A Comparison of Field Emission Properties of Carbon Nanostructures Deposited By the Microwave Plasma Enhanced Chemical Vapor Deposition Technique

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Abstract
This paper reports the comparison of field emission properties of different carbon based nanostructures deposited by the microwave plasma enhanced chemical vapor deposition MW PECVD technique. The carbon nanostructures comprised of Carbon Nanotubes (CNTs), graphene and hybrid of CNTs and graphene. These carbon nanostructures have been deposited at different pressures of 5, 20, 30 Torr, temperatures of 500, 600, 700 ºC, negative substrate biases of 150, 250, 350 V and by two step method. The various nanostructure films show the changes in the morphology with the change in deposition conditions. The presence of graphene seems to increase the field emission properties of these nanostructures. The lowest turn on field of 1.6V/μm is accompanied with the highest emission current density of 2.8 mA/cm² in the CNT grown on graphene film with the help of Ni nanoparticle. The field emission has also been realized using phosphor screen.

Key words: CNTs; Graphene; Hybrid film; MW PECVD; Field Emission

Introduction
In the recent scenario, carbon has proved its remarkable applicability in different scientific and technological field. Out of different carbon allotropes, sp² hybridized carbon based allotropes, e.g., carbon nanotube (CNT), graphene has been emerged as a subject of intense research due to their unique chemical, electrical, mechanical and thermal properties [1-11]. Field emission is the electron ejection due to the electrostatic field. A good field emitter should have high thermal and electrical conductivity, mechanical strength and melting point. Due to the high aspect ratio, thermal and electrical conductivity, mechanical strength, easy growth and high chemical stability, CNTs have emerged as a promising candidate for field emission [12-14].

With these properties, CNTs have futuristic application in the field, where a cold cathode is needed e.g., electron source in the X-ray tube, field emission display (FED) etc. Another form of sp² bonded hexagonally arranged carbon has emerged as graphene [15,16]. A drawback of perfect graphene is the absence of band gap, which inhibits its applications in the semiconductor industry.

Introducing defect centers in graphene produced band gap and such material is called graphene-like. Graphene is not so promising material for field emitter but its presence along with CNTs can give good results. For better field emission results, the sharp edges of graphene sheets and CNTs should be in the direction of an applied field. The lateral distribution of graphitic sheets may not contribute in the field emission but help to interconnect the CNTs to provide highly conductive channel for electron emission.

The hybrid material can be termed as CNT rich or graphene rich, depending on the quantity of individual allotropes. Graphene can act as filler to the voids present in the CNTs network and can provide better electrical connectivity. Graphene in lateral alignment have a low field enhancement but the vertical graphene has found all the capabilities for a good field emitter [17,18]. Beside vertical orientation, graphene combined with different materials is of significant use as field emitter. Chaoxing et al. [19] used the combined graphene with zinc oxide with its edge as field enhancer.

In this paper, we have reported and compared the field emission properties of different carbon based nanostructures deposited by the microwave plasma enhanced chemical vapor deposition (MW PECVD) technique. The carbon based nanostructures include flowered CNTs, CNT rich hybrid and graphene rich...
hybrid films. Direct deposition on the metal helps to dissipate heat produced due to the Joule heating effect.

**Experimental details**

**Sample preparation**

The carbon based nanostructured films were synthesized in a custom designed and indigenously built MW PECVD system. It consists of 1.2 KW microwave power supply, magnetron, circulator for power adjustment and three stub tuners for tuning microwave power. Microwave system with waveguide is separated from the deposition chamber by a quartz window. The deposition chamber is equipped with a turbo molecular-rotary pump combination and a base vacuum of ~3×10^{-7} Torr is achieved. High deposition pressure is achieved using a throttle valve and monitored by a high pressure gauge. Nickel and copper foil were used as substrate for the deposition of these nanostructures.

The substrates were cleaned by the sonications in isopropyl alcohol (IPA) and acetone up to 5 min each and then subsequently treated it with hot IPA followed by the deionized (DI) water. The substrate temperature was raised with the heating rate of 30˚C / min. The samples were further cleaned by flowing H₂ gas in the chamber and plasma to remove the surface oxide from the substrates. After the deposition, the samples were naturally cooled down. The deposition conditions for the samples have been summarized in Table 1.

CNT rich hybrid films have been deposited at 5, 20 and 30 Torr pressures with a fixed temperature of 600 ºC and at different temperatures of 500, 600, 700 ºC with a fixed pressure of 20 Torr. Flowered like CNTs have been grown at different negative substrate biases. Graphene rich hybrid films have been grown by the two step method, first depositing graphene on Cu foil and post graphene growth of CNTs with the help of Ni nanoparticle.

The field emission properties were measured in a diode geometry using 150μm teflon spacer. The current density and corresponding turn on field were measured by a high voltage source meter (Keithley, Model 2410). The carbon nanostructured film on the metal was used as the cathode and phosphor coated Indium Tin Oxide (ITO) was used as an anode. The sample arrangement for the field emission is shown in Figure 1.

The morphology and microstructure of the samples were examined by high resolution scanning electron microscope (SEM) (JEOL-JSM-7100F) and high resolution transmission microscope (HRTEM) (Tecnai G20, F-30-ST WIN) with field emission electron gun source operated at the electron accelerating voltage of 300 kV. For HRTEM study, the samples were prepared by etching nickel in HNO₃ and HF mixture and collecting the remaining film after diluting the mixture with the DI water on the carbon coated copper grid.

**Result and discussions**

**Surface morphology**

Figure 2 a,b,c and d give the typical generalized morphological view (SEM image with inset of HRTEM) of carbon nanostructures. Figure 2 a and 2b show CNTs rich hybrid films. The density was found to be the highest after applying negative substrate bias as it enhanced the energy to attract more carbon radical more rapidly as shown in Figure 2c.

The flowered nanostructured have also been correlated by the increased substrate bias. The graphene rich hybrid shows

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition conditions</th>
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<tbody>
<tr>
<td></td>
<td>Pressure (Torr)</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
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<td>20</td>
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<td>9</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>5.5 x 10⁻²</td>
</tr>
<tr>
<td>12</td>
<td>5.5 x 10⁻²</td>
</tr>
<tr>
<td>13</td>
<td>5.5 x 10⁻²</td>
</tr>
</tbody>
</table>

Table 1: Deposition conditions for different samples.
the lowest CNTs density, but CNTs may be related to be interconnected by the graphene sheets as shown in Figure 2d. The inset shows the HRTEM image of the samples. The details about the deposition of various samples have already been reported [20-24]. There are different mechanisms of the growth of carbon nanostructures on different substrates. Carbon has the high solubility in Ni comparable to Cu. At high temperature, some carbon atoms from the plasma diffuse into Ni with the simultaneous growth of CNTs. After the fast cooling, the diffused carbon atoms segregated on the Ni surface arranging in sp² bonded graphitic sheets. This may be the reason for the growth of CNTs accompanied with the graphitic sheets at high temperature, while at low temperature the carbon atoms do not diffuse into Ni and only CNTs have been grown. Whereas, on Cu substrate due to the low solubility of carbon, graphitic sheets are directly grown on the surface. The bonding between the CNT and graphene is strongly attributed to their high intrinsic affinity due to the same graphitic nature [25].

Field-emission properties

Field-emission is a quantum-mechanical tunneling phenomenon in which electrons tunnel out of the cathode, when a very high electric field is applied. It is a non-linear process, in which the field emission current density (J) versus electric field (E) characteristics are usually described by the classical Fowler-Nordheim (FN) equation [26]:

$$J = \frac{A(\beta E)^2}{\phi} \exp\left(-\frac{B\phi^{3/2}}{\beta E}\right)$$  \hspace{1cm} (1)

Where J is the current density, $\phi$ is the barrier height (taken as the work function), E is the applied electric field, $\beta$ is the field enhancement factor and A and B are the constants and have the values of 1.54 x 10⁶ Av² and 6.83 x 10⁹ Vm⁻¹eV⁻⁴/², respectively. Figure 3 a,b,c show the variation of J versus E characteristics of samples 1 to 3. Figure 4 a,b,c show the variation of J versus E characteristics of samples 4 to 6. Figure 5 shows the variation of J versus E characteristics of samples 7 to 10 and Figure 6 shows the variation of J versus E characteristics of samples 11
to 13. The plots of log \((J/E^2)\) versus \(1/E\) of all these samples are straight lines which confirm that the J-E characteristics follow the F-N relation [20,21,23,24].

The field enhancement factor is defined as the ratio of local electric field to the applied electric field. The field emission strongly depends on the field enhancement factor \((\beta)\) as the local field generated along the emission site is evaluated by \(E_{loc} = \beta E_{appl}\), where \(E_{appl}\) is the external applied field. The field enhancement factor depends on the morphology of nanostructures presented in the film. The nanostructures with the high aspect ratio have the high field enhancement factor \(\beta\) which can be calculated from the slope of the curve \(\ln (J/E^2)\) versus \(1/E\) by

\[
\text{Slope} = -\frac{B\phi^{3/2}}{\beta}
\]

--- (2)

Table 2 summarizes the field emission properties of these nanostructure samples involving the turn on field (defined corresponding to the current density of 1 µA/cm² in samples from 1 to 10 whereas in samples from 11 to 13 with symbol star
marked in the Table 2 is defined corresponding to the current density of 10 µA/cm²) and the maximum current density (Jmax).

It is clear from the table that the turn on field is the lowest and the current density is the highest for the graphene rich hybrid films. For all graphene rich hybrids films the current density (J) is the highest among all the samples. This may be due to the higher amount of graphene interconnector. The CNTs network on the metal substrate has large numbers of voids, which in turn lowers their interconnectivity.

Graphene fills these voids and provide a better interconnectivity, which in turn increase the electron transport. Samples from 7 to 10 are CNTs deposited at different negative substrate biases. Although there is hardly any presence of graphene in these samples since these samples have been deposited at low temperatures. The cause of comparable field emission properties of these samples is due to the flowered morphology deposited at different negative substrate biases.

Table 2: Turn on field and current density of different samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Turn on field (V/µm)</th>
<th>Maximum current density (Jmax)(A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.7</td>
<td>1.2 x 10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>2.3 x 10⁻⁶</td>
</tr>
<tr>
<td>3</td>
<td>5.5</td>
<td>3.5 x 10⁻⁷</td>
</tr>
<tr>
<td>4</td>
<td>4.7</td>
<td>3.8 x 10⁻⁷</td>
</tr>
<tr>
<td>5</td>
<td>3.6</td>
<td>1.0 x 10⁻⁶</td>
</tr>
<tr>
<td>6</td>
<td>2.7</td>
<td>1.0 x 10⁻³</td>
</tr>
<tr>
<td>7</td>
<td>5.5</td>
<td>1.3 x 10⁻⁷</td>
</tr>
<tr>
<td>8</td>
<td>4.3</td>
<td>6.0 x 10⁻⁵</td>
</tr>
<tr>
<td>9</td>
<td>2.6</td>
<td>4.7 x 10⁻⁴</td>
</tr>
<tr>
<td>10</td>
<td>1.9</td>
<td>5.3 x 10⁻⁴</td>
</tr>
<tr>
<td>11</td>
<td>5.0*</td>
<td>1.5 x 10⁻³</td>
</tr>
<tr>
<td>12</td>
<td>4.0*</td>
<td>2.5 x 10⁻³</td>
</tr>
<tr>
<td>13</td>
<td>1.6*</td>
<td>2.8 x 10⁻³</td>
</tr>
</tbody>
</table>

Figure 7: Turn on field of different samples.

These types of vertical and edged nanostructures are required for better field emission properties. Samples 1 to 6 have been deposited at high temperatures so there is the presence of graphene with CNTs but these nanostructure films are CNTs rich films as the quantity of graphene like nanostructure is low in these films and these films are having unique morphology. Paulson et al., [27] depict the dramatic change in the contact resistance on CNT-graphene interface as discrete Fermi surface allow states only in the specific direction and the relative angle between the lattices. Figure 7 shows the turn on field of different samples. The lowest turn on field of 1.6 V/µm is obtained in sample 13 which is having the highest emission current density of 2.8 mA/cm².

Figure 8 depicts the phosphor image of different samples observed during the field emission. In case of the low emission
current density, the emission is non-uniform. At high emission current density, the brightness and uniformity of the phosphor has improved. It is clear from the figure that earlier the current being low, the phosphorescence is non-uniform. For the graphene rich hybrid samples there is uniform brightness. Phosphors, involves the substitution of cations in the lattice with the activator ions to produce luminescence, which produce a mismatch of the charge and crystal lattice due to the different valence state and ion radius which, in turn produce the unwanted defects e.g., vacancy, gap, crystal lattice distortion, and strain [28].

In the case of low emission, electron energy is not efficiently transferred to the lattice and electrons accumulate on the surface of phosphor, which in turn generate non-radioactive transition due to the recombination with defects. So for high and uniform brightness in the samples, it is evident that the high emission current density is needed in the samples.

**Conclusion**

The synthesis of different sp² based carbon nanostructures using the MW PWCVD technique with the controllable field emission properties has been reported. With the control of temperature, we can control the presence of graphitic sheet. It has been observed that the electron emission depend upon the CNTs nanostructure along with the presence of graphitic sheets. Maximum emission current density of 2.8 mA/cm² accompanied with the minimum turn on field of 1.6 V/µm was achieved for the CNTs grown on graphene film with the assistance of Ni nanoparticles. The phosphor image during field emission shows the high contrast with the sustained emission. Due to the flexible nature of the thin substrate, the cathode can be used in the large area flexible devices.

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**Reference**


