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# Field emission properties of $Fe_{70}Pt_{30}$ catalysed multiwalled carbon nanotubes

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Multi-walled carbon nanotubes were grown on nanocrystalline $Fe_{70}Pt_{30}$ film using low-pressure chemical vapour deposition (LPCVD) method. The growth time was varied between 5 min to 30 min. SEM micrograph of this film revealed that the size of nanoparticles varied from 5 nm to 10 nm. The diameter of the carbon nanotubes varied from 20 nm to 50 nm as verified by TEM. HRTEM image confirmed that the carbon nanotubes are bamboo-shaped multiwalled carbon nanotubes (MWNTs). Field emission characteristics of MWNTs at various growth times (5 min, 15 min and 30 min) with working distances (50 μm, 100 μm and 150 μm) were also studied. The carbon nanotubes grown for 30 min with working distance 150 μm exhibited the lowest turn-on field of 2.45 V/μm. The turn-on field increases from 2.45 V/μm to 6.21 V/μm as the growth time decreases from 30 min to 5 min whereas for lower working distances (100 μm and 50 μm), the turn-on field increases from 4.74 V/μm to 6.74 V/μm and from 8.79 V/μm to 14.49 V/μm respectively. The turn-on field ($E_{to}$) and field enhancement factor ($\beta$) were studied as a function working distance (d) and growth time respectively to see the effect of these parameters on field emission properties. The field enhancement factor ($\beta$) was also studied as a function of radius of apex curvature ($r$) . It was found the field enhancement factor ($\beta$) decreases with the increase in radius of apex curvature ($r$) and growth time whereas the value of field enhancement factor ($\beta$) increases as working distance (d) increases. On the basis of the dependence of $\beta$ on radius of apex curvature ($r$) a relationship of $\beta \propto r^{-1/2}$ is fitted.

*Keywords*: Carbon nanotubes; SEM; TEM; HRTEM; Growth time; Working distance ($d$); Radius of apex curvature ($r$); Turn-on field ($E_{to}$); Field enhancement factor ($\beta$)

## 1. Introduction

There is a considerable interest in the development of field emitting cathodes; much effort is being devoted to the fabrication of arrays of field emitters for use in flat

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screen displays. Carbon nanotubes (CNTs) have been considered as one of the best electron-emitting materials and thus extensive studies has been devoted to the field electron emission characteristics of carbon nanotubes. The high conductivity, sharp tips, long and narrow shape of CNTs suggested to a number of groups that they might make useful emitters, and some promising results have been achieved. de Heer *et al.* [1] carried some of the first experiments on field emission properties of carbon nanotubes. Field emission emitters operating at room temperature have great potential for miniaturization and hence portability of a device. The external field almost solely controls the emission current, which opens up several new applications in carbon nanotubes. CNTs have been proposed as new materials for field emitters in panel display [2], single molecular transistors [3], quantum wires [4], scanning probes [5], microscopic tips [6] and gas and electromechanical energy storage [7]. CNTs exhibit remarkable emission characteristics due to their high aspect ratio, electrical conductivity and mechanical stiffness. They are also of particular interest for FED (Field Emission Display) application due to their low operation voltage. They are capable of emitting high currents (up to $1\,\mathrm{A\,cm^{-2}}$) at low fields ($\sim 5\,\mathrm{V/mm}$). The controlled deposition of nanotubes on a substrate has recently become possible through combined use of CVD methods and catalyst patterning techniques. Khan *et al.* [8] performed the field emission measurements of carbon nanotubes grown under different growth times. They found out that carbon nanotubes grown for a longer time showed a superior turn-on field than those grown for a relatively short period of time. The major factors that determine the field emission properties of the tube are radius of apex curvature and the position of the occupied levels with respect to the Fermi level, which depends primarily on the tip geometry i.e., the tube chirality and diameter as well as the presence of defects [9, 10]. Indeed, only tubes with a band state just below or just above the Fermi level are good candidates for field emission. It is worth mentioning that the presence of such localized states greatly influences the emission behaviour [11].

In the present study, we have employed $Fe_{70}Pt_{30}$ nanocrystalline thin film, elevated growth temperature ($\sim 800^{\circ}$C) with $N_2$, $C_2H_2$, $H_2$ as gas mixtures and different growth times varying between 5 min and 30 min, to achieve multiwalled bamboo-shaped carbon nanotubes. We have also compared the field emission parameters: field enhancement factor ($\beta$), turn-on field ($E_{to}$) and maximum current density ($J$), for carbon nanotubes grown for different growth times and for different working distances (50 µm, 100 µm and 150 µm).

## 2. Experimental details

The catalyst $Fe_{70}Pt_{30}$ nanocrystalline films were deposited on Si substrate by vapour condensation technique. A mixture of $N_2$:$C_2H_2$:$H_2$ with flow rates of 300:50:50 sccm respectively, were introduced into the quartz tube (fitted inside the CVD system). The reaction temperature was kept at 800°C and duration was varied between 5 min and 30 min. The morphologies of the as-grown CNT film were obtained using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and High Resolution Transmission Electron Microscope (HRTEM). TEM and HRTEM were employed to observe the diameter and wall structure of multiwalled carbon nanotubes.

The field emission properties of these CNTs were investigated by using a cathode-anode arrangement. The anode probe is made of stainless steel, and has a flat surface in a disk shape. The measurements were carried out in high vacuum chamber. The anode-cathode distance (working distance) was varied from 50 μm to 150 μm.

## 3. Results and discussion

### 3.1. *Morphology*

SEM image of nanocrystalline $Fe_{70}Pt_{30}$ film is presented in figure 1. It is evident from this image that the size of these nanoparticles varies from 5–10 nm. SEM and TEM images of CNTs grown on $Fe_{70}Pt_{30}$ catalysed film are shown in figures 2 and 3.

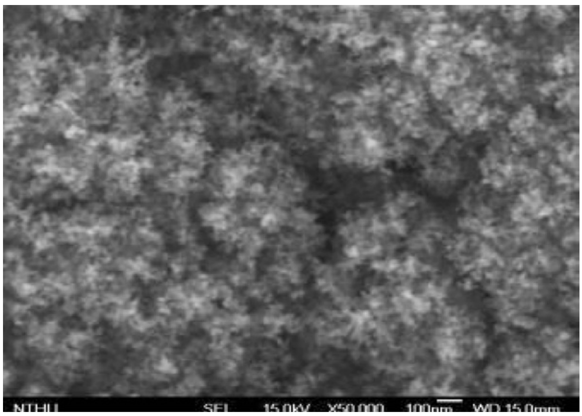

Figure 1. SEM image of $Fe_{70}Pt_{30}$ nanocrystalline film.

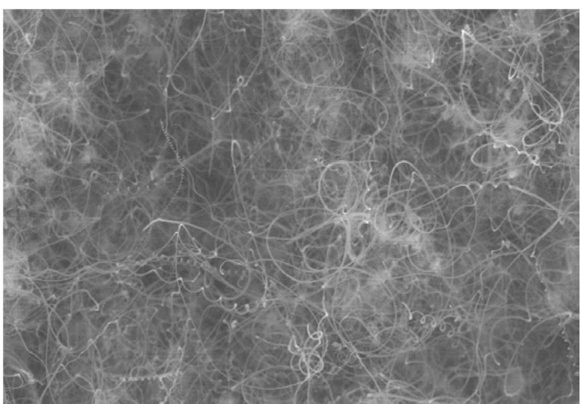

Figure 2. SEM image of CNTs grown on $Fe_{70}Pt_{30}$ nanocrystalline film.

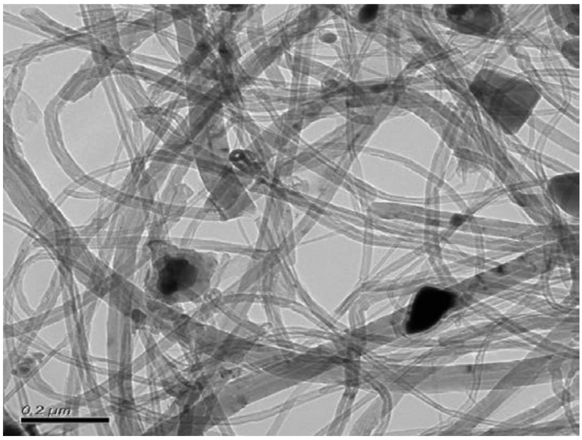


Figure 3. TEM image of CNTs grown on $Fe_{70}Pt_{30}$ nanocrystalline film.



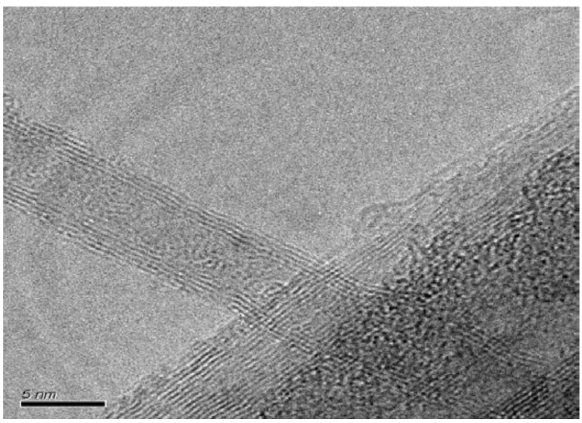


Figure 4. HRTEM image of CNTs grown on $Fe_{70}Pt_{30}$ nanocrystalline film.

The diameter of these CNTs varies from 20 nm to 50 nm and the length of these CNTs is of the order of several microns. From TEM image (figure 3) of the CNTs, it is observed that these are multiwalled nanotubes. The metal catalyst encapsulated at the tip of the CNTs can be seen. The growth for this kind of CNTs can be explained by tip growth mechanism [12, 13]. Figure 4 represents the HRTEM image of CNT. It is clear that the graphite layer lattice fringes are straight, continuous and parallel to tube axis. The inner diameter of this CNT is about 5 nm and numbers of graphene layers are about 30 nm with the interlayer spacing of 0.34 nm.

### 3.2. *Field emission studies*

In the past years, extensive studies have been devoted to the field emission characteristics of CNTs [14–19]. The Fowler-Nordheim theory [20] is the most

Table 1. Field emission parameters of carbon nanotubes grown on $Fe_{70}Pt_{30}$ nanocrystalline film for 5 min, 15 mins and 30 mins with working distances 50 μm, 100 μm and 150 μm.

| CNT | Working distance ($d$) (μm) | Growth time (min) | Turn-on field ($E_{to}$) (V/μm) at 10 μA/cm$^2$ | Field enhancement factor $\beta \times 10^6$ cm$^{-1}$ | Max. current density ($J$) (mA/cm$^2$) |
|---|---|---|---|---|---|
| Bamboo shaped MWNTs | 50 | 5 min | 14.49 | 2.18 | 0.399 |
| | | 15 min | 10.68 | 1.66 | 14.07 |
| | | 30 min | 8.79 | 1.48 | 23.03 |
| | 100 | 5 min | 6.74 | 6.63 | 3.909 |
| | | 15 min | 5.27 | 4.45 | 19.31 |
| | | 30 min | 4.74 | 2.65 | 95.53 |
| | 150 | 5 min | 6.21 | 9.32 | 39.9 |
| | | 15 min | 3.60 | 5.20 | 19.31 |
| | | 30 min | 2.45 | 4.26 | 23.0 |

commonly used model for the emission of cold electrons from a metal under a strong applied field. The F–N plots for the samples yielded a field emission parameter by simple slope and intercept method [21]. Small variations of the shape or surrounding of the emitter and/or the chemical state of the solid or of its surface have a strong impact on the emitted current.

One can also estimate the field enhancement factor ($\beta$) from measurements, provided that they follow the F–N model. The field enhancement factor ($\beta$) is calculated from the following simplified equation, assuming work function ($\phi$) to be 5 eV as for carbon [22].

$$\beta = 2.83 \times 10^7 \left[\frac{\phi^{3/2}}{S}\right] \mathrm{cm}^{-1} \tag{a}$$

where, $\phi$ = Work Function, $S$ = Slope of the F–N plot.

The turn-on field ($E_{to}$), (defined as the applied field needed to generate a current density of 10 μA/cm$^2$), and maximum current density ($J$) were obtained from $J$–$E$ curves plotted for different growth times and for different working distances.

The role of $\beta$ is to enhance the applied macroscopic electric field such that under the action of local electric field, tunnelling of electrons from the Fermi level, into the vacuum, through the potential barrier becomes possible. The interpretation of $\beta$ (a dimensionless quantity if electric field rather than voltage is used in analysis) is therefore, of great importance. Thus, it is important to increase the field emission enhancement factor in order to fabricate a field emission electron source with low operation voltage and high current.

Table 1 shows the calculated values of the field emission parameters. Figures 5–10 display the $J$–$E$ curves and the F–N plots of CNTs grown for 5 min, 15 min and 30 min for the working distances of 50 μm, 100 μm and 150 μm respectively. All the plots are approximately a straight line indicating that the emission mechanism is likely to be of the Fowler-Nordheim Fermi level tunnelling type.

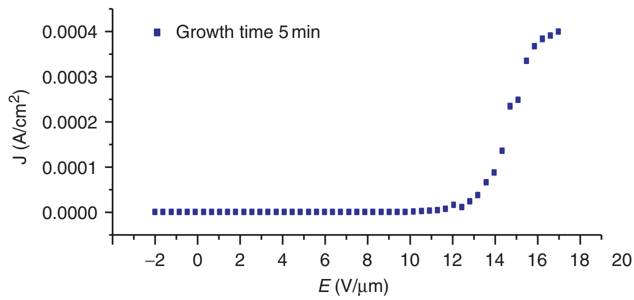


Figure 5. $J$–$E$ curves for CNTs grown for 5 mins, 15 min and 30 min, respectively, with working distance $(d) = 50\ \mu m$.

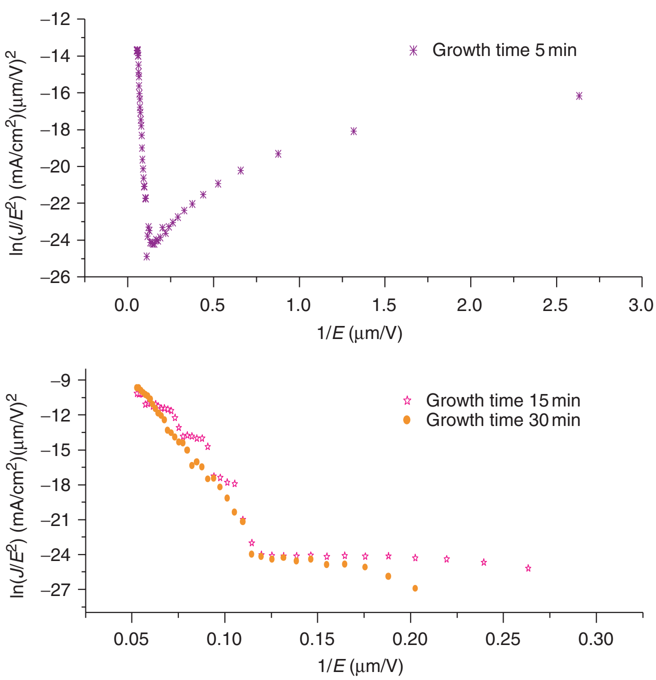


Figure 6. F–N plot for CNTs grown for 5 min, 15 min and 30 min, respectively, with working distance $(d) = 50\ \mu m$.

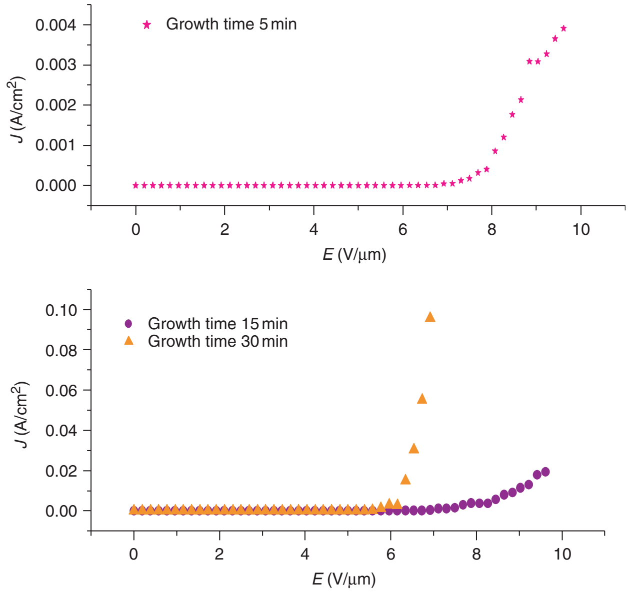


Figure 7. *J–E* curves for CNTs grown for 5 min, 15 min and 30 min, respectively, with working distance ($d$) = 100 µm.

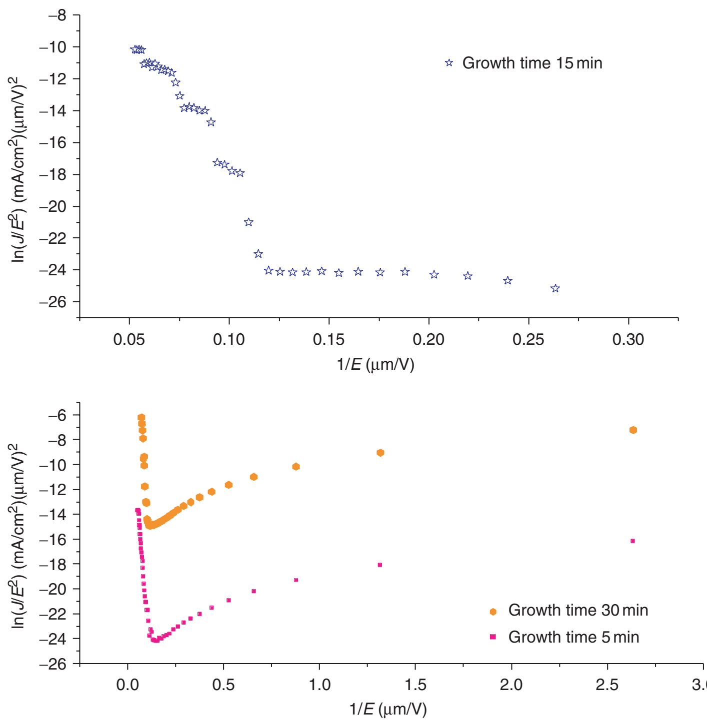


Figure 8. F–N plot for CNTs grown for 5 min, 15 min and 30 min, respectively, with working distance ($d$) = 100 µm.

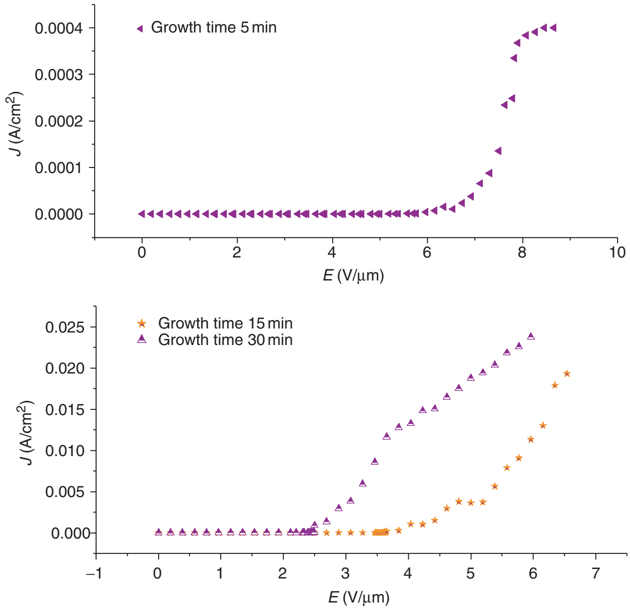


Figure 9. *J–E* curves for CNTs grown for 5 min, 15 min and 30 min, respectively, with working distance $(d) = 150\,\mu m$.

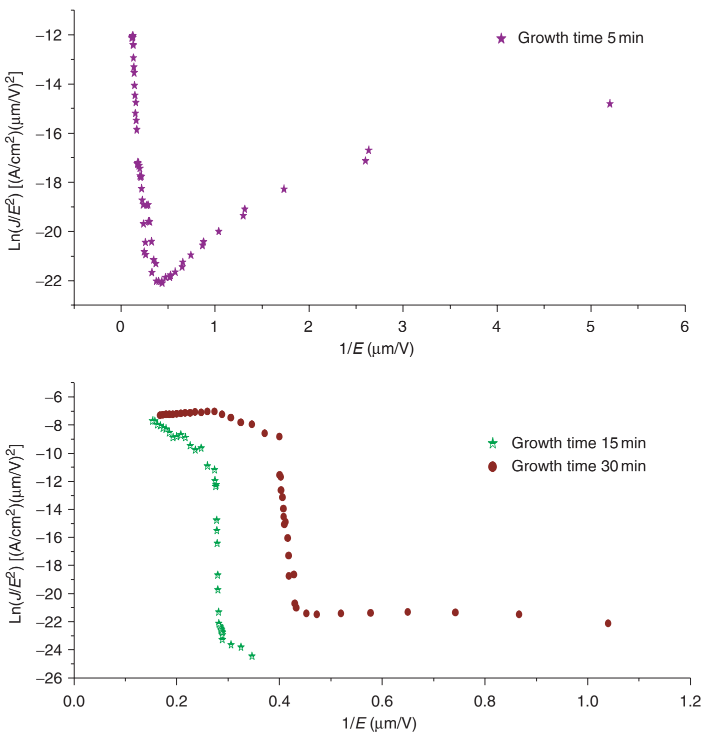


Figure 10. *F–N* plot for CNTs grown for 5 min, 15 min and 30 min, respectively, with working distance $(d) = 150\,\mu m$.

**3.2.1. Dependence of turn-on field ($E_{to}$) and field enhancement factor ($\beta$) on working distance ($d$).** Field emission parameters were calculated for working distances 50 µm, 100 µm and 150 µm and for different growth times 5 min, 15 min and 30 min respectively. Figure 11 shows a plot between turn-on field ($E_{to}$) and working distance ($d$). We find that the turn-on field ($E_{to}$) decreases with the increase in the working distance ($d$). The lowest turn-on field ($E_{to}$) 2.45 V/µm is obtained for working distance $d = 150$ µm at a current density of 10 µA/cm$^2$ for CNTs grown for 30 min. Maximum current density 39.9 mA/cm$^2$ is observed at 8.65 V/µm for CNTs grown for 30 min whereas the highest turn-on field ($E_{to}$) 14.49 V/µm is obtained for working distance ($d$) 50 µm at a current density of 10 µA/cm$^2$ for CNTs grown for 5 min. Maximum current density 23.03 mA/cm$^2$ for this working distance is observed at 8.79 V/µm for CNTs grown for 30 min.

The dependence of the field enhancement factor ($\beta$) on the working distance (d) is also studied. The value of field enhancement factor ($\beta$) is estimated from the F–N slope in the low current regime taking working function ($\phi$) as 5 eV for graphite and $C_{60}$. It is found that *field enhancement factor* ($\beta$) *increases with the increase of the working distance* ($d$) *from 50 to 150 µm* as shown in figure 12. The maximum calculated value of the field enhancement factor ($\beta$) is $9.32 \times 10^6\,\mathrm{cm}^{-1}$ for working distance ($d$) 150 µm for CNTs grown for 5 min whereas, the lowest value of field enhancement factor ($\beta$) is calculated to be $1.48 \times 10^6\,\mathrm{cm}^{-1}$ for working distance (d) 50 µm for CNTs grown for 30 min.

Lee *et al.* [23] studied the field emission properties of CNTs and showed that the turn-on field was 4.8 V/µm at an emission density of 10 µA/cm$^2$. Saito *et al.* [24] calculated the field enhancement factor in the range of $10^4\,\mathrm{cm}^{-1}$ to $10^5\,\mathrm{cm}^{-1}$ for MWNTs. Jo *et al.* [25] studied the field emission of carbon nanotubes (MWNTs) grown on carbon cloth and obtained a field enhancement factor of $3.5 \times 10^4$ cm. This suggests that our results are in good agreement with the other workers [23–25].

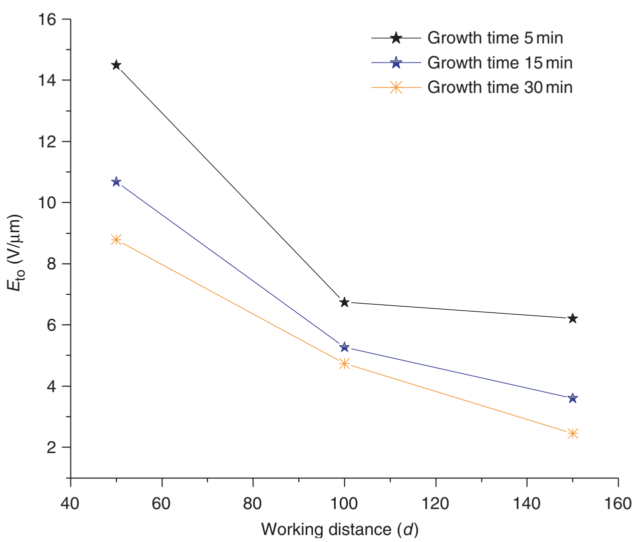


Figure 11. Working distance ($d$) vs. turn-on field ($E_{to}$) for CNTs grown for 5 min, 15 min and 30 min, respectively, for working distances ($d$) = 50 µm, 100 µm and 150 µm.

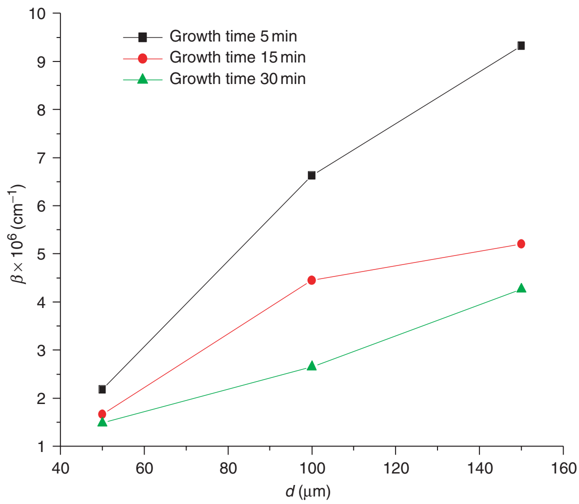


Figure 12. Working distance ($d$) vs. field enhancement factor ($\beta$) for CNTs grown for 5 min, 15 min and 30 min, respectively, for working distances ($d$) = 50 µm, 100 µm and 150 µm.



Therefore, we see that the best field emission parameters with lowest turn-on field ($E_{to}$) and highest field enhancement factor ($\beta$) are obtained for working distance ($d$) 150 µm.

**3.2.2. Dependence of turn-on field ($E_{to}$) and field enhancement factor ($\beta$) on growth time.** A plot between growth time verses turn-on field ($E_{to}$) and field enhancement factor ($\beta$) respectively are also presented (figures 13 and 14). It is observed that the value of turn-on field ($E_{to}$) and field enhancement factor ($\beta$) decreases with the increase in the growth time. The $E_{to}$ increases from 2.45 V/µm to 6.21 V/µm as the growth time decreases from 30 min to 5 min for working distance ($d$) 150 µm and the value of field enhancement factor ($\beta$) increases from $4.26 \times 10^6\,\mathrm{cm}^{-1}$ to $9.32 \times 10^6\mathrm{cm}^{-1}$ as growth time decreases from 30 min to 5 min for the same working distance. Excellent field emission properties of CNTs result certainly from the large field enhancement factors and elongated shape of the CNTs [26, 27]. In our case as the growth time decreases the values of $\beta$ and $E_{to}$ increases, which indicates that large field enhancement factor results from low growth time. Therefore, growth time may be believed to play a vital role in the field emission properties of CNTs.

**3.2.3. Dependence of field enhancement factor ($\beta$) on radius of apex curvature ($r$).** We have also studied the dependence of field enhancement factor ($\beta$) on the radius of apex curvature ($r$). It indicates that $\beta$ increases with the decrease in $r$, as shown in figure 15. It is clear from the figure that the tube radius plays a key role in the field enhancement. This relationship between $\beta$ and $r$ can be approximately fitted to $\beta \propto r^{-1/2}$, which is consistent with the result reported by other workers [28].

Xu *et al.* [29] found a linear dependence of field enhancement factor $\beta$ on the distance $d$ between the nanotube tip and the anode. Their theoretical calculations show that the tube lengths have little influence on $\beta$, while the radius of emission apex $r$ is an important factor in field emission with a relationship of $\beta \propto r^{-1/2}$.

Comparing the parameters for the CNTs with working distances 50 µm, 100 µm and 150 µm, we can interpret that the best field emission property with the lowest turn-on field ($E_{to}$) is exhibited by CNTs with working distance 150 µm whereas the highest $E_{to}$ was observed in the FE characteristics of CNTs with working distance 50 µm. This change in the values of the field emission parameters can be interpreted in terms of formation of some amorphous carbon resulting from the growth process, which plays an important role in the electron field emission properties. It also seems that radius of apex curvature ($r$) plays an important role in the field emission characteristics with a relationship $\beta \propto r^{-1/2}$. For good emission characteristics, large amplification factor, arising from the small radius of emission apex of the nanotube tips plays an important factor in field emission. Further the plot between growth time and field enhancement factor ($\beta$) shows that the growth time also has an influence on field enhancement factor ($\beta$). Therefore, growth time could possibly play a significant role in the emission properties of the CNTs. The difference in the emission properties may result from the different diameters, geometry and the graphitized structure of the CNTs.

In our case also, the presence of unorganised carbon plays a vital role in the field emission parameters. We observed that the field emission properties are superior for working distance $(d) = 150$ µm whereas the values of field emission parameters for smaller working distances ($d$) (100 µm, 50 µm) are lower. The lower values of field emission parameters may result due to detachment of some of the CNTs from the substrate for smaller working distance (50 µm) resulting in poor field emission properties.

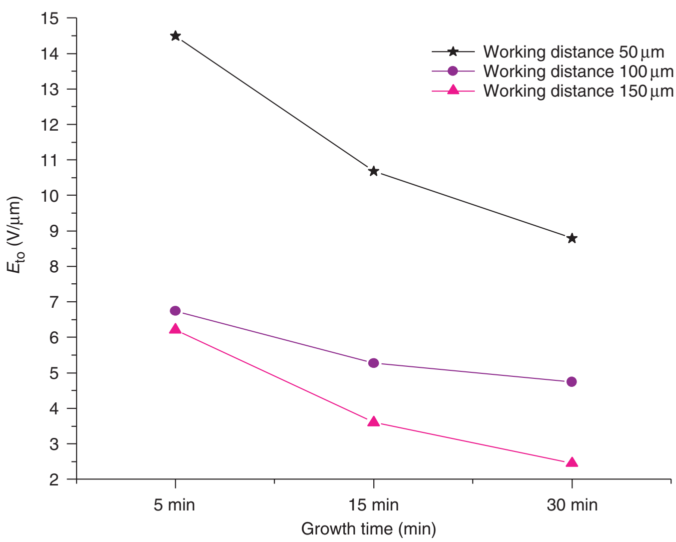


Figure 13. Growth time vs. turn-on field ($E_{to}$) for CNTs grown for 5 min, 15 min and 30 min, respectively, for working distances $(d) = 50$ µm, 100 µm and 150 µm.

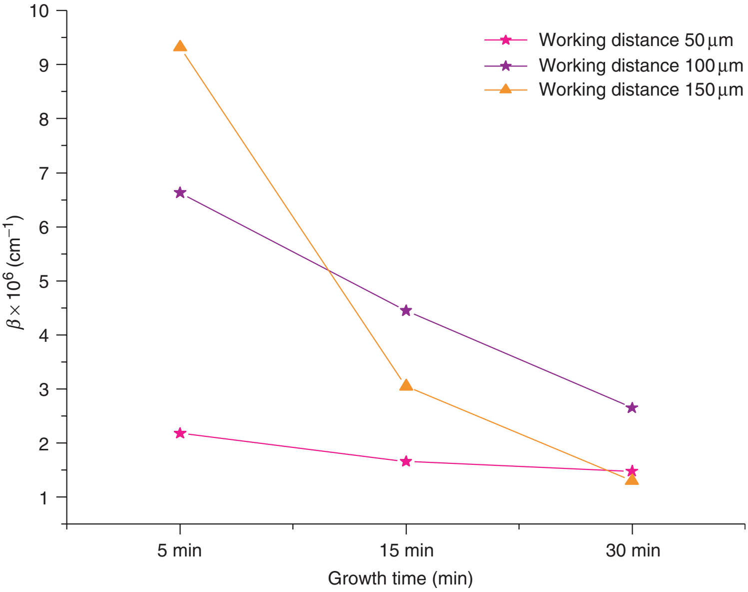


Figure 14. Growth time vs. field enhancement factor ($\beta$) for CNTs grown for 5 min, 15 min and 30 min, respectively, for working distances ($d$) = 50 µm, 100 µm and 150 µm.

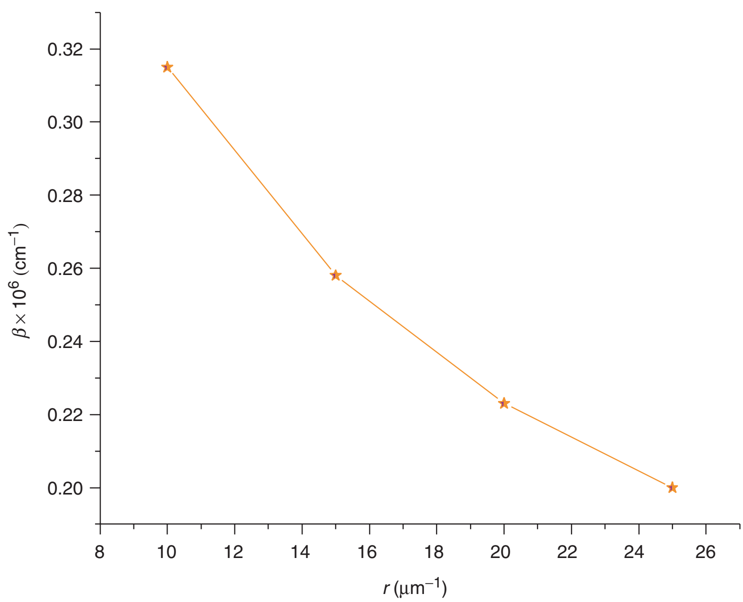


Figure 15. Radius of apex curvature vs, field enhancement factor ($\beta$) for CNTs grown for 5 min, 15 min and 30 min, respectively, for working distances ($d$) = 50 µm, 100 µm and 150 µm.

## 4. Conclusion

MWNTs were grown on $Fe_{70}Pt_{30}$ nanocrystalline film. The *J–E* characteristics curves and F–N plots of carbon nanotube field emitters were measured using a cathode-anode arrangement. Amongst all the other parameters (growth time and working distance ($d$)), carbon nanotubes grown for a longer time (30 min) show a superior turn-on field ($E_{to}$) of 2.45 V/μm ($d = 150$ μm) when current density achieves 10 μA/cm$^2$. It may be concluded that the CNT with the lowest turn-on field ($E_{to}$) and high field enhancement factor ($\beta$) corresponding to different growth times and working distances ($d$) shows good field emission properties. The presence of unorganised carbon may be responsible for the change in the field emission properties. The effect of growth time on the field emission characteristics plays an imperative role resulting in good field emission properties. As the working distance ($d$) increases from 50 μm to 150 μm, the field enhancement factor ($\beta$) increases. The relationship $\beta \propto r^{-1/2}$ results in an important conclusion that the radius of apex curvature ($r$) is one of the important factors for attaining good field emission properties.



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