

## **Final Report: GR/R40333.**

### **AEROFED: An evaluation of a Research Opportunity to Realise a Low Voltage, Field Emission Display for use as a multifunctional Avionic Flat Panel.**

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This grant provided part funding for a four centre collaborative project involving Smiths Industries Aerospace (lead industrial partner), Brimar Ltd., and the Universities of Bristol (Chemistry and Physics) and Bath awarded under the Optical Systems of the Digital Age (OSDA) LINK programme. Progress was severely compromised by the withdrawal of Smiths Industries in spring 2003, and their release of employee and project co-ordinator, Dr N.A. Fox. Subsequent negotiations with the DTI, though time-consuming, ultimately led to the release of a further funding stream that provided one years salary for Dr Fox to continue (mainly in Bristol), and a project restart on 1/9/03 (albeit with somewhat re-defined objectives) – with Brimar now acting as lead (and sole) industrial partner.

The original and the revised objectives of the complete package of work are detailed on the IGR form. Bristol's targets within the programme were:

- research and materials characterisation to develop laser induced nanodiamond (ND) doping and activation treatments to enable processing of large arrays of diamond pixel emitters;
- novel encapsulation techniques and material processing of candidate phosphors to improve low voltage performance, and establish the physical nature and electronic properties of the interfaces between material layers;
- the development of a suitable vacuum packaging solution to enable the field emission device (FED) components to be assembled to operate in a stable, reproducible ambient environment;

Resources granted by this award were two years PDRA funding, partial support for Mr John Rowden, the glass workshop technician in Physics, a contribution towards the cost of a new vacuum chamber associated with the pulsed excimer laser ablation (PLA) / deposition (PLD) experiment and upgrades to an existing field emission test station in Chemistry, and consumables costs. The PDRA appointed to the project, Dr Simon Henley, worked in Bristol through the period 9/01–8/03, focussing particularly on PLA/PLD opportunities and materials characterisation. He subsequently accepted a second PDRA position in the group of Prof. Ravi Silva at the University of Surrey. Other Bristol contributors to the programme, or to related activities, included Mr Owen Evans (Ph.D. CASE student, supported by Smiths Industries, on a project focussing on SEM and TEM analysis of phosphor materials in the group of Prof Cherns) and Mr Lamine Bougueroua (Physics M.Sci. undergraduate, whose industrial placement year was spent with Brimar, modelling FED packaging (using finite element analysis methods)). We can report substantial progress towards all of the above objectives.

### **Production, characterisation and evaluation of Rival Emitter Materials**

Initial activities centred upon investigations of a range of potential emitter materials. Bristol focussed particular attention on doped and undoped ND samples and ZnO, while other non-carbon materials such as LaB<sub>6</sub> and AlGaN were investigated at Bath. Commercially available ND powders (from Microdiamant and from De Beers) emerged as the front-running emitter material, and a variety of post-processing strategies for enhancing its emissivity were explored. PLD methods were used to deposit nitrogen doped diamond-like-carbon,<sup>1</sup> boron nitride, MgB<sub>2</sub>, LiF,<sup>2,3</sup> and doped<sup>4</sup> and undoped<sup>5,6</sup> ZnO films. Each process was investigated and characterised in some detail, by studying optical emission from the ablation plume and/or by applying a range of analyses to the deposited material.

Carbon nitride (CN<sub>x</sub>) overcoatings – here formed by 193 nm PLA of graphite in low background pressures of N<sub>2</sub> – have been reported to enhance the emissivity of carbon emitters. We were unable to confirm previous reports regarding the electrical characteristics of this material, however. Spectral analysis of the optical emission accompanying the PLA process revealed the presence of C<sup>+</sup> ions, C atoms, C<sub>2</sub> and CN radicals and N<sub>2</sub><sup>+</sup> molecular ions within the plume of ejected material. Films

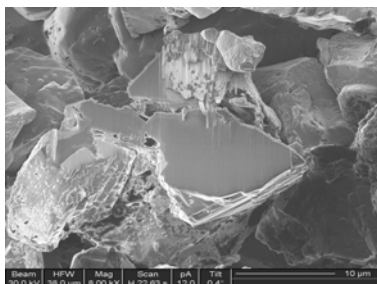
deposited at low substrate temperatures ( $T_{\text{sub}}$ ) were found to be amorphous, with N/C ratios  $\sim 20$  at.%. Raman analysis showed that  $\text{CN}_x$  films grown at higher  $T_{\text{sub}}$  were increasingly nanocrystalline. X-ray photoelectron spectroscopy (XPS) revealed that  $\text{CN}_x$  films grown at higher  $T_{\text{sub}}$  also had less overall N content. Such observations were rationalised<sup>1</sup> by assuming an increased propensity for sputtering or desorption of more labile CN species from the growing film surface at elevated  $T_{\text{sub}}$ , resulting in a higher fraction of C–C bonding – probably in the form of graphitic nanocrystallites embedded in an amorphous matrix. Electron emission from these films was found to be irreproducible, however, and this activity was shelved quite early in the project in order that we might concentrate on coatings involving lithium compounds or ZnO.

LiF coatings were investigated in the expectation that they might lower the effective workfunction for electron emission from a diamond surface. Thus the morphology, composition and crystallinity of LiF thin films grown on both silicon and quartz substrates by 193 nm PLA of a LiF target were examined and deposition parameters for optimal growth suggested. Hydrodynamic sputtering was shown to be the dominant mechanism of material ejection from this ultra-wide bandgap material, at high laser fluences. Mounting the substrate off-axis from the ablation plume (*i.e.* at  $\sim 60^\circ$  to the target surface normal) was shown to yield deposits with the correct (*i.e.* 1:1) Li:F ratio, fewer asperities, and a much improved film morphology.<sup>2</sup> Coatings deposited at  $300^\circ\text{C}$  onto thin film, undoped diamond cathodes were tested for field emission at Bath and found to emit current at reduced turn-on voltages, but their conductivity was rather disappointing, with significant charging and arcing occurring during operation. Nonetheless, these findings served to trigger much subsequent work and the eventual selection of Li doped commercial diamond dusts as our emitter material of choice. Subsequent PLA studies of LiF at 248 nm, using ps and fs laser pulse durations at the UV laser facility at FORTH, Heraklion, have served to highlight the advantages of fs ablation (from the viewpoint of minimising the density and size of unwanted droplets in the deposited film), and the extreme perturbation of the optical emission spectrum by radiation trapping within the ablation plume.<sup>3</sup>

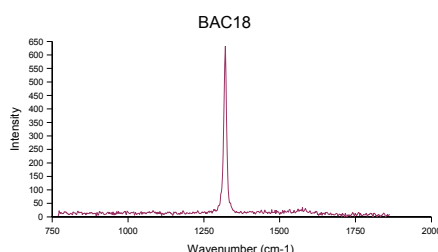
Insulating and conducting ZnO films were investigated because of their potential use as, respectively, gate dielectric layers and as transparent conducting layers (*i.e.* an alternative to indium tin oxide, ITO) in the faceplates of prototype FED devices. Undoped ZnO films, and Al- and Ga-doped ZnO (AZO and GZO) films, were thus grown on sapphire, Si and NaCl substrates by 193 nm PLA of targets of, respectively, ZnO, ZnO+2%(by wt.) $\text{Al}_2\text{O}_3$  and ZnO+5%(by wt.)Ga, in low background pressures of  $\text{O}_2$ . All samples demonstrated improved crystalline quality with increasing  $T_{\text{sub}}$ , as evidenced by the full width half maxima (FWHM) of the ZnO (0002) rocking curve and the (0002)  $2\theta$  peak in the respective XRD spectra. The best crystallinity was observed for undoped films deposited at  $T_{\text{sub}} \geq 300^\circ\text{C}$ . Such films have since been used as templates for subsequent growth of ZnO nanorod arrays by both PLD<sup>7</sup> and hydrothermal methods.<sup>8</sup> Addition of Ga or Al resulted in conducting films. Multi-wavelength ellipsometry provided a reliable means of determining film thicknesses which, in turn, enabled determination of the absolute resistivities,  $\rho$ , of the as-grown ZnO films. AZO films deposited at the highest  $T_{\text{sub}}$  then attainable ( $\sim 450^\circ\text{C}$ ) gave the lowest values ( $\rho \sim 9.7 \times 10^{-4} \Omega \text{ cm}$ ); AZO films grown at  $25^\circ\text{C}$  exhibited  $\rho$  values some  $4\times$  larger.<sup>4</sup> The best resistivity values obtained for GZO films were somewhat larger ( $\rho \sim 1.6 \times 10^{-3} \Omega \text{ cm}$  for material grown at  $T_{\text{sub}} = 450^\circ\text{C}$ );  $\rho$  values for GZO films deposited at  $25^\circ\text{C}$  were some  $100\times$  larger. Thus we concluded that, though Ga is reportedly the better dopant for producing high quality *n*-type ZnO, doping with Al may be more viable economically given the lower process temperatures that can be used and the more reproducible conductivities that can be achieved. The resistivity of AZO is still too high to be used as an efficient injecting layer for emitter cathodes, but it should be a compatible material for use with phosphor screens – to improve their conductivity. For this application, the thin film material would be deposited at the highest glass-compatible temperature (*e.g.*  $420^\circ\text{C}$  or  $640^\circ\text{C}$  for lead glass or borosilicate, respectively) so as to obtain the lowest resistivity. The aluminised phosphor layer would be fabricated on top of the AZO film. Electrical connections to the phosphor layer could then be made via the AZO film, thereby obviating the need to make direct connections to the perforated aluminium coating on top of the phosphor layer.

PLD is not suited to the deposition of uniform coatings over large areas. As the present work illustrates, however, the technique allows rapid investigation of a wide variety of depositions and process conditions (*i.e.* target material and composition, substrate material,  $T_{\text{sub}}$ , presence or otherwise of any background gas, and its pressure). The LiF PLD studies led to our focussing on lithiated ND as the emitter material of choice, while the ZnO PLD results stimulated investigations of larger area deposition of ZnO films using the Nordiko Ion Beam system in Wang's group at Bath.

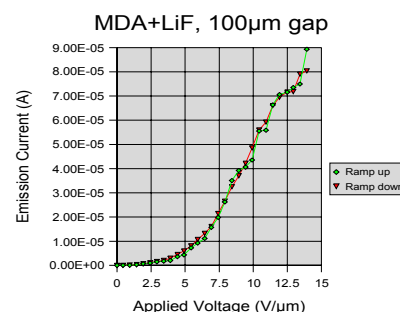
Thin films of commercial undoped ND powders were deposited on conducting substrates, hydrogenated by exposure to an H<sub>2</sub> plasma in a microwave CVD reactor, and then subjected to electrical and field emission measurements in order to provide a benchmark for emission measurements involving metal-doped ND powders. Thermal diffusion, ion plating and spray pyrolysis were then each evaluated as potential routes for infiltrating Li (in the form of LiF) into commercially available ND powders. The first two methods were implemented experimentally. Thermal diffusion – whereby the diamond powder is ball-milled with LiF, then heated, in steps, to 1100°C in vacuum – was found to be more reproducible, and to be more amenable to scale-up (to yield the 1-5 g quantities necessary for making test devices). Material was ultimately produced from three grades of processed diamond powder: ND (<10 nm grain size), and micron size powders with typical grain sizes in the ranges 1.5-2.5 μm and 15-25 μm, respectively. ND showed a tendency to agglomerate under processing, but all of the processed powders were found to be highly conducting (volume resistivity ~15.7 Ω cm for the ~2 μm material, *cf*  $7.8 \times 10^{13}$  Ω cm prior to lithiation) and emissive. UV (325 nm) Raman spectroscopy showed the post-processed material to retain a strong diamond signature, with no significant conversion to non-diamond phases and little visible photoluminescence. Figs. 1 – 3 show illustrative results.



**Fig. 1** Fast ion beam sectioning of a 20 μm lithiated diamond crystal.



**Fig. 2** 325 nm Raman spectrum of doped diamond powder sample.



**Fig. 3** I/V plot for lithiated diamond film.

The fabrication of emitter cathodes requires a reliable method of depositing such lithiated diamond particles, uniformly, and at sufficient density, across operationally useful (>1 sq. in.) areas. Both dusting and ink-jet printing methods were investigated in Bristol, while industrial partner Brimar explored spin-coating strategies also. Of the two former methods, dusting has produced much higher particle densities on metal- (*e.g.* Al-) patterned glass substrates and, with the best (~2 μm grain size) Microdiamant samples, current densities well in excess of the 100 μA cm<sup>-2</sup> that would be required for successful phosphor illumination. Such performance has been achieved with demountable samples, using the field emission test station in Chemistry. Attempts to replicate these emission characteristics from cathode structures operating in a vacuum environment with a 5 kV phosphor screen proved problematic, however. The first such bottle tests highlighted several shortcomings in the test procedures, which necessitated a reappraisal of the methods used in conditioning the bottle parts for vacuum operation, and the development of more reliable electrical contacts within the bottles. Bottle tests thereafter showed improved reproducibility, with the best operating as diode devices and generating >10 μA cm<sup>-2</sup> at applied fields of <10 V μm<sup>-1</sup>, but this current is seen to be unevenly spread across the area of the cathode as a result of the low density of stable, active emission sites.

### Processing of candidate phosphors to improve low voltage performance

FEDs can utilise cathodoluminescent (CL) phosphors developed previously for CRT-based TV

displays. The operation of a FED differs from a CRT, however, in that it uses an array of addressable e-beam sources operated in a line modulated mode rather than a scanning e-beam spot to illuminate phosphor pixels. The accelerating voltage applied to a TV screen is usually  $>20$  kV, to take advantage of the more favourable CL conversion efficiency ( $\sim 20\%$ , P22; ZnS family). To achieve the desired display luminance on a TV tube the e-beam gun delivers up to  $1 \mu\text{W}$  to each phosphor pixel in a dwell time of 250 ns. Such short dwell times ensure that the phosphor pixel experiences little heating and is not damaged. In contrast, an FED with the same resolution and screen diagonal would require at least twice the beam current, and a  $100\times$  increase in dwell time if it is to operate with the same luminance at the desired anode voltage of 5 kV. If these requirements are not met, the emitter array will not deliver the same level of excitation energy to each phosphor pixel. The longer dwell time and higher current requirement will accelerate the degradation of the phosphor material, and reduce the operating lifetime of the device. To circumvent this problem, the phosphor can be given further protection – either by increasing the thickness of the Al film deposited on the phosphor, or by incorporating an additional encapsulating material layer. However, a thicker Al layer will lead to greater absorption of the 5 kV electrons, less penetration into the phosphor layer, and hence reduced phosphor efficiency. FED developers have proposed use of an electron transparent, encapsulating film of a wide band-gap material (*e.g.* AlN, SiO<sub>2</sub>) as a possible means of protecting the phosphor. To establish the usefulness of such encapsulation to the present project,  $\sim 10$  nm thick layers of AlN were deposited onto both aluminised and non-aluminised phosphors by PLD, and then sent to Brimar for evaluation. AlN overcoating was determined to be very beneficial: the coating process caused no change in the phosphor efficiency, and slowed the aging characteristics. This test established that an AlN film could be a simple means to stabilise a FED phosphor screen against rapid degradation under high beam current densities. Inclusion of such a film is likely to have the added benefit of being an effective physical barrier that limits the mobility of compounds evolved from the phosphor layer into the vacuum.

#### Development of a suitable vacuum packaging

Emitter structures were fabricated on lead glass discs supplied by Brimar. Lead glass was selected because it was a standard stock item used for fabricating miniature CRT faceplates, and also suitable for inclusion in the test bottle, being compatible with all other component parts. Figure 4 shows a completed test bottle under test. Emitter cathodes 2 cm in diagonal were prepared with the various grades of doped ND and assembled with aluminized P15 or P43 phosphors having an integral stand-off of  $500 \mu\text{m}$ . The bottle design was revised a number of times to incorporate modifications made to the construction and support of the anode and cathode plates, and the electrical contact to them. The configuration of the getters and pumping ports was also altered to allow bottles to be heated and bombarded at  $250^\circ\text{C}$  while running an air discharge, or a cleaning gas, and finally vacuum pumping to eliminate residual contaminants. The pin-out for the diode bottles was standardized so as to be plug-compatible with a valve base connector integrated into pulsed dc test equipment built and tested in Physics. This equipment has been used to operate all completed bottles.



**Fig. 4** Bottle testing using a pulsed DC diode test kit

#### Development of suitable gated emitter structures.

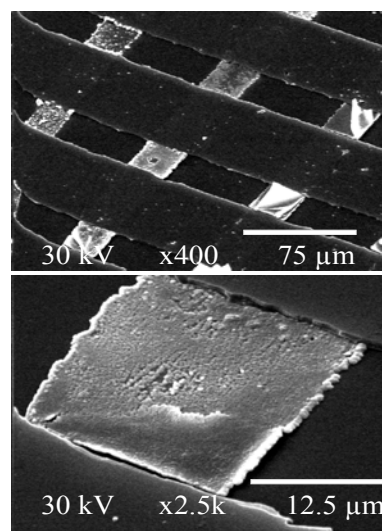
Though not part of the original Bristol remit, this work package was taken on by Bristol with the transfer of Dr Fox from Smiths. Gated cathode emitter structures were fabricated on lead glass and borosilicate discs. Several thin film material combinations that could serve as the  $1 \mu\text{m}$  high cathode-insulator-gate stack were evaluated. A multi-layer composed of nichrome, aluminum, silicon dioxide and aluminium was first investigated. A spin-on dielectric (Nanoglass E (NGE) from Honeywell) was

used for the SiO<sub>2</sub> layer in some of these structures, but found to be too fragile. Thus a thin film metal-dielectric-metal material stack that could be deposited in an available Balzer 510 system was adopted for all subsequent work. The evaporable dielectrics routinely used in this system are silicon and titanium monoxides, both of which exhibit good adhesion to glass and nichrome. A structure composed of a nichrome cathode (30 nm), a silicon monoxide/ titanium monoxide insulator layer (950 μm) and a nichrome gate (30 nm) was thus tested. The electrical tests yielded an average pixel capacitance of 0.19 pF for a 0.96 cm<sup>2</sup> array containing 15,862 gate structures. The nichrome address lines had a sheet resistivity of 30Ω/□.

Establishing a procedure for placing the emitter material selectively onto the gated electrode structures while avoiding electrical shorts between the cathode and gate has proved challenging. The shorts are caused by conductive particle clusters, >10 μm in diameter, that are present in the printable suspension. Comparing the quality of printed dots produced using a commercial polishing suspension and the doped ND powder led us to conclude that formulation of the doped ND material into an agglomerate-free, printable 'ink' would require the help of a specialist, commercial company. Several companies were approached, but none were able to offer a solution within the timeframe of the project.

Two alternative plating methods were thus identified and developed. The first was an electrodeless, silver-plating solution based upon the Brashear process, which was modified to incorporate the lithiated diamond powder. This method is quite wasteful with regard to material, and does not provide a means to plate onto patterned structures selectively, but it is a very straightforward process for forming large area, conformal coatings on glass and metal structures. The Brashear process relies upon substrate cleanliness and rigorous agitation to obtain a good quality coating. To consolidate the coating on glass a vacuum bake is required. This method was found to work well for sub-μm diamond powders and the incidence of clusters could be limited by the degree of agitation during coating. The method was thus used to form thin films containing a large density of doped particles. Coatings on glass and on Ni wires were produced and analysed. The coatings on the wires were evenly distributed and were deemed to be suitable for a gated emission test in a bottle. This device has now operated continuously for >3 months without any sign of degradation. To make this plating method selective, we can envisage a situation where the components of the plating solution could be formulated as two printable 'inks', to be dispensed from an inkjet onto a metal-patterned substrate. A solution containing the activator solution would first be dispensed onto the pixellated, metal areas, which would then be over-printed with the second ink, containing the ND and the metal salt.

The second plating method employed a commercial nickel electro-plating solution, into which the ND material was dispersed (by sonifying for several hours). It allowed selective plating of metal and diamond onto metal-patterned structures. A gated line structure was adopted, with the cathode linewidth smaller than that of the gate lines. Gated cathode arrays containing areas of exposed nichrome cathode lines were plated with ND and nickel. SEM (see fig. 5) confirmed selective deposition onto the metal cathode, but also revealed partial delamination of the plating layer from the nichrome, and unevenness in the plating layer thickness. Plating nichrome alloys is known to be more challenging than plating pure nickel, but formulations are available to circumvent this.



**Fig. 5** SEM analyses of electro-plating tests with doped ND. Top: illustration of particle clustering, variable density coating and delamination effects in three adjacent pixel lines. Bottom: example of the desired film morphology for a selectively plated pixel area.

## Research Impact, and Further Research and Dissemination Activities

Work supported by this grant was described in a number of presentations at international conferences (e.g. COLA'03 (Crete, 2003), the 30th International Conference on Metallurgical Coatings and Thin Films (San Diego, 2003) and the 14th European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, Nitrides and Silicon Carbide (Salzburg, 2003)) and at several national meetings.

The project has not realised a prototype display device, but has generated technology demonstrators in the form of test bottles and a significant knowledge-base on the diamond emitter material and the processes required to fabricate, test and package it in a FED device. The lithiated ND material has been shown to offer improved operational stability in bottle tests and has been patterned selectively into gated structures by novel printing and plating methods. Both methods should be readily scalable to large display panel sizes and resolutions. The maximum current density recorded with BAC18 at 5 V/ $\mu\text{m}$  was 400  $\mu\text{A}/\text{cm}^2$  for a 1 mm<sup>2</sup> pixel emitter. Achieving the original target figure (100  $\mu\text{A}/\text{cm}^2$ ) with this material would require an extraction field of just 2V/ $\mu\text{m}$ . The output luminance of the screen is determined by the efficiency of the phosphor. Based upon the results on phosphor test bottles, P53 (green) produces a luminance of 2000 cd/m<sup>2</sup> at 5 kV when irradiated with an e-beam current of 100  $\mu\text{A}$ . The area illuminated by the e-beam in these tests was  $\sim 6.5$  cm<sup>2</sup>. The current density may thus be estimated at  $\sim 15$   $\mu\text{A}/\text{cm}^2$ . The desired output luminance of 6000 cd/m<sup>2</sup> could easily be achieved using this phosphor simply by choosing a different particle size of phosphor material and/or adjusting the thickness of the Al backing layer. Tests on the phosphor (by Brimar) show this to be feasible, without having to raise the accelerating voltage or the emission current drawn from the emitter cathode. Throughout, the project the metrics that have been hardest to achieve (with a diode device) have been the active emission site density and the related metric of luminance uniformity – a problem that can be traced directly to the lack of control of the surface morphology. Surprisingly, the inkjet printed emitter films turned out to exhibit the poorest control. The incidence of agglomerated, doped ND particles was unacceptably high (typically  $\sim 2$  per 10  $\mu\text{m}^2$ ). The hybrid electroplating techniques investigated towards the end of the project offer the most promising route to controlling the surface morphology of the deposited ND films.

Had more project time and manpower been available, there is little doubt that the pre-fabricated gated emitter arrays could have been furnished with BAC18 material using the plating method to enable preliminary testing of 1 cm<sup>2</sup> emitter pixels containing >15000 addressable sub-pixels. With Brimar's consent, Bristol have taken steps to protect the intellectual property generated by the project on ND emitters. A PCT application was filed on 29/8/04 in which the method of making lithiated ND emitters was disclosed. Efforts to exploit the IP were initiated in the last quarter of the project by the Research and Enterprise Department (RED) unit at University of Bristol. The goal of this exercise is to fund a second phase of development that will culminate in the fabrication of a 15" diagonal, high definition display device that utilises the ND emitter material developed by the AEROFED project. To this end, a contract has been drawn up between Bristol University and Advance Nanotech (a US-based investment fund) to pursue a 2-year, £1M development project to realise a FED prototype.

## Publications arising from the project

- <sup>1</sup> G.M. Fuge, C.J. Rennick, P.W. May and M.N.R. Ashfold, *Diamond Rel. Mater.* (2003), **12**, 1049.
- <sup>2</sup> S.J. Henley, M.N.R. Ashfold and S.R.J. Pearce, *Appl. Surf. Sci.* (2003), **217**, 68.
- <sup>3</sup> S.J. Henley, G.M. Fuge and M.N.R. Ashfold, *J. Appl. Phys.* (in press).
- <sup>4</sup> S.J. Henley, M.N.R. Ashfold and D. Chems, *Surf. Coat. Technol.* (2004), **177-8**, 271.
- <sup>5</sup> F. Claeysens, A. Cheesman, S.J. Henley and M.N.R. Ashfold, *J. Appl. Phys.* (2002), **92**, 6886.
- <sup>6</sup> S.J. Henley, M.N.R. Ashfold and D. Chems, *Thin Solid Films* (2002), **422**, 69.
- <sup>7</sup> Y. Sun, G.M. Fuge and M.N.R. Ashfold, *Chem. Phys. Lett.* (2004), **396**, 21.
- <sup>8</sup> S.J. Henley, M.N.R. Ashfold, D.P. Nicholls, P. Wheatley and D. Chems, *Appl. Phys. A.* (2004), **79**, 1169.

PCT Patent Application filed 29/8/04: Field Emitter - P101797PC00