Optimisation of CNTs and ZnO Nanostructures for Electron Sources

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***Abstract*- The aim of this paper is to review our recent results on the growth and optimization of carbon nanotubes (CNTs) and CNT/Zinc Oxide nanostructures and present and discuss their suitability for various applications such as cold cathode electron sources for use in x-ray sources and lighting.**

I INTRODUCTION

Carbon nanotubes (CNTs) are a unique form of carbon filament/fibre in which graphene walls are rolled up to form a cylindrical structure with diameters typically between 1 and 50 nm depending upon whether they are single-walled or multi-walled CNTs. They can have lengths up to several millimeters. There are several properties which make CNTs suitable for use as cold cathode electron emitters. They exhibit high in-axis electrical conductivity at room temperature. They have a high aspect ratio which is an ideal geometry for field emission and because they have small tip radii, typically less than 30 nm, the potential to form a small point source can be realised. They also have a high thermal conductivity and can be very stable emitters even at high temperatures [1]. This is in contrast with metal emitters where the resistance increases with increasing temperature leading to short life times. The resistance of the CNTs reduces with increasing temperature which limits heat generation for a given emission current. Table 1 compares the properties of various types of electron sources. The use of CNTs as electron sources for electron microscopes, microwave sources, flat panel displays and x-ray sources has been well described elsewhere[2].

In fact, X-ray sources providing a current density of 0.1 A/cm^2 based on CNTs have been already fabricated and commercialized [3,4]. For such applications Xintek and XinRay systems produce sources based on the random deposition of CNTs.

We have also been working on the production of CNTs for X-ray source applications and in our work, the emitter is based on a regular array of CNTs such as those shown in Fig 1. Using such an array we have previously reported exceedingly high emission currents at 1.5 GHz [5]. Although this gives the current density required for our x-ray application, in order to obtain better control of the current, together with a much higher stability and lifetime we have developed the ballasted array shown in figure 2. The objectives here were to develop a cathode that is able to deliver a stable current density of >1 A/cm^2 at DC and even higher in pulsed mode for x-ray sources. We will also report on the use of a novel hexagonal mesh structure which has a threshold field of 1.5 V/micron defined at an emitting current density of 1mA/cm^2.

Property	Thermionic (tungsten/LaB_6)	Schottky (tungsten+ZrO)	Metal cold FE (tungsten)	Carbon nanotube FE
Virtual source size (nm)	10,000	<20	<10	<10
Energy spread (eV)	1	0.7	0.2 - 0.3	0.2 - 0.35
Brightness (A/m^{2}srV)	10^6-10^7	10^8	10^8	10^9
Stability (%)	<1	<1	4-6	<0.5
Operating temp	1500 – 2100 C	1500 C	25 C	25 C – 400 C
Lifetime	100 - 1000 hrs	>1 year	>1 year	>1 year

Table 1: Typical properties of various types of electron sources

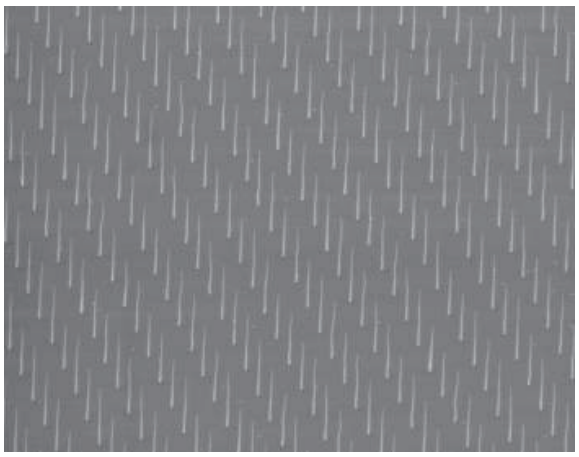

Figure 1: Ordered Array of Vertically aligned MWCNTs

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II EXPERIMENTAL DETAILS

The CNTs in the arrays described below are vertically aligned, 5 μm in height and 50 nm in diameter with a pitch of 10 μm. In order to attain large current densities with reasonable uniformities and long lifetimes, it is necessary to prevent the best CNT emitters in the array from emitting a current larger than the current which induces their destruction (around 100 μA). To solve this problem, a ballast resistor must be integrated. The ballast resistor must be connected in series with each CNT *individually* to enable this to happen. This is because the resistor must act to prevent all the current going through one CNT.

Tungsten deposited between the CNTs in a grid pattern acts as the electrode, with the resistive silicon in between the CNT and tungsten acting as the ballast resistor as shown in figure 2 below.

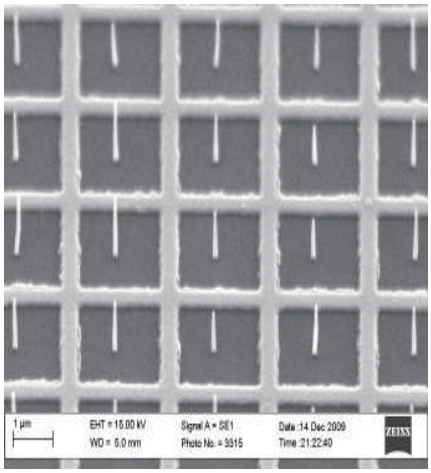

Figure 2 Ballasted CNT array Aligned MCNTs

Our initial efforts to achieve the ballast resistor structure/CNT array were based on an SOI (undoped-Si/SiO_2/Si) substrate employing electron beam lithography and plasma enhanced chemical vapor deposition (PECVD). First, a catalyst dot array was produced using e-beam lithography and Ni metal sputtering. The CNT array was then grown in a cold wall CVD system to obtain the CNTs as shown in Fig.1. Finally, a top-contact layer of tungsten was used to bias the CNTs, with the gap between the tungsten and CNT of undoped Si acting as the ballast resistor. The emitted current density from such a structure provided ~1A/cm^2 at a threshold field of 23 V/μm. This makes such a structure suitable for x-ray applications. However, the fabrication process for this structure is very complex which, whilst acceptable for x-ray applications, is not suited to applications such as displays and lighting.

In order to circumvent this we have designed a novel, but simpler structure, incorporating a combination of Carbon Nanotubes and ZnO nanowires.

Firstly a CNT array such as the one described above was produced and then ZnO nanowires were grown onto this using a hydrothermal method as reported previously [7]. The final array combining both the CNTs and the ZnO is shown in Fig 3.

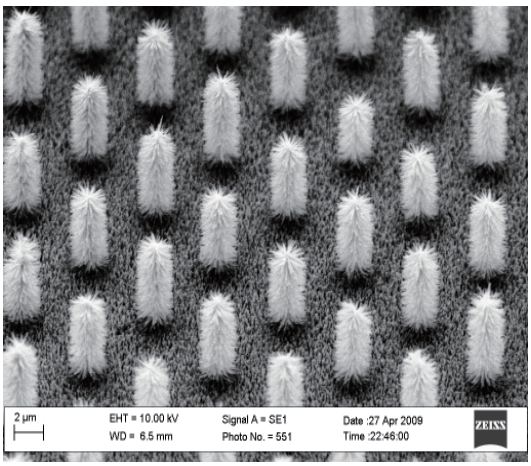

Figure 3 ZnO/CNT Nanostructure Array[6]

The field emission from the CNT array and the CNT/ZnO combination is compared in Fig 4 in a Fowler Nordheim plot, where the ballasting effect of the ZnO wires is obvious. The comparison illustrates the difference in the threshold voltage required to initiate field emission. The ZnO grown on top of the CNTs clearly perturb the field profile around the CNT, further increasing the field enhancement resulting in a turn-on field roughly a third of that required to turn on the CNT-only array [6].

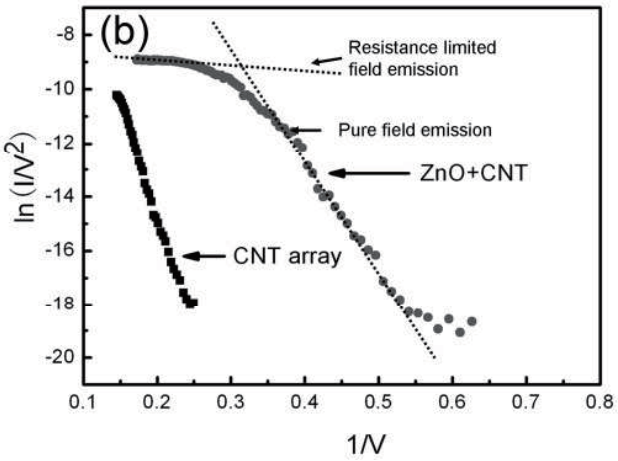

Figure 4 Fowler–Nordheim plot of Emission Current Density for CNT and CNT/ZnO arrays [6]

However, in this case the emission current densities were of the order of a few mA /cm^2 whereas before the ballasted CNTs could produce close to 1 A/cm^2. Consequently, these values are too low for our x-ray source application but would be suitable for application in lighting etc. The average field enhancement factors of the CNT array and CNT/ZnO combination were calculated to be 820 and 2400, respectively. A further effect of the ballasting ZnO wires was to improve the lifetime/stability of the array. This is the key barrier to field emission-based lighting devices. Field emission requires pressures of 10^{-9} mbar for operation, much lower than those found in CRTs for instance. We have, thus far, conducted lifetime measurements at a pressure of 5×10^{-6} mbar with an initial emission current density of 10 mA/cm^2. These lifetime tests have found [6] that the CNT/ZnO combination has a much longer lifetime than that of the CNT-only array. We postulate that it is the limited carrier concentration in the zinc oxide which controls the current emitted and thus protects the emitters from damage at high pressure, which opens up the possibility of using such a structure in lighting.

However, this structure still currently requires the use of expensive e-beam lithography in order to pattern the catalyst prior to CNT growth. Such a process will prevent the technology competing with alternatives. Therefore, we searched for a solution which produces even simpler structures for this application.

We recently began work on the use of novel hexagonal mesh structures which typically have a threshold field of 1.5 V/micron defined at an emitting current density of 1mA/cm^2. In this instance a combination of an imprint lithography process with low temperature growth was used to reduce costs and eliminate the complication of the e-beam processing needed for the above CNT arrays.

Highly doped n-type silicon wafers were patterned using imprint lithography to produce 1 micron-wide mesh lines on which 10 nm of Al was deposited followed by a further 1 nm of Fe catalyst by sputtering. Subsequently, the vertically aligned CNT meshes (VACM) were synthesized by thermal CVD in an AIXTRON Black Magic cold walled CNT growth system. First, the sample was annealed in Argon at 420 °C for 40 s to form the catalyst nano-particles. Then, CVD growth was carried out at a temperature of 450 °C and at a pressure of 14 mbar with a flow rate of 200 sccm of acetylene (C_2H_2), as reported elsewhere [8].

Based on previous work on square mesh arrays, which demonstrated that emission from the edges of the arrays dominates, we investigated the use of hexagonal meshes in an effort to increase the contribution of the edges to enhance the field profile and hence to obtain a higher current density at lower fields. To investigate this particular cathode geometry, we first carried out finite element electrostatic simulations using COMSOL MULTIPHYSICS. The electric field distribution around the honeycomb structure is as shown in Fig.5.

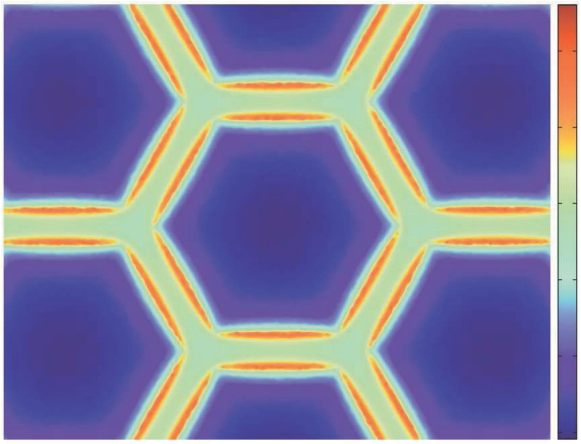

Figure 5 Simulation of Electric Field Profile [8]

.As with our previous work, the highest field enhancement can again be observed at the edges (indicated in orange) and there appears to be good uniformity of the electric field along the edges of the hexagons. We therefore expect that all the VACM walls will behave as edges to enhance the electric field equally.

Fig.6 shows the top view of the honeycomb-shaped CNT mesh in low and high magnification. The hexagons are 6 microns across and are ~5 microns high [8].

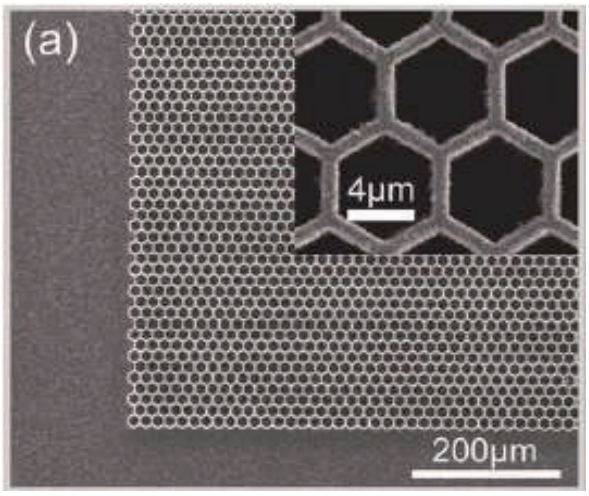

Figure 6 Top view of Honeycomb structure [8]

The FE properties of the VACMs were determined using a simple diode configuration in a vacuum chamber at a pressure of 10^{-8} mbar. The VACM cathode was placed beneath an ITO-

coated glass anode, separated by spacers with a thickness of 0.25 mm. Prior to FE measurements, a rapid annealing process was carried out to remove amorphous carbon and absorbed gaseous species from the array. Such a process increases the stability of the field emission and the lifetime of the cathode.

The FE measurement set–up is shown in figure 7(a) and the current versus applied electric field characteristic (I vs E) is shown in Fig.7 (b). In this case the threshold field for a current density of 1 mA/cm^2 was found to be 2-5 V/μm, and a maximum current of order 1 A was obtained at a field of the order of 4-5 V/μm. The corresponding Fowler-Nordheim (FN) plot is shown in the inset of Figure 7(b) along with the emission image on a phosphor coated ITO layer at 1 mA/cm^2 current density [8].

We also investigated the use of the hexagonal mesh structures for x-ray sources but found that although the emission currents were high enough for such an application the emitted beam from the array edges diverged too much and they could not be sufficiently focused to provide the required current densities.

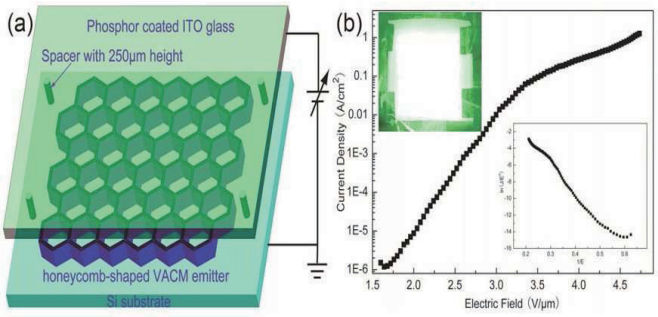

Figure 7 (a) FE set up and (b) Emission Current vs Applied Field [8]

Stability measurements were also made on these structures at 10^{-6} mbar with total current densities of approximately 10 mA/cm^2. Under these conditions the cathode was also found to exhibit stability over long periods of time, exhibiting a similar stability to that observed from the CNT/ZnO arrays. Inspection of the cathodes indicated no significant degradation in the cathode structure, though we postulate that because the grown CNTs are so high and so dense, that should a CNT break down, this wouldn't be translated into an effect seen in the emission characteristics for some time. Consequently, this is another potential method which could be used to realise low-power field-emission-based lighting.

III CONCLUSIONS

This paper reports the production of a selection of CNT-based electron emitter structures. The initial work concentrated on an array of vertically aligned MWCNTS ballasted using a Silicon on Insulator ballast resistor. However, this production technique is complicated and in order to simplify the manufacturing methods we have also investigated ZnO nanowire-coated CNTs for application as electron sources. The ZnO nanowires act as a "front-end" ballast resistor limiting the current densities obtainable from the arrays. However they do lead to more stable and longer lifetime emitters measured at pressures of order 10^{-6} mbar. In order to make even simpler emitter structures we also investigated the use of hexagonal mesh edge emitting structures which show excellent emission current densities but are not useful for x-ray purposes as the divergence of the emitted beam is too great. Such emitters can however be used in back lights or other lighting applications.

IV ACKNOWLEDGMENTS

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