Carbon nanotubes for Field Emission Displays.

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Abstract

The Field Emission Display is potentially an excellent display with high brightness and low power consumption with wide viewing angle but more work is still needed in order to identify the ideal electron emitter for such displays. This paper will review the work that we have carried out in Cambridge over the past couple of years on optimisation of Carbon nanotubes for use as the cold cathode emitters that are possible candidates as the electron sources in second generation FEDs.

1. Introduction

The Field Emission Display (FED) has received significant industrial, government and venture capital attention throughout the 1990's and into the current millennium. This is because the FED is essentially a thin, flat cathode ray tube and so in principle offers the many advantages of the CRT – lambertian viewing characteristics, best colour gamut, high brightness, acceptable contrast, no motion artefacts on video and a potentially lower manufacturing cost than LCD or PDP.

As early as the 1960's workers [1] at Stanford Research Inc (SRI), described the possibility of using sharp metal tips operating in a high electric field, to generate a source or sources of electrons using Fowler-Nordheim quantum mechanical tunnelling - a source of electrons from a cold substrate. Such a cold cathode had been the "Holy Grail" of the electron devices industry since the turn of the last century and offered the possibility of a flat thin TV.

The FED operates on the same principle as a CRT where electrons are used to excite a phosphor screen to generate light but instead of having one electron gun it has an x **x** y array of individual electron sources. The CRT is bulky because depth is needed to allow the single electron beam to be able to raster across the phosphor screen. In the FED on the other hand by utilising an array of individual electron emitters at each pixel that can locally scan different areas of the phosphor the depth is eliminated.

As indicated above, in order to aid the emission efficiency low work function materials are utilised and to further aid the process they are usually in the form of sharp tips that cause field enhancement. Several different emitting materials have been used including Mo, W and Si .

In the 1990's it had also become clear to some that thin films of diamond or diamond like carbon might be used as flat or planar electron emitting films and significant resources were committed to research in this area.

These latter approaches use one type of broad area emitter structure or another (or as has often been suggested- "2nd Generation FEDs") and they had mainly changed market focus – increasingly looking at large area TV. This change in focus arose due to the realisation that large TV requires relatively large pixels which can utilise screen or ink jet printing – so promising low cost and offer the motion quality needed for TV.

A major effort has also been made to investigate the use of carbon nanotubes (CNTs) for field emission applications. Carbon nanotubes exhibit extraordinary field emission properties because of their high electrical conductivity, ideal high aspect ratio whisker-like shape for geometrical field enhancement, and remarkable thermal stability. Samsung have recently announced development of a 38" FED based on a Carbon nanotube Technology [2]. For large areas where pixel sizes are large Carbon nanotubes (CNTs) can be screen printed (see figure 1).

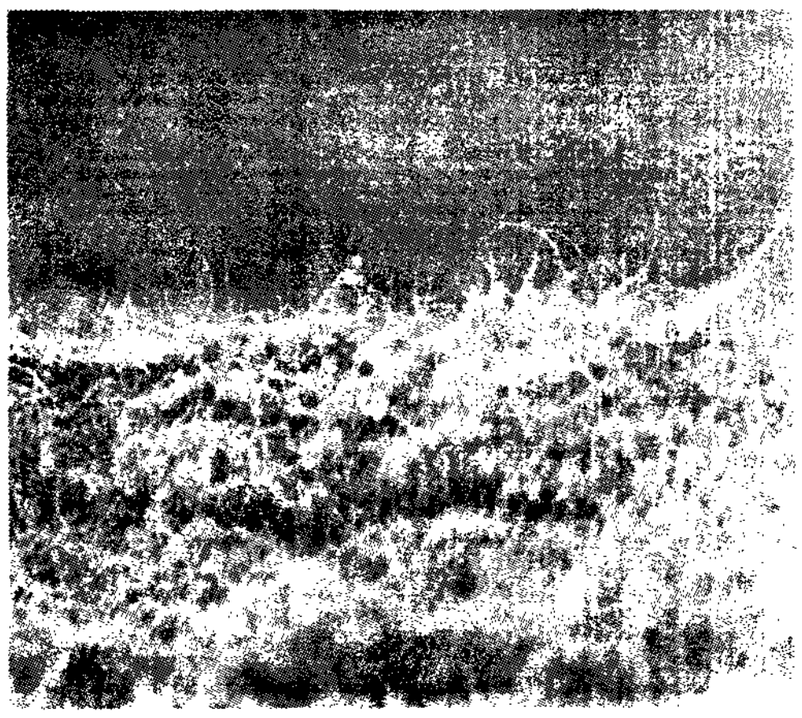

Figure 1 Screen Printed CNT Film (courtesy of Iljin)

However for smaller high definition displays where pixel sizes are much smaller the emitted current from a sub-pixel must be highly directed so as to minimise inter pixel 'cross talk' and maximise colour definition. See figure 2.

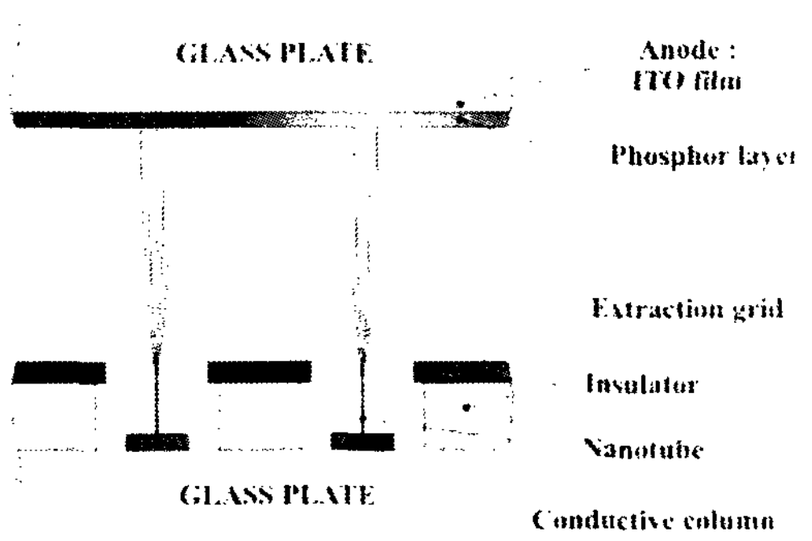

Figure 2 FED utilising CNTs as electron sources

They must therefore be deposited by other means – plasma enhanced chemical vapour deposition (PECVD) is a prime candidate for this.

2. Experimental

In Cambridge we use the direct current PECVD method as first reported by Ren and co-workers [3] to deposit our aligned multiwall carbon nanotubes (MWCNTs). We use acetylene and ammonia as the process gasses. The CNTs can be deposited on a range of substrate materials at temperatures from 500 up to 1000°C in our system using acetylene and ammonia gas mixtures. Initially we have used Ni as the catalyst and this is sputter deposited. The thickness of the Ni layer controls the size of catalyst particles when the substrates are heated to the growth temperature [4].

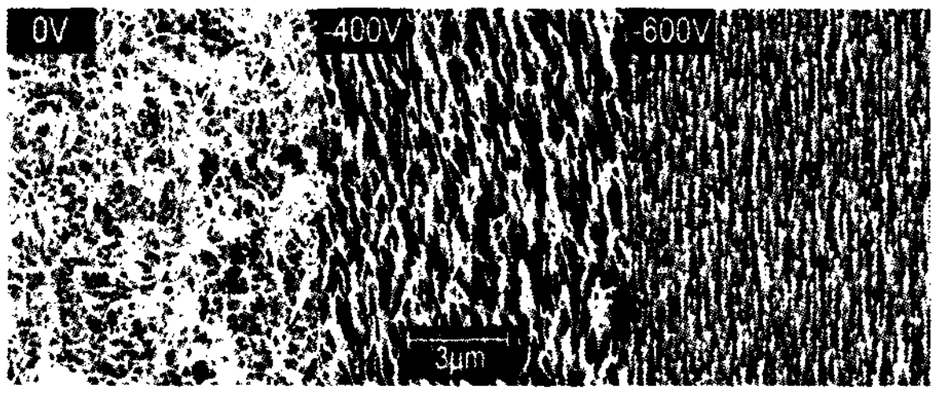

Figure 3 SEM Images of CNTs grown at 0V/micron

Figure 3 shows the effect of field on the nanotube growth. Nanotubes grown at 3 different fields whilst keeping all other growth parameters constant are highlighted. At 0V bias there is no plasma and CNTS grow via a thermal composition of the C_2H_2. No electric field is present and tubes grow rather like "spaghetti". If a small bias is applied, a weak plasma is generated and some alignment begins to occur and when fields of order 0.35 V/ m are applied the tubes become perfectly aligned. Although the figure does indicate the effect of field on alignment it must also be noted that the plasma characteristics (bias current, degree of ionisation/excitation) under the various bias conditions are expected to be significantly different in terms of the types and amounts of species responsible for the growth.. Further details of the growth process are given in reference [5].

As stated earlier such well aligned CNTs should make excellent field emitters. However as has been shown by e.g Nilson et al [6] and Bonard et al [7] such close packed arrays of CNTs are not necessarily ideal for FE applications as the close packing of the tubes screens the applied field effectively reducing the field enhancement of the high aspect ratio tubes.

Thus for some applications it is necessary to have individual vertically aligned tubes spaced well apart to minimise field shielding effects in order to optimise emitted current densities. We and others [8],[9] have produced such controlled arrays using e-beam lithography techniques to produce the Ni catalyst dots. The size of the Ni dot determines the diameter and number of CNTs per dot. Provided the diameter of the Ni catalyst dots are < 100 nm each dot produces one MWCNT as shown in. A typical array of multiwall nanotubes is shown in figure 4

For yet other applications such as parallel e-beam. lithography systems or high definition displays, integrated gate structures may also be needed.

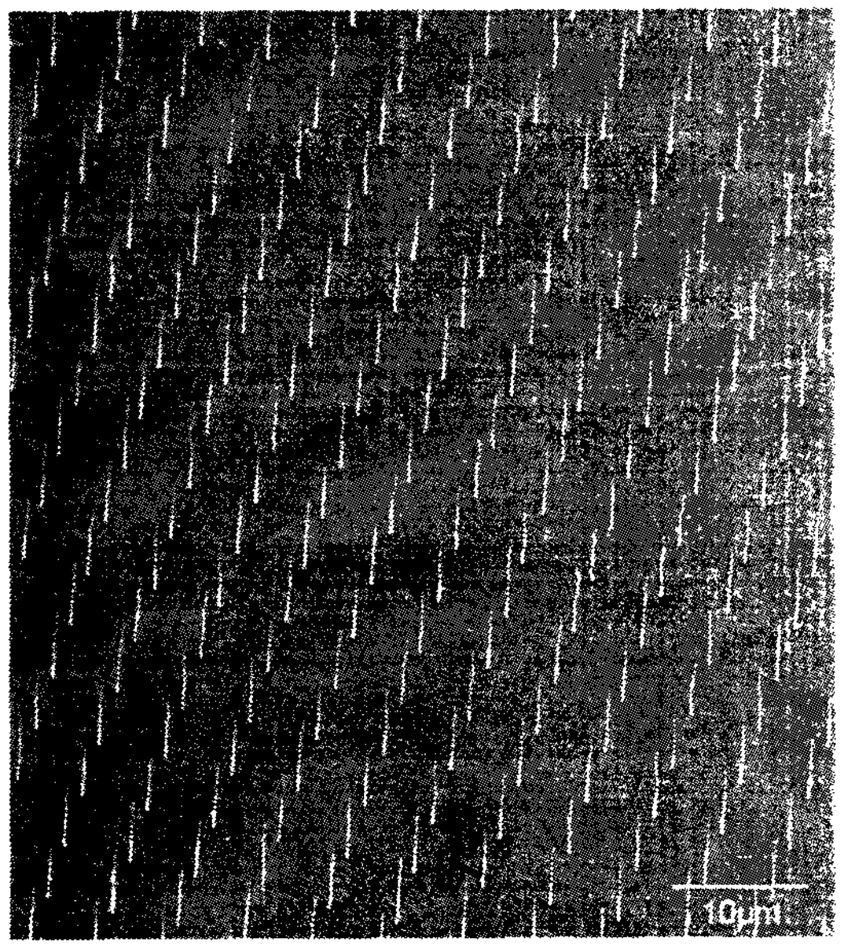

Figure 4 Array of MWCNT

Figure 5 shows an array of such integrated structures (each including a forest of aligned CNTs) produced in our laboratory on glass at 550°C.

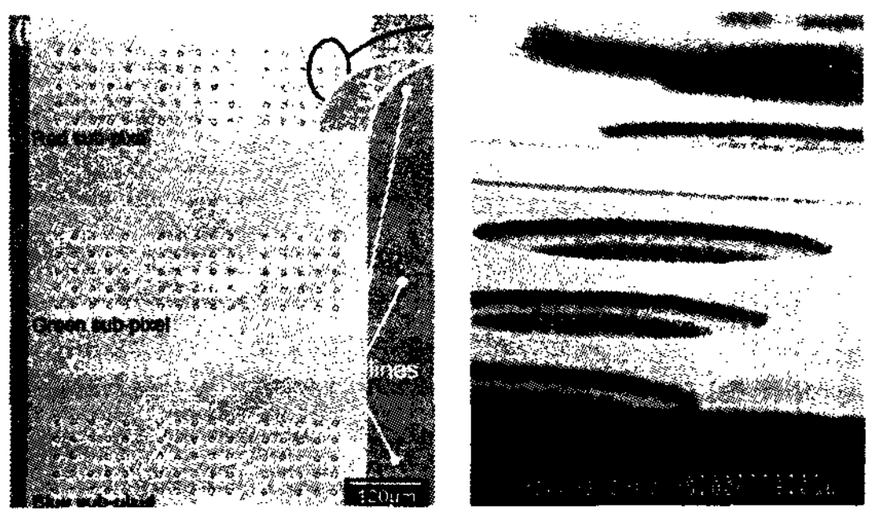

Figure 5 Gated Arrays of CNTs on Glass Back Planes for FED production

For future mass production of cathodes on a wafer/large scale, electron beam lithography is clearly unsuitable. Thus. we have examined other methods to meet future production requirements. Large area techniques to obtain an array of 'dots' include laser interferometry, nanosphere lithography and nanoimprint. We did not pursue laser interferometry because the mark:space ratio is typically 1:1 (highest contrast of a sine wave/interference pattern is at 50%), when higher mark:space ratios are required for optimum field emission arrays. Nanosphere lithography, in which a mask of self-assembled polystyrene spheres is created, has therefore been investigated. In theory, the spheres can be assembled in

a monolayer (or a double layer) as shown in Figure 6(a). Ni catalyst is then deposited through the mask and lift off is performed by dissolving the polystyrene spheres in toluene. Next, CNT growth is performed and patterned CNTs, with good uniformity in terms of height and diameter, are obtained as shown in Figure 6 (b).

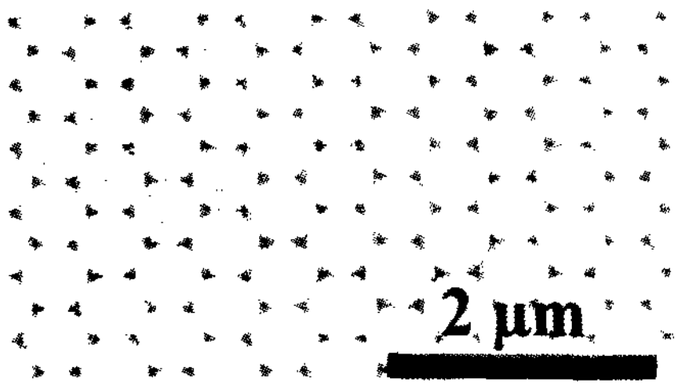

Figure 6(a) Array of co-polymer Spheres

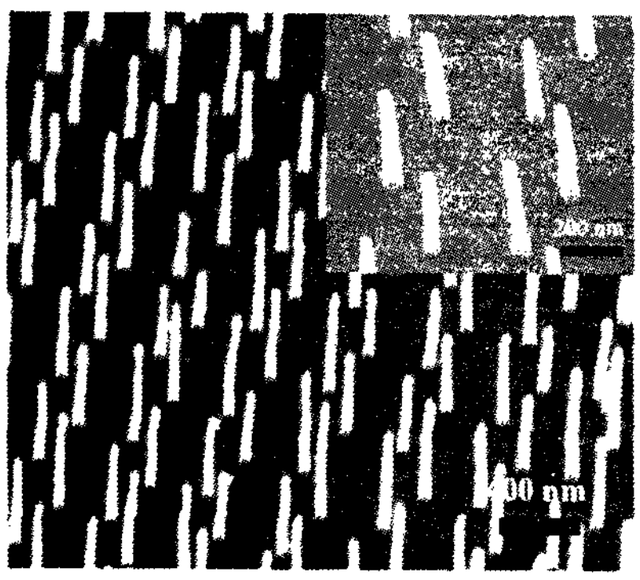

Figure 6(b) MWCNT array

Photolithography can also be used with nanosphere lithography to confine the CNT growth as seen in figure 7. It is also evident from Figure 7 (a) that the 200x200µm area of CNTs contains various types defects (point, grain boundaries) due to imperfections in the self-assembled nanosphere mask.

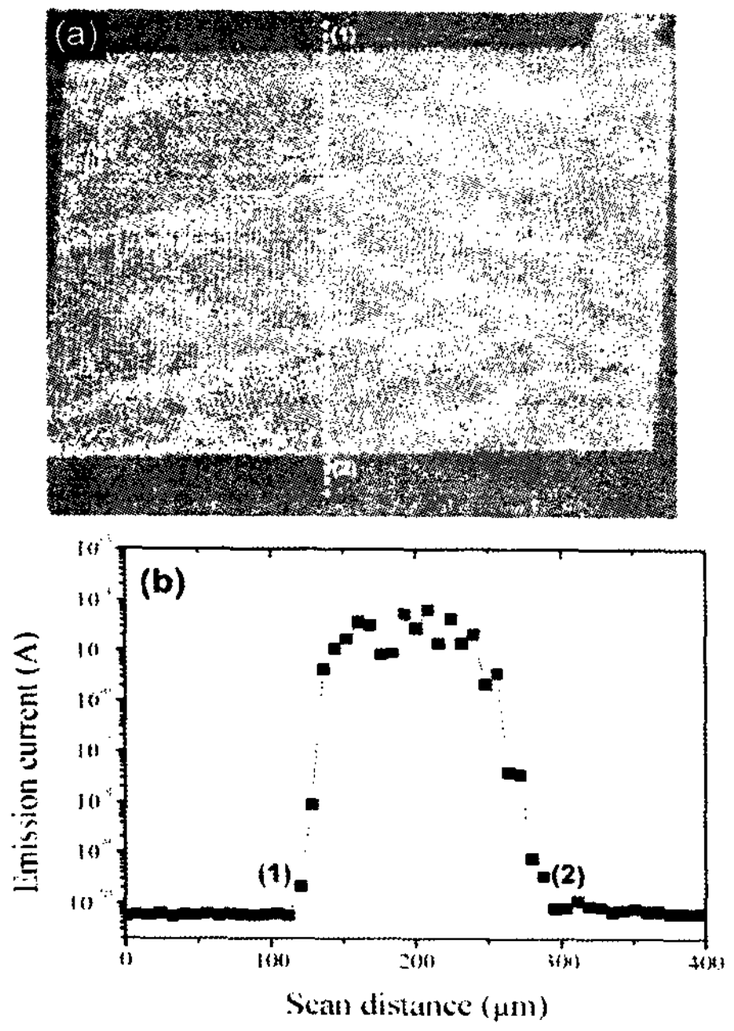

Figure 7. Photolithography used with nanospheres to confine the CNT growth to a 200µmx200µm region

We have carried out field emission current measurements over such an area and these show that the emission current is confined to the patterned CNT area. The emitted current from a scan along line (1) to (2) in figure 7(a) is shown in Figure 7(b). Although more suitable than laser interferometry, nanosphere lithography still only has the mark:space ratio of ~1:6 at best, and hence although high aspect ratio CNTs can be obtainedusing long growth times, the overall field enhancement may still be limited due to electrostatic field shielding from adjacent CNTs. Nanoimprint lithography was thus investigated as an alternative means of producing large arrays of CNTs, which can possibly have ideal mark:space ratios with CNTs which are spaced appropriately apart to avoid electrostatic field shielding. In the nanoimprint process, a stamp master is pushed against a wafer containing the same resist as in the e-beam lithography process. Under high pressure (50bar) and sufficiently high temperatures above the glass point of the resist, the resist would flow to form holes at pillar locations of the stamp master. When the master is released from the wafer, the pattern is reproduced. An oxygen plasma step is then used to remove resist (if any) from the bottom of the holes of the pattern, followed by diffusion barrier (TiN or ITO) and catalyst (Ni) deposition and lift off, as per the normal CNT growth process. The nanoimprint process is shown pictorially in Figure 8(a) and figure 8(b) shows preliminary results which have produced a series of 1 micron wide lines with a 5 micron pitch produced using this technique. We are currently working on optimisation of this procedure and results on uniform arrays will be reported soon.

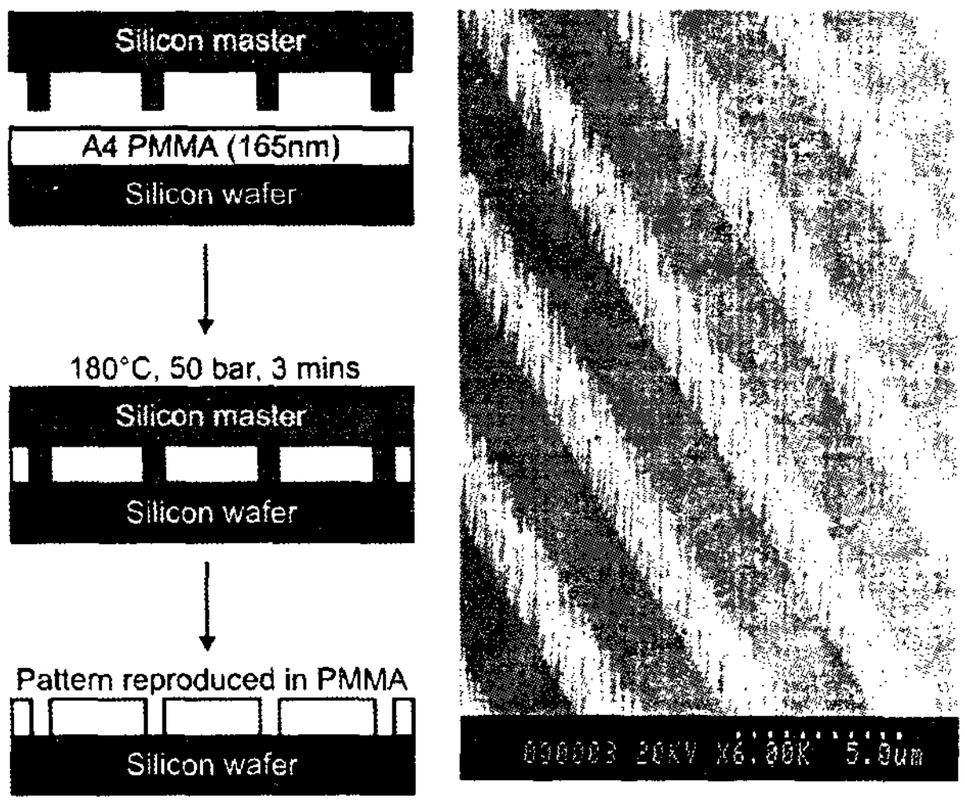

Figure 8 Nanoimprint lithography process

3. Conclusions

The various methods of producing arrays and single CNTs for use in Field emission based displays have been described

and their advantages and disadvantages discussed. The FED is potentially an excellent display with high brightness and a wide viewing angle. However its disadvantage still mean that to date there are no FEDs in the market place although Samsung are causing major interest in the technology with their 38" prototype CNT based FED.

4. Acknowledgements

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