 'quantised'—one electron or proton was either transferred or not and the only way round the diagram was around the edges. In the case of the reported experiments, quite a number of electrons were transferred and they did not all have to be transferred at once. Furthermore there was a whole range of motions and they did not all have to start at once. So in this case it was not necessary to go along square or cube edges—one could go diagonally. That was a crucial difference because it was no longer just a matter of counting how many ways there were for going round edges of a cube. That would be an underestimate since one could go through the inside of the cube too. Hillman agreed that in principle the square model was simplistic, but pointed out that if the time scales of two processes are very different (as in the present case) then it was energetically unfavourable to take diagonal pathways. However, in looking at some pyrrole electrochemistry of this sort with anions and cations of different sizes and using the cube model to look at ion solvent and salt transfer, it was indeed possible to model cation transfer as a diagonal. In principle also one could have 3 solvation states, or even a continuum of solvent states, not just 2. In effect, it was a question of using the simpler model where its approximations were justified.

Etchenique said he thought it was very dangerous to try to extract density, thickness, G' and G'' from QCM measurements. In his opinion this was not possible, because there were only three measurables but four parameters. One measured the inductance (L), resistance (R) and C_0 . L and R were the parameters related directly to the viscoelastic properties of the material attached to the quartz. These two parameters then had to be put into a model to obtain the mechanical properties of

the film. Using Martin's equation one sought to obtain thickness, density and the two moduli but one only had two experimental parameters. For semi-infinite materials it was possible to measure the density, and if α was assumed constant, or if the thickness was measured directly, then it was perhaps possible to estimate some of the parameters. But it was still a problem. In principle there was an infinite set of the four parameters which could all give the observed measurable values. He illustrated these basic points with reference to equations and model calculations presented in detail with the aid of overheads.

Hillman replied that some of the things said were true quite generally, some of them were true under special circumstances and some were true in a mathematical sense but in practice did not quite apply in the way suggested. He illustrated this in a number of ways, of which the following are examples. Concerning the number of parameters, it was quite correct that there were four film parameters to be determined from two measurable parameters. But from coulometry it was possible to make a reasonable estimate of film thickness—although solvent could present complications. In terms of density, knowing the density of the monomer and solvent it was possible to estimate the density of the films within limits. Therefore although when viewed in isolation Etchenique's point was correct, if the other available information was considered it was not so bad as it seemed. The final point was the issue of how accurately it was necessary to know, for example, the film thickness in order to obtain a significant value for the shear modulus. Model calculations showed that in certain regimes of parameter space, for certain values of shear modulus, there was unbelievable sensitivity to film thickness but that in other areas it was possible to tolerate errors even up to a factor of two in film thickness. The case of the reported systems fortunately corresponded to a region where the modulus was not highly sensitive to variations in thickness.

Turning to Jones' paper, Holmes commented that there was a lot of interest in the interfaces in doped films. For example recently the interface between polystyrene sulfonic acid doped polythiophene at an interface with a light-emitting polymer was looked at, and the issue that was proposed was that the protons were diffusing into the emitting phase and even to the ITO and releasing indium. He asked if there was any hope for looking with neutron reflectivity at such systems at this level of doping and then at the influence that it might have on polymer morphology and behaviour. Jones replied that he thought there was hope. There was a potential problem that small molecule dopants travelled a long way and did not give sharp interfaces. If the dopant moved to an interface and accumulated there, that would be quite easy to see. The bigger the species the more it would segregate because the less entropy it had to lose. For polymer mixtures segregating to an interface, even quite small differences in driving forces could cause quite large amounts of segregation.

Roser asked whether the roughness of the air/solid interface was included in the calculation, and Jones replied that it was, and that it was typically about 8 Å. Roser then asked what information could be obtained from off-specular scattering. Jones replied that in off-specular scattering, the beam comes in at a glancing angle and one observes neutrons that are scattered slightly out of the specular angle. The kinematics of scattering shows that this is going to be sensitive to structures on quite large length scales of 0.5–1 µm. So the particular problem that he was talking about could perhaps be addressed in this way, though the bundles that might occur in the substrate could be too small to see. Dispersion forces acting at the polymer/polymer interface might destabilise it and at a particular wavelength in the capillary wave they could grow and that could lead to de-wetting (de-lamination). In fact he had successfully used off-specular scattering to look at that because

the capillary wave involved had a wavelength of between 1 and 2 μm .

Cook asked if there was an optimum film thickness for this technique. Jones said that since neutrons are very penetrative, quite thick films can be used. There isn't really an optimum thickness. For films less than about 0.5 μm thick strong interference occurs from the front and back. For films thicker than that, the interference is washed out by the loss of coherence of the neutrons as they go through, but that can be fitted and allowed for. The key thing was for the films to be uniform.

Turning to Ryder's paper, Cook commented that the nitrile group on the end of the chain was interesting, and asked what he hoped to do with that eventually. Ryder replied that he was looking to attach it to transition metals.

Hanly asked how large was the film conductivity. Ryder replied that the conductivities were quite high—0.1–5 $\Omega^{-1}\text{cm}^{-1}$ —but they were not yet reproducible. There were not yet any obvious trends in relation to the chemistry.

Etchenique commented that in Fig. 2 the cyclic voltammograms first grew then decreased in amplitude, and asked if this was due to formation of an insulating layer at the electrode. Ryder agreed that this was quite possible, and that it was known to occur quite commonly.

Session VI—Chairman: Professor R. M. Metzger

The effect of alkyl chain length and terminal group chemistry on the attachment and growth of murine 3T3 fibroblasts and primary human osteoblasts on self-assembled monolayers of alkanethiols on gold, E. Cooper, L. Parker, C. A. Scotchford, S. Downes, G. J. Leggett and T. L. Parker (p. 133)

Coupling of protein sheet crystals (S-layers) to phospholipid monolayers, M. Weygand, M. Schälke, P. B. Howes, K. Kjaer, J. Friedmann, B. Wetzler, D. Pum, U. B. Sleytr and M. Lösche (p. 141)

In situ characterisation of phospholipid coated electrodes, P. N. Bartlett, K. Brace, E. J. Calvo and R. Etchenique (p. 149)

This session contained the papers presented by Leggett, Lösche and Bartlett, and was focussed on biological thin films. Discussion began with Willis asking Leggett about the nature of the attachment interactions for the fibroblasts: were they multi-point attachments and were they controlled by hydrogen bonding? Leggett replied that they were certainly multi-point since the fibroblast cells had sizes of about 20 μm , *i.e.* orders of magnitude larger than the substrate molecules. However the important thing to realise was that proteins first adsorbed to the monolayer and then the cells attached to this protein layer. The influence of the monolayer was indirect. A variety of proteins adsorbed from the serum in the cell culture, and the composition of that protein layer, in particular the conformations of the adsorbed protein molecules, ultimately determined the cell behaviour. The next stage of the work was to try to understand how the monolayer influenced the composition and structure of this adsorbed layer. The interactions between the proteins and monolayer were not only *via* H-bonding; there were also hydrophobic interactions, charge–charge interactions, *etc.* Willis said he had found that phosphonic acids bound much better than carboxylic acids, and Leggett said he thought this had not yet been tried for these systems, but seemed a good idea.

Russell commented that two different types of medium (foetal calf serum and new-born bovine serum) had been used, and asked if there were differences in composition between these. Leggett replied that he did not think there would be a vast difference. Both of those media would contain large numbers of proteins (including fibronectin, vitronectin and

albumin) at high concentrations, although even for the same kind of serum there were variations from batch to batch. Russell then asked if differences of cell attachment were due to different affinity for the surface of different proteins, or to different amounts of adsorption of a single protein, or to different conformations of the adsorbed protein. Leggett said it almost certainly involved the conformations. He had found that the amount of fibronectin (which encourages cell attachment) on the surface followed the trend in numbers of attached cells, but he had also found that albumin, which is known to discourage cellular attachment, followed exactly the same trend as fibronectin. Surfaces which adsorbed large amounts of fibronectin also adsorbed large amounts of albumin, so he believed it was due to conformation or competitive adsorption. Metzger asked if it was possible to measure the changes in biological activity of proteins which occurred when they were bound to a surface. Leggett replied that there were a number of approaches for studying protein conformations on surfaces. Physical approaches used, for example, infra-red spectroscopy—*e.g.* changes in the amide stretching frequency—while biochemical approaches involved, for example, using monoclonal antibodies binding to specific parts of the protein such as the cell binding domain and using that as a way of probing the accessibility of those domains.

Discussion of Lösche's paper began with Sato asking if there was an explanation for the preferential adsorption of proteins to the disordered part of the film membrane. Lösche replied that he had no explanation, and this was purely an experimental observation. There was clear evidence from fluorescence microscopy double label experiments, with one label on the lipid and another on the protein which is absorbing. The lipid fluorescence revealed mesoscopic phase separation into disordered and ordered lipid regions during the first-order phase transition observed in monolayer isotherms. On binding the protein, the protein label fluorescence appeared in between the ordered lipid regions. Sato then asked if the same phenomenon occurred when the membrane was in water. Lösche replied that whenever the membrane was put into water it had to be attached to some sort of solid substrate, and it was well known that this led to reorganisation of the phases so that this state would be different from the self-organized state prepared on the air–water surface.

Roser enquired how large the two-dimensional protein crystalline layer domains were in relation to the size of the phospholipid domains, and Lösche replied they were similar. Jones asked if anything was known about the nature of the interaction between the proteins in the layers, and how that might affect, for example, the surface rheology (which clearly was affected because that was stabilising the vesicles). They had been represented as distinct non-interacting species and he wondered if there could be stronger interactions between them which contributed to the stabilisation of the layer. Also, how compact was the protein layer? Lösche replied that this was an unsolved problem. Two-dimensional crystalline protein layers were observed, but not three-dimensional crystals. Although the amino acid compositions could be determined, these were large proteins (≈ 120 kDa), and their primary structure was not clear and even less so the three-dimensional structure. For the two proteins that he had investigated, the reflectivities were very complicated patterns with undulations due to the protein layers. For the best investigated protein species, analysis of the electron density distribution yielded a mass density distribution which gave an idea of the contour of the protein along the surface normal. In this particular two-dimensional protein crystal, some 60% of the volume was filled by the protein at -30 Å and then there was a cavity in the protein, then at -90 Å some 70% of the volume was filled with protein and 30% with water. Jones asked about the fitting of the reflectivity data, commenting that data had been shown extending to very high Q and very low reflectivity and asking whether it was all

significant. Lösche replied that he was confident that he could describe every wiggle that had been observed. The data were good, with low error bars, and the model fitted well, *c.f.* Weygand *et al.*, *Biophys. J.*, 1999, **76**, 458.

Metzger referred to micrographs of a one-layer thick S-layer protein sheet which Lösche had shown in his presentation of the paper, and asked if there was any evidence of a second or third layer forming. Lösche replied that there was evidence of 30% of a secondary layer forming that was derived from the detailed analysis of the data. For the analysis of the protein–lipid interaction that was at the focus of interest in this paper, this detail seemed of minor importance.

Turning to Bartlett's paper, Russell asked whether he had considered using phospholipids that had been thiolated. These were now commercially available and could be deposited directly onto the surface. Bartlett said although bilayers could be deposited directly on gold they were not stable when the potential was applied. Good discrimination was essential between the cases of phospholipid present or absent on whatever was on the surface. A rather porous layer was needed, but one which would still allow the phospholipid to assemble. In this case he used a tertiary thiol in order to give a rather disrupted surface. Use of something like *n*-dodecanethiol gave a well packed layer but there was no difference between the electrochemistry with and without the lipid layer. His concern would therefore be that attaching the phospholipid to a thiol would give a well-packed layer which would block the electrochemistry.

Lösche then asked whether order in the lipid layer promoted or discouraged the lipase action, and whether this could be controlled. Bartlett commented that the biological system did not have a lipid layer made of a single phospholipid. This raised questions about the organisation of the lipids in the layer and about where the phospholipases actually reacted. One of the things that people in hospitals would like to do was to know what the population of phospholipase enzymes was in their samples. There was a range of different ones. He would like to make measurements with different phospholipase layers or mixtures so that he could assess the kinetics. So far he had only been working with model systems and his choice had been guided by collaboration by biochemists. Lösche asked if it was possible to estimate the activity of the phospholipase and whether or not it was comparable to the attachment to vesicular systems. Bartlett answered that he could not yet compare the activity on his systems with that on vesicles—it could be an order of magnitude less for his systems. One of the problems was how to model the data so as to be able to extract the kinetics from it. Probably the best way forward would be to use the impedance data, but that would require a good model for the impedance which took account of the pinholes and defects which were definitely in the structures. He had kinetic data, but it was then a question of how to extract enzyme activity information. He had made measurements as a function of temperature and concentration, and had obtained results which were comparable with measurements on fluorescent vesicle systems, with the same sort of temperature dependence and the same sort of concentration detection range. However, it could well be that his systems were one order of magnitude slower when the rates were derived.

Finally, Ryder asked how the enzyme interacted with the exposed alkane thiol surface after all the lipid has reacted, and whether it might bind to this surface and block further electrochemical response. Bartlett said that if the electrochemical experiments were continued for a long time, voltammetry characteristic of the thiol was seen. There was therefore no evidence that any lipid was left or that the enzyme was blocking the surface. If there was anything left on the alkane thiol surface it would have to be very porous and open.

Session VII—Chairman: Professor A. B. Holmes

Design of conjugated molecular materials for optoelectronics, T. Sano, Y. Nishio, H. Takahashi, T. Usuki and K. Shibata (p. 157)

Organic electroluminescent devices: enhanced carrier injection using SAM derivatized ITO electrodes, S. F. J. Appleyard, S. R. Day, R. D. Pickford and M. R. Willis (p. 169)

Dual-layer light-emitting devices based on polymer Langmuir–Blodgett films, G. Y. Jung, C. Pearson, M. Kilitziraki, L. E. Horsburgh, A. P. Monkman, I. D. W. Samuel and M. C. Petty (p. 163)

This session was concerned with materials for electroluminescent devices, and provoked lively and informed discussion which clarified many of the key current trends.

Discussion was opened by Petty who distinguished several different approaches to electroluminescent devices. There were polymer and small molecule devices; and there were very simple structures and very complex structures (with electron transporting and hole transporting layers and maybe also an insulator layer to enhance injection). He asked which were going to be the better devices for commercial exploitation. Sano said the physics of both classes of materials was very similar, but the processing was different. Small molecule materials could be purified by sublimation and had some advantages for colour patterning, while the thermal stability of polymers was very good. Both types of material had advantages, and he predicted they might be combined in future hybrid devices. Shirota added that while polymer thin films could be made by spin coating, small molecules could usually be vacuum deposited. He thought the performance of devices using small molecules had until recently been better than that of polymer devices, but recently the driving voltage for polymer devices had been very much reduced, and as a result luminous efficiency had increased. Holmes showed a plot of progress in luminous efficiency over the years. The inorganic III–V compounds took a long time to get above about 1 lm W^{-1} , and the small molecules did very well, although polymers had slightly overtaken them in the last year or so. The only inorganic system which was a spectacular development was In–Ga nitride, which had rapidly risen to a working brightness of $10\,000 \text{ cd m}^{-2}$. (For comparison, a TV display emits about $200\text{--}300 \text{ cd m}^{-2}$.) This could be used in traffic lights and outdoor displays. At the moment he did not believe there was any chance of an organic material competing with that on brightness and voltage, although size was something where small molecules and polymers could possibly compete. Brightness was also an issue in relation to the problem of addressing the display. Pioneer actually had a product on the market using a multi-colour organic electroluminescent display costing about \$600. This used passive matrix addressing, which required up to $10\text{--}100 \times$ the current steady-state intensity during the period that the pixel was switched on, and this limited the size beyond which the current density became unmanageable. The other alternative was to use TFT addressing. Cambridge/Seiko-Epson were doing this. There were no really good red small molecule systems yet, but polymer devices could make a red.

Cook enquired what was the current situation regarding stability and lifetimes. Holmes said lifetimes for some of the polymers were thousands of hours, and Sano confirmed that optimised devices using Professor Shirota's materials were stable for over 25 000 hours. Later in the discussion, Holmes returned to this issue, pointing out that lifetime was related to the total number of coulombs passed through the film. In polymers, breakdown was associated with reduction of conjugation, but this could not be invoked so easily for

small molecule systems. Sano said his materials did not have double bonds, but moisture was a problem. The best stability was obtained using a smooth carrier flow in a cascade of interfaces each involving small jumps at the interfaces. Holmes drew the analogy with biocatalysis which often proceeded in a series of small jumps. Willis remarked that there seemed to be little standardisation in the definitions of lifetime reported by different workers in this field. Holmes said that commercial devices were all encapsulated and measured in air under standard conditions—it was the academic community which was less standardised.

Wright asked how far it was possible to predict electroluminescent properties by calculation. Did the secret lie in the energy levels of the molecules or were there other factors involved that could not be predicted? Sano replied that although it was difficult to calculate the efficiency, the band energy/colour could be calculated and predicted, but at present experiment must come first.

Willis took up the issue of efficiency, pointing out that when an electron and hole arrived at the same molecule the spins were random, so both singlet and triplet states were formed, but the triplet generation was 3 times more likely than singlet. At present the triplet phosphorescence was no use, so efficiency was limited to a maximum of 25%. He proposed using either a ligand or a central metal which had an unpaired electron on it, so that the excited state became a doublet. In that case there would be no forbidden transitions and efficiency would potentially be much higher. Examples might be organic magnet materials, nitroxides and metal complexes. Shirota said this was a very interesting idea. Holmes said he did not think that anybody had taken a material, measured its photoluminescence efficiency and then made it into a single-layer electroluminescent device with an efficiency of greater than 25%, although polymers were now reaching the 25% efficiency level. He said Heeger claimed to have obtained efficiencies where the ratio of singlet:triplet approached 1:1. Many of the best results were for multi-layer devices, where it was possible to adjust the barrier to hopping to the correct level. It could be that the excited state was spread over quite a wide range of the material at the interface, it could be that there was some spin physics at work, or it could be singlets emerge from triplet recombination. One of the nice experiments that had been done recently for small molecule and polymer materials was to capture some of the triplet energy with a Dexter transition from the excited triplet state and obtain phosphorescence by energy transfer to a phosphorescent material. That had mainly been done using porphyrins, which had a suitable triplet lifetime and energy and could accept energy from the triplet-generated electroluminescent states. This would only work for emission in the red region.

Nabok asked whether any structural studies had been done on the materials, and what were the structural requirements. Sano suggested that in future devices the carrier transport layer might be more crystalline, but the fluorescent molecules should be more isolated. Holmes added that light scattering by crystalline materials presented a problem, so order without crystallinity was really the requirement.

Turning to Willis' paper, Sano asked what was the thickness of the SAM layer. Willis replied that he had not measured it, but the molecules were assumed to stand almost vertically, in which case the layer thickness would be the length of the molecule, 10–20 Å. It was a very thin layer. He pointed out that he was interpreting the effect entirely in terms of the dipole which existed in the isolated molecule. He added that, the previous day, Iwamoto's paper had demonstrated electron transfer between a substrate and a molecule on its surface, and presumably that would be an additional effect, though its magnitude had not been estimated in this context. Petty said there was another reason for using very thin layers in addition to using them to change the work function. On moving from a

Schottky barrier to a metal–insulator–semiconductor structure the Fermi level in the metal became able to move with respect to the band structure of the semiconductor, which was not possible at a Schottky barrier. Provided the film was thin enough, injection of one type of carrier or the other could thus be enhanced. Willis took up this point and said he had been quite surprised to obtain such a large improvement using Al as electrode but not with a magnesium/silver electrode. He explained this in terms of the distribution of field in the device. The oxide-coated aluminium electrode was not a particularly good electron injector and formed the most resistive part of the device. When the voltage was applied, the field concentrated there and increased non-linearly, leading to increasing electron injection until eventually the field shifted across to the less resistive electrode, inducing hole injection and the onset of electroluminescence. That was why aluminium had the best effect. Shirota commented that he thought this result provided very important information that in this device the minority carrier was the electron, and the SAM changed the distribution of the strength of the internal electric field, increasing the field in the AIQ layer and enhancing the electron injection. He asked if this could be controlled by, for example, changing the thickness of the AIQ layer. Willis agreed that control of the onset of the second carrier was crucial.

Bartlett asked whether the field distribution had been measured experimentally in these systems. One approach would be to make one electrode much smaller than the other. For example if one made the Al electrode 1 cm² but the ITO electrode a few μm², the current–voltage characteristic would be entirely dominated by the processes at the smaller electrode. Reversing this would similarly permit study of the rate of electron transfer at the other electrode. Willis replied that the influence of the electric field on some spectroscopic properties had been studied. Some probes were therefore available. Holmes said that the Philips group had studied the processes at one interface by changing the work function enormously at the other, but had not used SAMs. Petty said that the field distribution in even the simplest of these devices was still the subject of debate. Possible models included Schottky barriers at the metal–organic interfaces, Fowler–Nordheim tunnelling, space charge injection, *etc.* No single model was yet accepted.

Holmes emphasised the importance of electrode surface coatings in levelling the often very rough surfaces of materials such as ITO. Willis said that in practise there were severe constraints on electrode materials, because one had to be transparent and conductive while the other had to have a very low work function and hence tended to be unstable. He reported Kelvin probe measurements which showed that the use of UV ozone to clean ITO electrodes gave an effect which proved to be temporary on exposure to air.

Turning to Petty's paper, Holmes asked what were the advantages of the LB film approach. Petty replied that industrial semiconductor manufacturers were reluctant to get involved with wet processes like dip coating or LB methods. Jung showed data indicating that LB films gave smaller currents, but a similar quantum efficiency, than spun films for a given voltage. The problem for LB films was that the films seemed too ordered and this limited the current. Holmes asked what solvent was used for spin coating, and Jung said he had used chloroform; Holmes pointed out that this usually contained significant amounts of HCl, which might lead to ionic conductivity contributions.

Willis commented that film thickness and uniformity was crucial. Variations in thickness gave variations in brightness, current, temperature and degradation. He asked whether LB or spun films were the smoother. Jung said in his opinion spun films were smoother, and the film thickness uniformity was within 10%. Petty pointed out that there were many effects of

changing film thickness, so that a 10% change in film thickness could lead to a doubling of current.

Session VIII—Chairman: Professor G. J. Ashwell

Condensation of organic vapours within nanoporous calixarene thin films, A. V. Nabok, A. Hassan and A. K. Ray (p. 189)

Optical transduction of chemical sensing by thin films of organic reagents and molecular receptors using piezo-optical and surface plasmon resonance methods, J. D. Wright, C. von Bültzingslöwen, T. J. N. Carter, F. Colin, P. D. Shepherd, J. V. Oliver, S. J. Holder and R. J. M. Nolte (p. 175)

Vapour sensing using hybrid organic–inorganic nanostructured materials, S. D. Evans, S. R. Johnson, Y. L. Cheng and T. Shen (p. 183)

The final session contained only two papers but many useful points were developed (the article by Evans *et al.* was prepared for the meeting but not presented). Nabok's paper was covered first, and Willis opened by asking if water vapour was present. Nabok said it was, but calixarenes were very hydrophobic, so water could not penetrate inside the cavities. Ziegler asked if any TDS measurements had been made to see if there was only one adsorption site. Nabok replied that he had not done this, and that he had no information on where the solvent was located in the film—it could be between the baskets or between hydrophobic chains. Some film swelling was observed. Taylor asked for some clarification of the SPR measurement methods used, and Nabok said he had used mainly fixed-angle measurements—although he had made some measurements of complete curves and done modelling to extract film thicknesses and refractive indices (which were sometimes difficult to separate). On injection of vapour a sharp response was observed then a decrease and stabilisation. On flushing with clean air there was fast recovery. The odd effects at the beginning were due to the way the vapour was injected with a syringe into the chamber. Saturated vapour gave a large peak, reducing on dilution. Using a continuous vapour flow system he saw no peak, just a fast step response and recovery. Metzger asked if the response in Fig. 3, with an initial peak followed by a drop to a steady lower value, could be due to an initial binding at only some of the calix sites followed by a redistribution over all the sites in the film. Nabok agreed, and said that at high concentrations there was accumulation on the surface followed by a redistribution. From the QCM data it was possible to calculate how many molecules were adsorbed, and this was much higher than one per calix, so swelling was expected.

Bartlett said the linear calibration curve in Fig. 2 was inconsistent with the proposed capillary condensation model because pores of just one size should give a function with a step at the pressure where capillary condensation occurs, since this was an equilibrium measurement. The only way the model could give a linear response was if there was a logarithmic pore-size distribution. Nabok said he believed there was a distribution of pore sizes, due to different cavities between molecules on the surface. Hillman said the absence of hysteresis also suggested that capillary condensation was not occurring. Nabok replied that in fact it was not a simple equilibration, since the vapour was injected suddenly. Using a vapour generator and changing the concentration in a continuous flow would be needed for such studies.

Nabok was asked whether repeated exposure and drying cycles of the LB films in solvent vapours led to any change in film structure as the process resembled a 2-dimensional recrystallisation. He replied that he had not done any structural studies or long term stability tests with repeated cycles for longer than two days. Jones said that neutron reflection would

give the overall thickness of the films as they swelled, any Bragg peaks from the layered structure would also come out, and if the gases were deuterated the number of molecules per unit volume of the film could be deduced—which was an expensive way of measuring an adsorption isotherm using neutrons! Any clustering in the layers would also be very clear in the neutron data. Nabok said he had only used X-ray diffraction, but saw at best only one broadened Bragg peak.

Wright was asked whether there were any problems with the polystyrene sulfonate competing with the phenols for the viologen sites. He replied that he had not seen any such effect but had not explored different types of counter-ion polyelectrolyte, *e.g.* different chain lengths. It was suggested that polyvinylsulfonate would be a good alternative as it had no benzene ring which might be involved in competing π – π interactions. Wright agreed that this might affect the speed and magnitude of the response and said he would like to increase the response speed. Whether the slow response was due to a low equilibrium constant for binding of phenol by viologen or related to the porosity of the matrix was not yet known. Matrix effects were extremely important. One effect of small pores in the matrix was condensation, as already demonstrated in Nabok's paper, but there were other effects. The solvent structure could be changed within the pore, influencing the whole thermodynamics of the reaction, for example entrapped metal complexation reagents showed very different selectivity for different metal ions from that of the reagents in aqueous solution.

In relation to the selectivity of the viologens for different phenols, Russell asked if they would respond to chlorophenol. Wright replied that many different phenols were detected but with different sensitivity. There was some evidence for trends. Two or three hydroxyl groups on the same side of the molecule led to greater sensitivity than just one, and detection of polyphenols was more sensitive than monophenols. He hoped that by using modified receptors such as the viologen-substituted cyclodextrin, different selectivity patterns could be obtained in future. However, since there was a need to detect all phenol-type pollutants in water, a generic method responding to some extent to many phenols was still useful.

Russell then asked how to optimise the thickness and wavelength in SPR to obtain the maximum sensitivity. Wright replied that in relation to wavelength, if there was a spectroscopic change on binding the analyte, the choice of wavelength became important. He illustrated this with data from films of 18-crown-6 substituted phthalocyanine exposed to NO_2 . Depending on the wavelength in relation to spectroscopic changes induced by the gas, either just a change of depth or changes in both depth and position were observed. If films swelled, fast changes in depth followed by slower changes in position had been observed, which had been interpreted as fast surface adsorption followed by slower bulk diffusion. In principle it would be possible to get a curve that went up and then down again, as seen in Nabok's paper, from such effects. (However Wright said he believed Nabok's suggested interpretation of condensation was more likely in that case.) Ideally full SPR curves should be recorded in real time using a CCD system during exposure to the analyte, and the data repeated for a series of wavelengths across the spectrum to determine the optimum fixed angle and wavelength. Concerning film thickness Russell asked how thick were the spun films, and was the observed slow response because of diffusional problems through the film? Wright replied that the film thickness was rather less than 1 μm , though he did not have an exact value. This work involved SPR in liquids so the resonance was much broadened, and it was necessary to be careful not to have too thick a film or the resonance became too broad to be measured reliably. Films were deposited with fast spin speeds, typically 8000 rpm, and in practice it was difficult to spin thinner films while still maintaining film coherence and uniformity. The evanescent field decayed exponentially from the metal surface,

and extended outward for of the order of one wavelength—*i.e.* several hundred nanometres, so most of the film thickness was probed by the field. Certainly there would be some diffusional limitation within this thickness, and from that point of view, the thinner the film, the better. But there was an optimum, determined by a compromise between being thick enough for good sensitivity and thin enough not to suffer too much diffusional limitation. He believed a monolayer was not optimum, because although the evanescent field was strongest at the surface, a monolayer did not give the full available response sensitivity.

Russell suggested it would be useful to do a study of sensitivity and response speed for a series of films of different thickness, perhaps LB films with different numbers of layers, to establish the optimum. Petty suggested that this might be done theoretically also.

Wright said another approach to optimising sensitivity was to modify the SPR measurement technology rather than optimising film parameters. He showed a modification of the normal SPR system, developed by Nikitin, in which the coupling of light was achieved by a grating instead of the usual prism. If the grating was made of silicon and coated with gold, at the resonance angle light was absorbed into a Schottky barrier, and a photovoltage developed between the silicon and the gold. This could be used to measure the SPR, leaving the reflected beam for other purposes, one of which was surface enhanced Raman spectroscopy. AFM showed the grating surface was rough, favouring enhanced Raman, and data were shown for SPR and Raman changes measured on the same phthalocyanine film on exposure to NO_2 . The other thing that could be done to increase sensitivity was to incorporate the SPR cell into an interferometer, because there was a phase change associated with SPR as well as the absorption of the light. In this way, refractive index changes as small as 4×10^{-8} could be measured, permitting measurement of very small concentrations using biological films. The potential problem with this system was sensitivity to thermal drift.

Ashwell asked about work in which Nikitin and Wright had reported seeing SPR changes when uncoated gold films were exposed to NO_2 . He said he had seen the same thing but could not reproduce it, so thought it was connected with the surface structure of the gold film. Wright replied that he had tried different ways of making the film, using different conditions and even different metal sub-layers, and did it both in Moscow and in Canterbury, and found the same results. Bartlett suggested this might be due to oxidation of the gold surface. He said that electrochemical oxidation of gold led to a surface oxide. His recent experiments with planar waveguide structures showed large optical changes following this oxidation. Wright replied that it was worth exploring but that he did not have the surface analytical facilities to check this. Etchenique commented that putting NO_2^- on gold can lead to etching. He had used this to clean the gold on QCM devices, and had seen from the change in frequency that one or two monolayers of gold atoms were removed.

Willis said that in the described variant of photoacoustic spectroscopy, Wright said quite restricted conditions were used—a fixed chopping speed and a fixed illumination frequency—but he had hinted that there was a lot more information available which was not being used, and it seemed that there was a lot of potential here for the study of films and sensing. One could in principle study the spectroscopy of optically opaque films, but one could also study rates of penetration of dopants for sensing, and also surface degradation of films. He wondered if Wright could say more about the limitations of sensitivity and wavelength range, *etc.*

Wright replied that he had altered the chopping frequency and looked at the shape of the response signal for some model systems which simulated some of the situations described by Willis. For example, he had taken a colour filter and put

decreasing numbers of transparent layers between it and the piezopolymer, so as to simulate the approach of a colour front to the actual sensing region. As expected, if the coloured layer was far away from the piezofilm, two things were seen. First there was a time lag between the time the light flashed and the generation of the piezosignal, because the heat was generated far from the surface and it had to come back before the stress could be generated, and secondly the response was smaller—heat could not pass through an infinitely thick object—it was damped out, as in insulation. Hence if colouration was non-homogeneous, the progress of the reaction front could be followed by looking at the increase in signal and change in phase lag in the lock-in amplifier. It was important to optimise that phase lag. For the case of uniform colouration of increasing depth for a completely uniform reaction within the spot, sometimes the shape of the response changed. A very intense colour led to a very sharp leading edge on the pulse as the heat developed very quickly; weaker colouration allowed deeper penetration of the light and a more gradual rise of the curve. There was an optimum chopping frequency: if the light was continuous there would be an initial rise but then no further change of stress so no further signal, so as chopping frequency decreased to zero the signal tended to zero: if chopping was too fast the leading edge rise of the signal was probed, resulting in a smaller signal. Concerning changing the wavelength, one must choose strongly absorbed light, and as the signal was quite small high-intensity LEDs were required, which fortunately were now available quite cheaply.

Nabok asked, in connection with the heat transfer, was the spot in direct contact with the PVDF? Wright replied that it was, and that this did limit the chemistry to some extent, because some things (*e.g.* acids) degraded the conducting ITO coating on the PVDF. In fact, for all the reagent spots so far studied, no serious phase lags had been seen because the spots were thin and heat reached the PVDF very quickly, and there was no evidence for non-uniform colouration. Nabok then asked if there were any effects of heat reaching the film directly from the LED. Wright said the LED outputs, which could vary by $\pm 25\%$, were normalised by first measuring the signal from a black coated PVDF film. Also, a laminated bimorph of PVDF was used, with two layers poled in opposite directions, so that any ambient temperature fluctuations were cancelled out. The spot was however only on one side of the bilayer so did give a signal when illuminated through the transparent ITO-coated PVDF film.

Metzger commented that the badge was exposed for a while then measured. He asked how quickly the signal developed if one wanted to measure *in situ*, and what were the prospects for producing a miniaturised portable measuring system to be worn with the badge?

Wright answered that the speed with which the colour developed depended on how the spot was made. Normally they were made to span a sensible calibration range over the 8 hour time-weighted-average exposure, but for glutaraldehyde, where there was a 15 min TWA exposure limit of 50 ppb, it was necessary to develop a spot which responded very fast. That had been done, and many hospitals were using that since it was one of the few ways capable of measuring 50 ppb of glutaraldehyde over such a short period. Problems of timing, which occurred since the exposure was not always exactly 15 min, were solved by reading the badge before and after use and the reader had an internal clock which allowed correction for the exact exposure time. Concerning miniaturisation, in principle this was possible, but in practice it might not be competitive with other sensor technologies. The small signals needed a great deal of amplification, and the electronic noise problem was difficult in a small portable configuration—not impossible but perhaps difficult enough to raise the question of whether it could be competitive. The question of competitiveness must always be addressed when choosing between different sensors.