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PII: S0039-6028(16)30797-X
DOI: http://dx.doi.org/10.1016/j.susc.2017.05.002
Reference: SUSC21025

To appear in: Surface Science

Received date: 26 December 2016
Revised date: 6 April 2017
Accepted date: 4 May 2017


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Study of Thermal-Field Emission Properties and Investigation of Temperature dependent Noise in the Emission Current form vertical Carbon nanotube emitters
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Abstract
We have investigated temperature dependent field electron emission characteristics of vertical carbon nanotubes (CNTs). The generalized expression for electron emission from well defined cathode surface is given by Millikan and Lauritsen [1] for the combination of temperature and electric field effect. The same expression has been used to explain the electron emission characteristics from vertical CNT emitters. Furthermore, this has been applied to explain the electron emission for different temperatures ranging from room temperature to 1500 K. The real-time field electron emission images at room temperature and 1500 K are recorded by using Charge Coupled Device (CCD), in order to understand the effect of temperature on electron emission spots in image morphology (as indicated by ring like structures) and electron emission spot intensity of the emitters. Moreover, the field electron emission images can be used to calculate the total number of emitters per cm\textsuperscript{2} for electron emission. The calculated number of emitters per cm\textsuperscript{2} is 4.5x10\textsuperscript{7} and, the actual number emitters per cm\textsuperscript{2} present for electron emission calculated from Atomic Force Microscopy (AFM) data is 1.2x10\textsuperscript{12}. The measured Current-Voltage (I-V) characteristics obey the Folwer-Nordheim (F-N) type behavior. The fluctuations in the emission current are recorded at different temperatures and, temperature dependence of power spectral density obeys power law relation \(s(f)=I^2/f^2\) with that of emission current and frequency.

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Figure: shows strong enhancement in the field emission current as well as new electron emission site due to temperature (a) AFM morphology for vertical CNT, (b) FEM image of vertical CNT at 1500 K and applied voltage of 1400 V, (c) I-V plots at RT, 1500 K, power spectral density versus temperature used for activation energy calculation.

**Keywords:** Vertical Carbon nanotubes, Thermal-field emission, Noise in emission current etc.

I. **Introduction**

Carbon nanotubes (CNTs) have attracted great interest due to their extraordinary electron emission properties. Recently many reports have shown the potential applications of these vertical CNTs [2, 3 reference], the controllable vertical alignment and tunable spacing between CNTs on different supports is found to be the most acceptable geometry for electron emission device applications such as cathode ray tube, electron source etc. There are several reports on field electron emission from vertically aligned CNTs [4-6] and thermionic emission from vertical
CNTs [7-9]. Even though there are few reports available on thermal-field emission study on vertical CNTs [10-13], the thermal-field emission phenomenon is not fully understood. In order to understand the thermal-field emission, a systematic study of temperature dependent electron emission from vertical CNTs is necessary. M. C. Kan et al reported that at 574 K temperature the electron emission from amorphous carbon with nano-tips and CNTs is 13 times higher than the electron emission at room temperature (RT) [14]. Previous theoretical reports have used approximations by series expansion and numerical methods, in order to understand emission patterns in various circumstances [15-18]. Among these studies, S. C. Lin et al adapted Christov general theory of electron emission to analyze the thermal-field emission from multi-walled CNTs [19]. None the less, Millikan-Lauritzen (M-L) thermal-field emission theory is equally applicable for theoretical explanation of vertical CNT type emitters. In general the M-L theory for electron emission assumes that the field emitted electrons are drawn from the cold metal by the application of large enough electric field at the surface to yield an appreciable probability that an electron will escape by the tunnel effect through the narrow potential barrier, with same assumption the generalized expression for temperature and electric field dependent current \( I \) is given by

\[
I = A(T + cF)^2 e^{-b} e^{T/cF} 
\]  

when \( F=0 \) the equation reduces to the usual thermionic equation, when \( T=0 \) (or is small compared to \( cF \)) it reduces to field emission equation, and when \( T \) is comparable with \( cF \) it yields computation effects between temperature and electric field, the constants \( b \) and \( c \) can be calculated from thermionic emission and, field emission data respectively [1].

The study of emission current stability and fluctuations in the emission current (i.e. noise in emission current) from vertical CNT emitters are not only important but also equally useful for long time device performance and sustainability. There have been few reports available on the measurements of emission current fluctuations from CNT emitters at room temperature [20-22]. To the best of our knowledge there is no report which presents emission current fluctuations and, calculates the activation energy at different temperatures from vertical CNT emitters.

In this work, we have reported the temperature effect on field emission from vertical CNT emitters, synthesized by water assisted chemical vapor deposition (WA-CVD) technique. The changes in turn-on field have been observed due to increase or decrease in temperature. The
actual number of CNT emitters per cm$^2$ at room temperature and at 1500 K has been calculated from AFM data and, field electron emission spot intensity images, obtained results are then compared. The fluctuations in emission current as a function of real-time are plotted at various temperatures. The calculated temperature dependence of power spectral density obeys power law of $s(f) = I^2/f^2$. The temperature dependent fluctuations in the emission current from vertical CNT emitters have been analyzed in the light of the bistable (two states) statistical model of electron emission.

II. Experimental detail

The details about the CNT growth using WA-CVD is discussed elsewhere [23, 24]. In short the process is as follows; a 17 nm thick aluminum (Al) (barrier) layer was initially deposited on tungsten (W) filaments by e-beam evaporation. Subsequently, 1 nm thick Fe (catalyst) was deposited on the same. The deposition rate was kept fixed at 0.1 A/s. These as processed W filaments were then used to grow vertical CNTs. The samples were then subjected to the homemade Ultra High Vacuum (UHV) system for all thermal-field emission measurements. The UHV system consists of main chamber, equipped with thermal field emission tube, ionization gauge and, a multi stage pumping system. This multistage pumping system consists of Ion pump, Turbo-molecular pump and, backing pump. The stable pressure of $10^{-8}$ Torr was obtained and the same pressure is maintained during all the electron emission measurements. The thermal field emission setup is made up of simple diode geometry in which tungsten cathode (a rectangular strip of dimension length ($l = 2$ cm), width ($w = 2$ mm) and thickness ($t = 0.1$ mm)) is connected to a 30 V, 10 A power supply and the molybdenum anode is connected (0.1 mm thick sheet of 2 cm × 2 cm size) to a highly stabilized 10 kV, 10 mA power supply (SEPLLMAN, Model SL10). The low voltage power supply was used for heating the filament whereas the high voltage supply facilitated current-voltage (I-V) measurements. The distance between the cathode and anode surfaces was ~5 mm. The measurements of emission current at different filament temperatures were carried out using HP multimeter (Model 5015) capable of measuring current with accuracy of 0.1%. Figure 1 represents the schematic diagram of thermal field emission experimental setup.
The filament temperature was determined by using the expression $R_t = R_0 (1 + \alpha t)$, where $R_t$ is the resistance of the filament at temperature $t$ °C, $R_0$ is the resistance at 0 °C and $\alpha$ is temperature coefficient of resistance. The resistance at room temperature was measured by passing 50 mA current through the filament after confirming that this much current does not heat up the filament [25]. The image formed on the phosphor screen is being captured using Sony hand held CCD having resolution of 12 Mega pixels. The program for the field electron emission current signal (emission current-time) acquisition is developed using National Instruments based Lab VIEW 8.2 software. The program has a facility to change the sampling rate, signal grabbing time and, the emission current. The grabbed signal can be analyzed online as well as offline.

III. Results and Discussion

Figure 2(a) and 2(b) shows the scanning electron microscopy (SEM) micrographs of vertically aligned CNTs before and after the experiment, the SEM micrographs shows the densely, well aligned vertical CNTs bundles. After thermal-field emission measurements the CNTs remain without any surface damage or surface modification. This suggests that after several temperature cycles the CNTs are stable and gives reproducible electron emission. Figure 2 (c) shows the field emission pattern on phosphor screen at RT and, at 1480 V applied voltage and at 0.001 mA emission current. Figure 2 (d) shows the electron emission pattern on phosphor screen at 1500 K temperature, 1480 V applied voltage and, 0.0021 mA emission current was
recorded. From the field emission images as shown in figure 2 (c) and (d) very intense bright ring like patterns are observed. Similar kind of field emission patterns on vertical CNT emitters are reported in our previous report and, which are compared with other morphology carbon structures such as carbon nanoflakes (CNFs), exfoliated Highly Oriented Pyrolytic Graphite (HOPG) flakes etc. [26]. The plausible reason for ring like pattern is the electric field effect of CNT bundles as well as the edge electron emission property of electron trajectory of the CNT bundles. The magnification of field emission pattern on phosphor screen is of the order of $10^4$ higher than the actual size of the CNT bundles. Further, the investigation about the formation of ring like pattern is in progress. In figure 2 (d) it is observed that, when temperature reaches 1500 K, the ring like patterns as well as more number of intense bright spots of electron emission are observed. This is probably due to the higher temperature (1500 K), at this temperature large number of vertical CNT emitters are involved in the electron emission processes. Due to several temperature cycles, cleaning of CNT surface takes place, thus the gas adsorbents on CNT surface gets removed, this can be one of the possible reason for increase in emission current and hence higher number of emission spots are observed on the phosphor screen. Earlier report says that, at RT the field emission from CNT emitters, is likely to be through adsorbates like H$_2$O and O$_2$ etc, provided that the emitters are not properly cleaned [27]. The fluctuations in the emission current from CNT emitters and understanding the origin of noise at RT gives better insights of electron emission processes across the clean CNT emitter surface.
In the standard F-N theory, the emission current is a function of the work function (Φ), voltage (V), voltage conservation factor (β), the emitting area (a) and is given by [28]

\[ I = aV^2\exp(-b/B)\text{amp/cm}^2, \]  

(2)

Where \( a = A\alpha\beta^2(1.1\Phi)^{-1}\exp[1.14\times10^{-7}(B\Phi^{-1/2})] \), \( b = 0.95\Phi^{3/2}B/\beta \), \( A = 1.54\times10^{-6} \), \( B = 6.87\times10^7 \).

The voltage conservation factor \( \beta \) is proportionality factor between applied voltage (V) and electric field (E) at the cathode apex, \( E = \beta V \). B can be split in two components, \( \beta = \gamma/d \), so as to separate the geometric enhancement factor (γ) from the anode-cathode separation (d). For flat anode and cathode the field enhancement factor is 1 and, the density of equipotential surfaces is constant between the anode and cathode. The geometric field enhancement factor arises from compression of equipotential surfaces around a protrusion on the cathode that leads to the maximum electric field being at the apex of the protrusion.
Figure 3. (a) Current versus voltage graph red color at 1500 K temperature and black color at room temperature, (b) F-N plot (c) number of emitters per cm$^2$ versus temperature both experimental and theoretical, (d) number of emitters per cm$^2$ versus voltage at room temperature and 1500 K.

Figure 3 (a) shows the plot of emission current versus applied voltage at RT and 1500 K, it is observed that the turn-on voltage reduced from 1220 V to 1100 V at 1500 K temperature.

Figure 3 (b) shows the corresponding F-N plot at RT and 1500 K temperature, the non-linear behavior of F-N plot indicates the semiconducting nature of CNT emitters at RT as well as at 1500 K without examining noticeable change in the slope. There are few reports on explanation of field emission from semiconducting CNT emitter as well as non-linear behavior of F-N plots [19, 29, and 30]. The F-N plot slope is directly related to the surface properties of the emitters such as Fermi energy, work function and, electron emission barrier height etc. From the morphology measurements before and after thermal-field emission experiment, the CNT surface remains same, except some adsorbents gets removed from the surface of CNT emitters. Figure 3 (c) shows the graph of number of emitters per cm$^2$ versus temperature, initially at 1200 K, roughly $\sim 1.17 \times 10^8$ number of emitters are observed, when the applied voltage is kept fix at 1100 V. As the temperature increases the number of emitters per cm$^2$ goes on increasing and at 1425
K, roughly ~4.5x10^8 number of emitters are observed. This indicates that as temperature increases, the number of emitting sites are also increasing, which ultimately results in the increased emission current. Red curve in figure 3 (c) indicates the graph of number of emitters with constant applied voltage at different temperature ranging from 1052 K to 1500 K, it can be seen that at higher temperature (1500 K) number of emitters are more as compared to the emitters at RT. To understand theoretically, black curve in figure 3 (c) indicates the graph of number of emitters versus temperature using statistical model of power spectral density as shown in equation (4). This indicates that both graphs show same behavior. Figure 3 (d) represents the plot of number of CNT emitters versus applied voltage at RT and at 1500 K, which shows similar behavior as indicated in figure 3 (c).

In general, the statistical model is based on the many emitting states of the electron emitting cathodes, in which the number of emitting sites are N(t), let λ_n(t) be the transition rate, where n is state number and t is time. The corresponding expression for the spectral density can be written as [31],

$$S_f(w) = \frac{AI^2}{\pi N_0 w^2}$$  \hspace{1cm} (4)

Where I=I_0N_0, I_0 is the square of the mean current from single site and N_0 is average number of emitting sites. The model for bistable fluctuations in field emission from individual site assumes that the multistable fluctuations in the field emission are results of independent emissive centers. The hypothesis suggests that there is linear relationship between transition rate λ and state number.

The comparison is valid between the number of emitters per cm^2 calculated from Atomic Force Microscopy (AFM) images with that of the number emitters calculated from field emission images taken at different temperatures. Figure 4 (a) shows the AFM morphology of the top surface of vertical CNT emitters, from AFM image the calculated number of CNT emitters per cm^2 are found to be ~1.27x10^{12}. This number is 10^4 times higher in magnitude than the actual CNT emitters (1.17 x 10^8) which are contributing into electron emission current as shown in figure 4 (b). In figure 4 (b), the sharp intense spot on phosphor screen is used for the calculation of the number of CNT emitters which are mainly contributing in the electron emission processes.
Figure 4 (a) shows AFM image of top surface of vertical CNTs, (b) shows the FEM image of vertical CNT emitters at 1500 K temperature and, at 1480 V applied voltage.

The ratio of the actual emitters is taking part in electron emission processes (calculated from field emission images) to that of the total number of emitters (calculated from AFM images) available for electron emission is,

\[
\frac{\text{Number of emitters per cm}^2 \text{ from FEM image}}{\text{Number of emitters per cm}^2 \text{ from AFM image}} = 10^{-4}
\]  
(5)

It is worthwhile to compare the calculated number of emitters per cm² on field emission images and that of AFM images and interestingly the ratio is $10^{-4}$, which suggest that the very less number of CNTs are taking part in the emission process out of larger number of CNTs which are present on the surface. This is due to F-N condition, only those fulfill the F-N condition takes part in electron emission process, other may require higher electric field in order to emit.

Figure 5 (a) shows the fluctuations in the emission current as a function of time at various temperatures ranging from 1053 K to 1500 K. It has been observed that the individual sharp spikes as well as sharp spikes density increase in the emission current after certain time interval and, as temperature increases from 1053 K to 1500 K. The sharp intense spike remains there for long time interval around 5 hours. This suggests that the spike in the emission current is due to the carbon atom trapping and de-trapping on CNT emitter surface. Furthermore, the intensity of spike in the emission current increases with increase in temperature and, it is high at 1500 K.
Similar type of observation is reported by Dong et al on ZnO nanowire emitter, after adsorbate removal at 1027 K, the apparently clean nanowire state shows lower emission current [32]. This suggests that the presence of adsorbates on the emitter surface tends to show more current as compared with clean surface, which is due to resonance tunneling through adsorbates. Figure 5 (a) shows the fluctuation in the emission current recorded at various temperatures and, the power spectral density is calculated from CNT emitter in a frequency range from 1 Hz to 6 kHz. The power spectral density is often used to study the current fluctuation mechanisms of an electron emitter. For example, in the study of noise in the tungsten field emitter, Collins and Zettl found that the noise spectra were of the $1/f^\beta$ characteristic as the impurity atoms of residual gases having lower work function diffuses over the emitter surface [22]. In most of the cases, an exponent $\beta$ is close to 3/2. In our experiment, the relationship between noise power spectral density and the frequency of CNT emitters are demonstrated as shown in figure 5 (b). From the slope the calculated exponent $\beta$ is around 1.78. Figure 5 (c) shows the logarithmic plot of power spectral density versus emission current in order to understand the power spectral density behavior with that of current, the slope of graph 1.82, which is nothing but the exponent gamma ($\omega$), the power spectral density of CNT emitters shows a $(I^{1.82}/f^{1.78})$ characteristic. These noise spectra suggest that current fluctuations of CNTs may also have resulted from diffusion of adsorbates of the CNT surface. In our previous report the aspect ratio of CNT emitters are high as compared to conventional tungsten cathode but the reported signal to noise ratios (I/dI) are ~16 % for CNTs, suggesting that in spite of comparable long term stability of CNT thermionic cathodes are noisier than tungsten cathode [25].
The activation energy of CNT emitters was calculated as shown in the figure 5 (d), the plot of power spectral density versus temperature is presented, fluctuations in the emission current starts from initial temperature 1052 K up to 1392 K. The power spectral density up to 1040 K is more or less stable and at temperature of 1052 K, it increases to its highest value reported in the present report. Inset of Figure 5 (d) shows logarithm of power spectral density versus 1/T, which fits straight line well. From the slope the calculated activation energy comes around ~3.5 eV and it matches well with the reported value.

IV. Conclusion

The thermal field electron emission from vertical CNT emitters have been carried out in the present report, it has been shown that the turn-on voltage for electron emission from vertical CNT emitters decreases as the temperature of CNT emitters increases. The temperature dependent electron emission analysis for vertical CNT emitter’s indicates that due to temperature the number of CNT emitters emitting sites as well as emission current increases. It has been
observed that the ratio of number of CNT emitters from field emission to the number of CNT emitters from AFM measurement is of the order of $10^{-4}$. This temperature dependent/thermally agitated electron emission is highly reproducible. The temperature dependent/thermally agitates electron emission suggests that the presence of defect band that allows electrons overcome the work function easily [14]. Furthermore, the analysis of F-N plots strongly support the semiconducting behavior of vertical CNT emitters. Fluctuations in the emission current suggests that the temperature dependent of power spectral density for CNTs emitters follows the power law $P(f) = A.f^2/f^2$. The calculated activation energy from arrhenius plot is $\sim 3.4$ eV and, which agrees well with reported values.

Acknowledgement

SK acknowledges UGC, Govt. of India and CSIR, Govt. of India for Research Fellowships.

References

Highlights

- Thermal-field emission measurements from vertical CNT emitter’s potential application as a cathode source in electron emission devices.
- It has been observed that, strong enhancement in the emission current as well as opening of electron emission sites from vertical CNT emitters due to temperature effect and it has been highly reproducible.
- The fluctuations in the emission obeys the temperature dependent of power spectral density for CNTs emitters and it follows the power law $P(f) = A.I^2/f^2$.
- It has been observed that the calculated activation energy from arrhenius plot is ~3.4 eV for CNT emitters.