Electrical Conduction Characteristics of a Thick-film Form Multiwalled Carbon Nanotubes for Field Electron Emitter

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ABSTRACT

Measurements of the direct current resistivity, on multiwalled carbon nanotubes(MWNT) for field electron emitter source that had been screen printed in a thick film form were made as a function of temperature T in the range of 1.7K-390K. In this measuring temperature range, the electrical resistivity for the MWNT show that the main contribution to the conductivity comes form carries that hop directly between localized states executing variable range hopping processes. This thick-film form system for large area display showed a high bright light emission as well as very low turn-on field as like an individual MWNT system at room temperature. Furthermore, the electron emission characteristics followed well typical Fowler-Nordheim conduction under the vacuum.

I. INTRODUCTION

During the past few years, carbon nanotubes attracted much attention due to their extraordinarily properties and possibilities for various applications, which may be utilized in electronic, medical, chemical fields[1]. Measurements of individual physical properties of though the potential applications of NT in nanotechnology are for the moment speculative and the production and purification of NTs having controlled structural and electrical characteristics will probably be required in a near future.

Due to high aspect ratio and small tip radii of curvature, carbon NT(CNT) may be suitable for electron field emission and therefore, great attention has been paid to field emission of MWNT due to its long-term stability and mechanical strength as compared to those of single wall nanotubes[2]. The electronic properties of MWNTs are of great interest, but they also appear to be the most challenging to measure. This work presents a detailed study of the structural and electrical properties of both purified MWNTs and a thick-film form MCNT film mixed with conductive paste for field electron emitter with large area.

II. EXPERIMENTS

The starting raw CNT material were provided by arc-deposition. Three batches (2g) of MCNT raw deposits were first placed on an alumina plate and heated to 600°C for 30min under normal atmosphere. After initial firing, the powders were removed from the furnace, weighted, regrounded in ethanol using ultrasonic cleaner. In order to remove metallic impurities, the MCNT powder were immersed in acid and then rinsed in deionized water, repeatedly. We measured a low magnification tunneling electron microscopy, X-ray diffraction analysis, raman spectra, and temperature-dependent conduction electron spin resonance spectroscopy for the MCNT powder before and after simple purification process used in this work. Electrical resistivity was obtained by using the conventional four probe measurement system in the temperature range of 1.7K-390K.

II. RESULTS AND DISCUSSION

Tunneling electron microscopy (TEM) was used to characterize the CNT thick films. Fig. 1 reveal that all the NTs are multiwall tubes with end capped at the tips, as shown, though no clear images was displayed and NTs have diameters ranging from 10-30nm without nanocarbon particles on tubes.

The ESR studies of CNT reveal many aspects of the material and also illustrates very well the issue of defects and sample preparation. The effect of the annealing can also be seen by comparing the intensity and g-value dependence of CESR peaks for purified and purified annealed NTs, as shown in Fig. 2(a)(b) and (c). At room temperature, ESR spectra for the unpurified sample is clearly composed of two signals. These two signals are characteristic of an inhomogeneous material containing broad signal and narrow signal. For the purified CNT, ESR signal in Fig. 2(b) is asymmetrical and the magnitude of the positive and negative peaks different. This deviation from Lorentzian lineshape may originates from the motion of paramagnetic centers and non-uniform distribution of the microwave electromagnetic field due to the skin effect associated with the metallic regions, which was well separated from such as the nanoparticle and carboceous materials covering NT surfaces through purification. The measured *g*-value of the CNTs after purification in Fig. 2(c) showed a nearly constant value at measuring temperature range of 125K-405K, as compared to that of the unpurified one. The fact that the g-value of the purified CNT sample becomes temperature independent upon purification can be understood if the large portion of our CNTs have closed cylindrical structures, which was confirmed at TEM images. If the open tubes are dominant, the interlayer spacing and therefore interlayer interactions will be more temperature dependent[3].

Electrical resistivity is the most important property of CNT for characterizing electronic structure and their possible applications. Fig. 3 (a) shows the change in R which were measured as a function of temperature over 4K-390K for the thick-film form MWNT with an averaged external diameter of 10-15nm. It is found that resistivity increases rapidly below 100K and nearly constant between 100K and 360K and reincreases with the temperature over 360K. Fig. 3 (b) shows the resistivity of the MCNT plotted logarithmically against $T^{-1/2}$ and, in the inset, against $T^{-1/4}$ over the higher temperature range. The MCNT obeys a $\nu=1/4(T^{-\nu})$ hopping law from 10K-100K in Fig. (c). However, a single line does not fit the data over the entire temperature range of 1.9K-100K. The linear dependence of lnρ(T) on $T^{-1/2}$ indicates that Efros and Shklovskii(ES) VRH conduction in our system is slightly appeared at low temperature below 40K. More direct observation was possible at near 10K. It is accepted that a steeply increasing resistivity of the high conducting CNT can be explained as a weak localization of electrons in metallic system at a low temperature range of 10K-50K. For non-interacting electrons ν=1/4 in 3-dimensional, ES argued that, including Coulomb interactions, that because of long-range interactions between localized states, the density-of-states near the Fermi energy tend to zero which yield a parabolic Coulomb gap. Our system showed the crossover between Mott and ES hopping regimes as a function of temperature .

Field emission measurements were carried on the thick-film form MWNT films with a Cr lines as a cathode electrode onto sodalimed glass substrate. The spacing between ZnO:Zn coated ITO glass and the MWNT cathode was fixed at 100μm using glass fiber spacers. Field emission measurements were performed at a pressure of $2x10^{-6}$ Torr. The emission current(I) versus electric field(V/μm) plots for three kinds of MWNT systems with external diameter of 20-60nm, 10-15nm are shown in Fig. 4.(LHS. These characteristics are relatively stable and repeatable without degradation of background vacuum. The nominal onset fields for an emission current are 4.5V/μm, 2V/μm, respectively. The I-V data plotted according to the typical Fowler-Nowdheim (F-N) relationship for field emission, is shown in Fig. 4 (RHS).

III. SUMMARY

In the present work, we tried to study the difference between a typical individual MWNTs and our non-aligned thick-film form MWNT. As a result, we obtained an evidence for metallic properties of our thick film form MWNT system through ESR study. At initial stage, we expected that the electrical characteristics will be deviates remarkably from those for an individual system and a sheet form pure MWNT film. Contrary to our expectation, nearly same behaviors were observed in whole measuring temperature range except below about 10K. In this work, it is evident that the thick-film form MWNTs can be successfully applied for the glass-based large area planar emitter.

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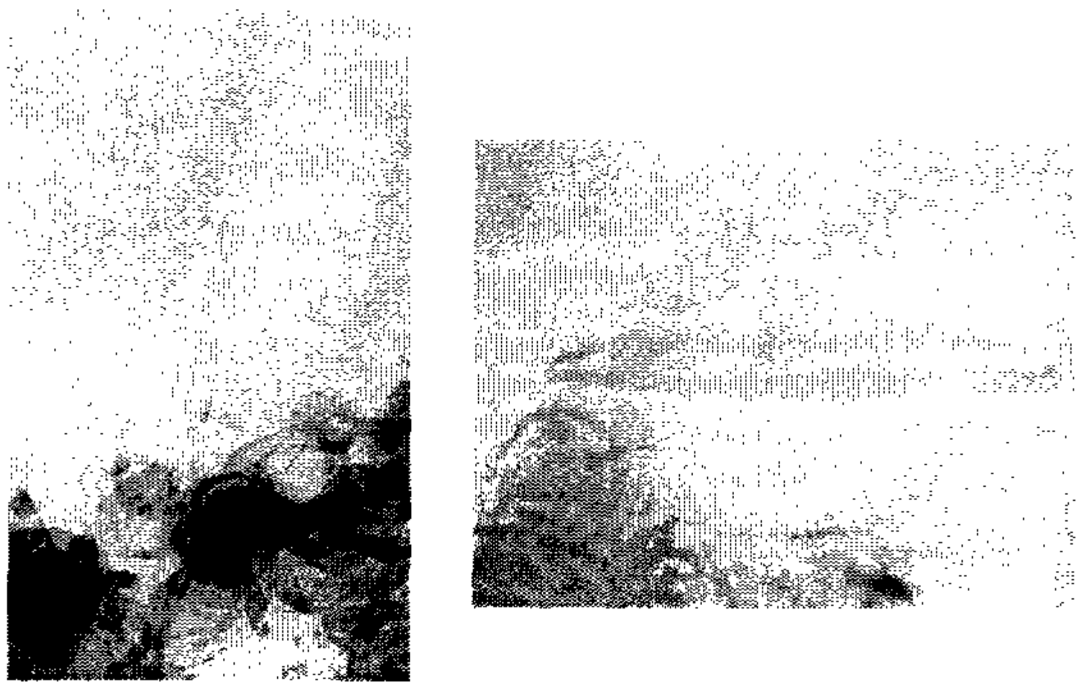

Fig. 1. A low resolution tunneling electron microphotograph for the MWNTs after purification process

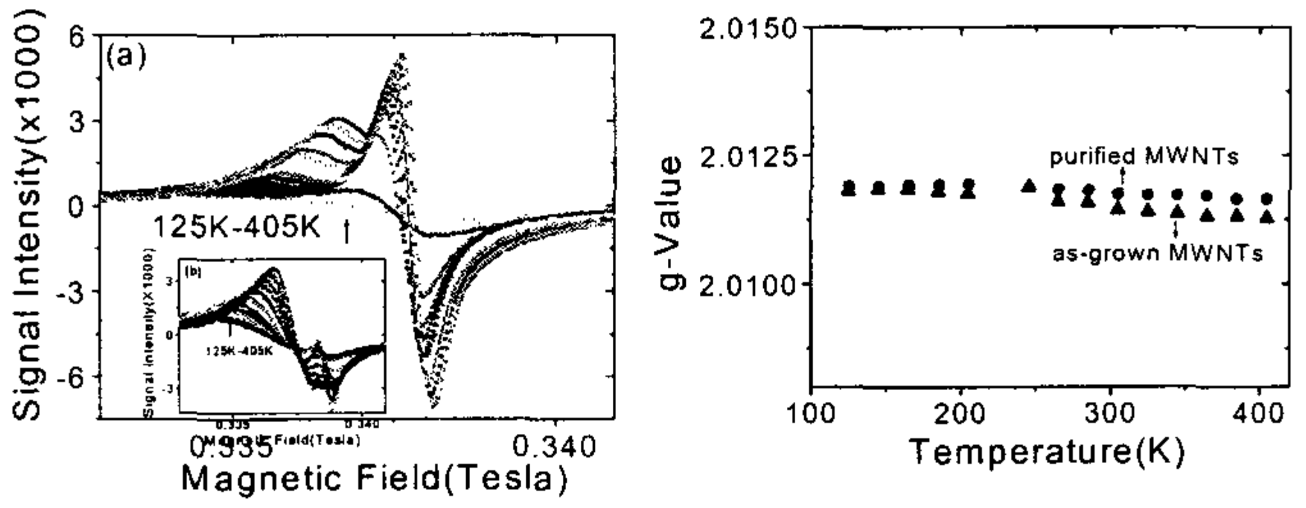

Fig. 2. ESR spectra of the MWNTs(LHS) and comparison of temperature dependence of g-value of ESR before and after (RHS) purification process.

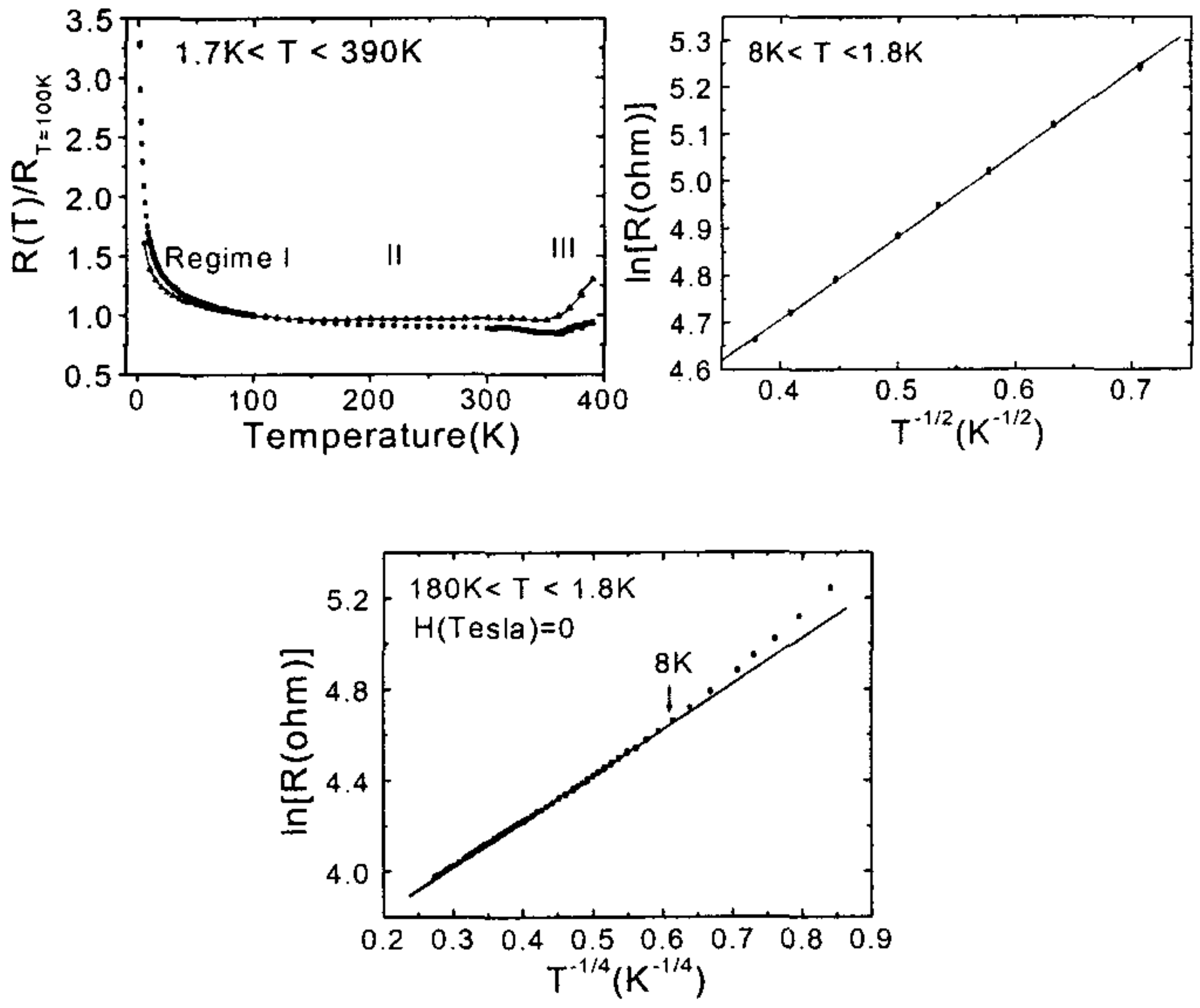

Fig. 3. (a) Log resistivity (R) vs. temperature for the thick-film form MWNT. (b) Temperature dependence of the resistivity of the thick-film form MWNT plotted as ln*R* vs $T^{-1/2}$(ES Law). (c) Temperature dependence of the resistivity plotted as ln *R* vs. $T^{-1/4}$(Mott's Law).

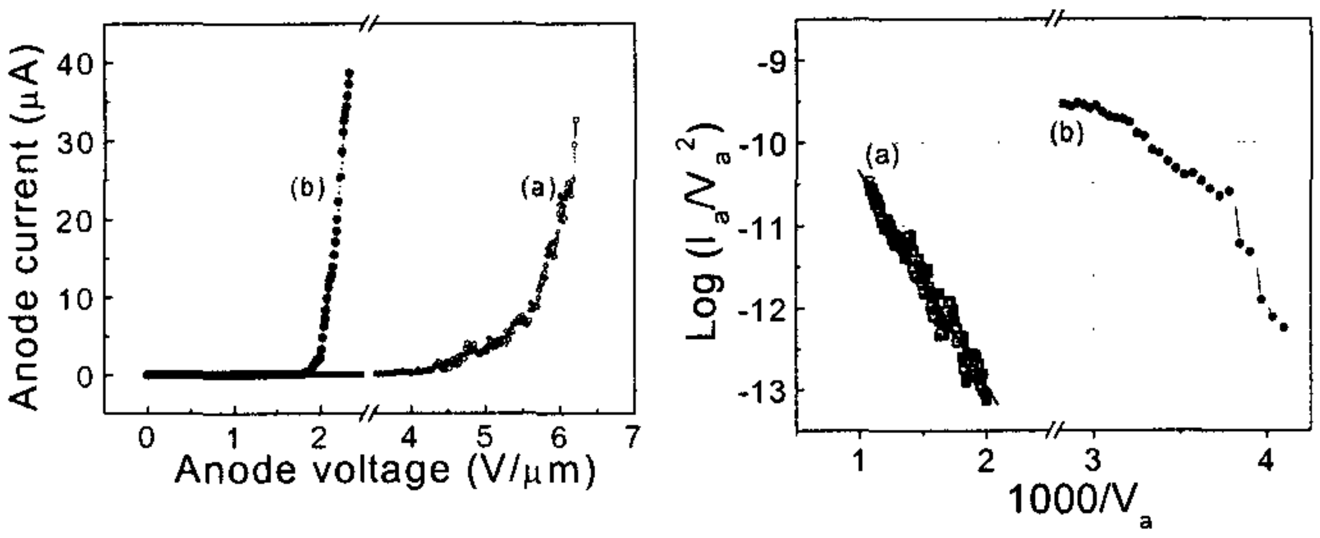

Fig. 4. The field electron emission characteristics for a thick film form MWNT under the high vacuum (LHS). Fowler-Nordhiem plot(RHS).