Carrier transport and electron field-emission properties of a nonaligned carbon nanotube thick film mixed with conductive epoxy

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We have studied the conduction characteristics of multiwalled carbon nanotubes (MWNTs), which were screen printed in a thick film form for field-emission displays. Resistivity and magnetoresistance were measured as a function of temperature T in the range of 1.7–390 K and magnetic field, respectively. The resistivity of the MWNTs for temperatures of 10–390 K indicates that the system is intrinsically metallic and the resistivity–temperature characteristics are well described by the Mott's $T^{-1/4}$ law in temperatures above 10 K, suggesting that the density of states at the Fermi level is constant in the range of 10–100 K. We found that the main contribution to the conductivity comes from carriers that hop directly between localized states via variable-range hopping. The temperature dependence above 10 K is in good agreement with that of an individual multiwalled carbon nanotube. However, below 10 K the resistivity is well fit to Efros $T^{-1/2}$ law, confirming the presence of a Coulomb gap for the system. With the decrease of temperature below 10 K the charge carriers in the system are localized by strong disorder, bringing a nearly insulating state. The thick-film form for large-area display resulted in a highly bright light as well as a very low turn-on field just like individual multiwalled nanotubes at room temperature. Also, the electron field-emission characteristics followed typical Fowler–Nordheim conduction under high electric field. © *2000 American Institute of Physics.* [S0021-8979(00)01117-8]

I. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by Iijima,[1] much effort has been devoted to the synthesis and characterization of carbon nanotubes. Among the fascinating properties of CNTs is that they may be suitable for electron field emission[2–9] under high field due to the high aspect ratio and small tip radii of curvature. Especially much attention has been paid to the field emission of the multiwalled carbon nanotube (MWNT), due to its long-term stability and mechanical strength as compared to single-wall nanotubes. The electronic properties of MWNTs are of great interest, but they also appear to be the most challenging to measure. Very recently, it has become possible to make a four-probe measurement on an individual CNT and to accurately evaluate the electric properties of the single CNT.[10–15] There is little literature concerning the electrical characteristics of MWNT systems, such as individual, thin-film form, sheet form, etc.[16–20]

Though several studies were performed to identify specific characteristics of an individual CNT,[10,15] reports on thick-film form CNTs for the large-area field-emission display are rare. CNTs are typically mixed with conductive binder and formed by a printing method and, unfortunately, only their field-emission properties[9] under a high-electric field of V/μm have been reported.

In this work we investigated the electrical transport properties of thick-film form MWNTs mixed with conductive binder for the field-electron emitter. The main interest for this work is to examine the difference in conduction behavior between an individual MWNT reported by others and our thick-film form MWNTs, and finally, to study the possibility of a promising cathode emitter for large-area display.

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II. EXPERIMENTS

Starting raw CNT materials were produced by arc deposition (Iijin Co., Korea). Three batches (2 g) of MWNT raw deposits were first placed on an alumina plate, then heated to 600 °C for 30 min under normal atmosphere. After the initial firing, the powders were removed from the furnace, then weighted and regrounded in ethanol using ultrasonic cleaner. In order to remove the metallic impurities, the MWNT powders were immersed in HNO_3 acid for 5 min, then rinsed in deionized water several times. The purified CNTs were mixed with conductive binder (silver epoxy) with a volume ratio of 1:1 using a stirrer, and then a 20-μm-thick MWNT film was formed on a bare glass substrate for four-probe measurements using the silk-screen method and Cr-coated 2×3 cm^2 glass substrate for field-emission study, respectively.

Electrical resistivity was measured using the conventional four-probe method in the temperature range of 1.7–390 K. For electrical contacts, four Al pads were formed by thermal evaporation and then highly conducting graphite adhesive was used for the contacting Al and wiring Au. The Ohmic contact down to the lowest temperature has been confirmed by checking the linear relationship between the voltage and current. The resistivity was measured using a Keithley 220 programmable current source and a 182 nanovoltmeter. The temperature dependence of the resistivity

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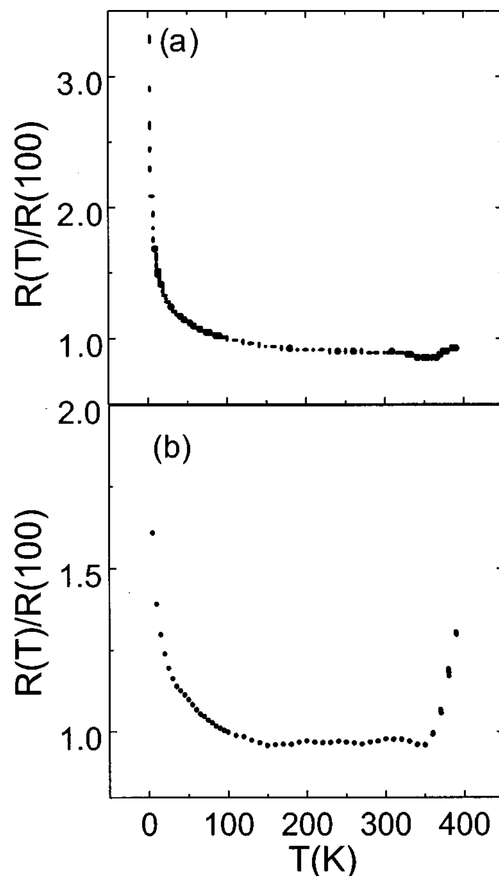

FIG. 1. Log resistivity (R) vs temperature for the thick-film form MWNT. The resistivity of the MWNTs increase rapidly below 10 K.

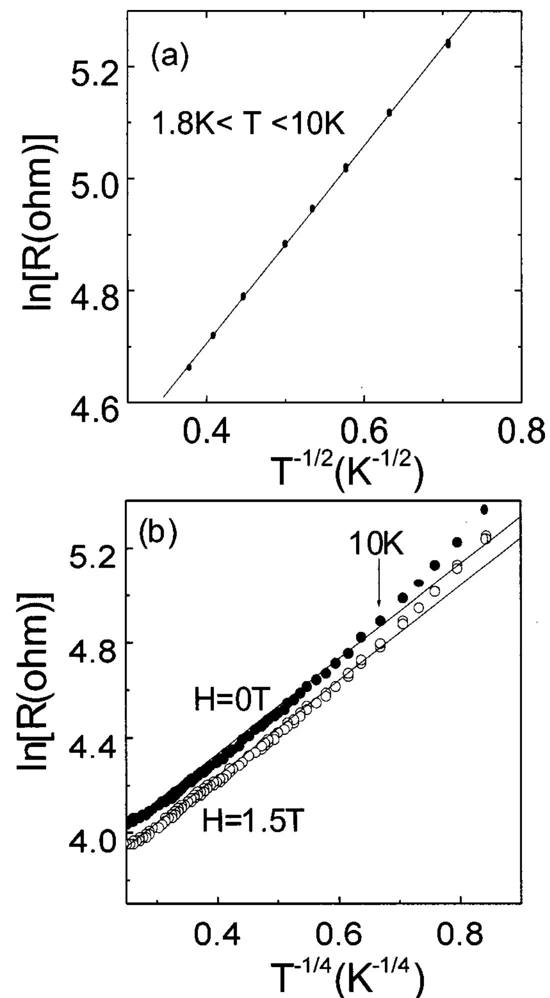

FIG. 2. (a) Temperature dependence of the resistivity plotted as in R vs $T^{-1/2}$. The solid lines are the best-fit lines with VRH conduction as predicted by Shklovskii and Efros. (b) Temperature dependence of the resistivity of the thick-film form MWNT plotted as $\ln R$ vs $T^{-1/4}$. The solid lines represent linear fits and show a large deviation with the increase of magnetic field.

and magnetoresistance (MR) as a function of temperature were measured in fields up to 5.5 T using a He^4 cryostat equipped with a superconducing magnet (Quantum Design). Based on these analyses, we will suggest what is the dominant conduction mechanism in the measured temperature range and discuss the differences of the electrical conduction characteristics between the thick-film form MWNTs and an individual MWNT or their sheet form reported previously.

Field electron-emission properties under a strong electric field were measured on thick-film form MWNTs on a sodalime glass substrate predeposited with Cr lines for the cathode electrodes. The spacing between the greenish-blue light-emitting ZnO:Zn phosphor-coated ITO glass and the MWNT cathode was fixed at 100 μm using glass fiber spacers.

III. RESULTS AND DISCUSSION

Electrical resistivity is the most important property of the CNT for characterizing the electronic structure and the possible applications. Figure 1(a) shows the change in resistance R, which was measured as a function of temperature over 1.7–390 K for the thick-film form MWNT with an averaged external diameter of 15–30 nm. It is found that the resistance increases rapidly below 100 K and nearly constantly between 100 and 360 K and reincreases with the temperature above 360 K. For different thick-film MWNTs with different external diameters of 25–60 nm, nearly the same trend was observed, as shown in Fig. 1(b).

The resistance versus temperature for $1.9\,\mathrm{K}<T<100\,\mathrm{K}$ was measured more precisely using four Al contacts on the plane of the MWNT sheet mixed with the conductive binder. Figure 2(a) shows the resistance of the MWNT plotted logarithmically against $T^{-1/2}$, and in the Fig. 2(b), against $T^{-1/4}$ over the higher temperature range. The MWNT obeys an $x=1/4$ ($x{:}T^{-x}$) variable-range hopping (VRH) law[21–23] from 10 to 100 K. This is shown in Fig. 2(b), and clearly, a single line does not fit the data over the entire temperature range of 1.9–100 K. On the other hand, the linear dependence of $\ln[R(T)]$ on $T^{-1/2}$, as shown in Fig. 2(a) indicates that Efros and Shklovskii (ES) VRH conduction[23] slightly appears at low temperatures below 40 K. More direct observation was possible near 10 K. One important thing in our thick-film form MWNT system is that the resistivity data follow the general hopping law expression in $\ln\rho \propto (T_0/T)^x$ with an exponent x changing from 1/4 to 1/2 instead of continuous variation from Mott's to Efros conduction.

It is accepted that a steeply increasing resistivity of the highly conducting CNT can be explained as a weak localiza-

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tion of electrons in the metallic system at a low temperature range of 10–50 K. Many authors have reported that at low temperatures the transfer of electrons between the nearest-neighbor sites may be less favored than between more distant sites of energetically accessible states to reduce the energy necessary for the transition. The low-temperature transport properties of disordered systems are governed by VRH between the localized states. Mott was the first to predict the key relation for the temperature dependence of conductivity for noninteracting carriers and for a constant density of states near the Fermi energy or a slowly varying function of energy. In disordered solids like our system of nonaligned MWNTs mixed with conductive paste, localized electrons can carry current at nonzero temperature but cannot screen the Coulomb interaction as effectively as in metals. Coulomb interactions in a many-electron system always deplete the single-particle density of states $N(\epsilon)$ near the Fermi energy ϵ_F, relative to the noninteracting case.[23] For a barely insulating material, charge transport occurs via inelastic hopping between the states localized in both space and energy. Mott showed that at low temperature electrons seek accessible energy states by hopping distances beyond the localization length, leading to variable-range-hopping conductivity $\sigma(T) \propto \exp(-T_0/T)^{\nu}$. For noninteracting electrons $\nu=1/4$ in three-dimension, Efros and Shklovskii argued that, including Coulomb interactions, the ground state is stable with respect to a one-particle excitation only if $N(\epsilon)$ has a quadratic dependence on ϵ near ϵ_F:

$$N(\epsilon)=\frac{3}{\pi}\left(\frac{\kappa}{e^2}\right)^3(\epsilon-\epsilon_F)^2,$$

where K is the dielectric constant. Because $N(\epsilon)$ vanishes only at ϵ_F, there is a ''soft'' Coulomb correlation gap with a width $\Delta_c=e^3(N_0/\kappa^3)^{1/2}$, where N_0 is the noninteracting density of states. In general, power law $N(\epsilon) \propto (\epsilon-\epsilon_F)^m$ results in a hopping exponent $\nu=(m+1)/(m+4)$ as $T \rightarrow 0$, so that the above equation gives $\nu=1/2$. When T is high enough for a hopping electron to explore an energy range $k_B[T^3T_0]^{1/4} > \Delta_c$, where $T_0=18/k_B\xi^3N_0$ and ξ is the localization length, the influence of the Coulomb gap can be neglected and the $\nu=1/4$ exponent is expected. However, below the temperature $T_x=0.38\,e^4\xi N_0/k_B\kappa^2$ only states inside the gap are accessible and a crossover to $x=1/2$ is predicted. This ES theory well fits to the present resistivity data, as shown in Fig. 2(a), suggesting the presence of Coulomb gap for about $T<10\pm4$ K and the transition to the nearly insulating state.

Considering the previous reports particularly regarding disordered metals and some doped inorganic semiconductors, our observation is not peculiar. Efros pointed out that because of long-range interactions between localized states, the density of states near the Fermi energy tends to go to zero, which yields a parabolic Coulomb gap. In last few years the crossover between Mott and ES hopping regimes as a function of temperature has been found experimentally. Very recently, it has been observed that some conducting polymers and conducting polymers mixed with a powder system[24,25] also show crossover from Mott to ES VRH conduction with a small Coulomb gap. Here, we would like to note that it is impossible to break up all the entanglements of the CNT materials with the conductive binder by the dispersion process used in our work and to remove all the carbonaceous materials, although the ultrasonic and the subsequent intensive grinding process of the mixed paste leads to an improvement of the dispersion of the CNTs in the binder. Therefore, our thick film MWNT shows one of the characteristics of the disordered system, and at the same time it should be noticed that these phases form a conductive three-dimensional network throughout the whole sample, as confirmed in resistivity measurements.

For the occurrence of a transition from Mott's to Efros's mechanism below 10 K, we can explain as follows: The competition between the interaction between electrons and the disorder of the system results in glassy dynamics that are often associated with very long relaxation times. A very recent report revealed that in the presence of strong disorder, electrons could indeed have very long relaxation times.[26] This occurs in a system with randomly placed electrons that have Coulomb interactions. Heavily doped semiconductors and disordered metals like our thick-film form MWNT system are assumed to be an example of such systems. Coulomb interaction between the localized states results in the so-called Coulomb gap in the single-particle density of states that is centered at the Fermi energy. In order to produce the Coulomb gap, electron rearrangement must occur and the associated hopping can involve very long time scales. These long relaxation times are consistent with recent reports[27–29] on thin-film semiconducting and metallic films which have shown that in the presence of strong disorder the electronic systems can relax very slowly, and the dip in the conductance (or rapid increase of resistivity) and the long relaxation times are present only at very low temperatures ($T<20$ K). As the number of phonons increases with temperature, there is an increase in the phonon-assisted hopping of electrons. This leads to a rapid rearrangement of electrons on time scales that are too short to observe experimentally. As a result, no dips in conductance or resistance were seen experimentally at higher temperature, and in our case, above about 10 K.

Figure 3(a) shows the magnetic-field dependence of the resistivity, showing a negative resistance $[R(H)-R(0)/R(0)]$ at lower fields in the temperature range from 9 to 50 K. We can observe an effect at low temperatures of 9–14 K, where the MR shows quadratic dependence on magnetic field (H) and when replotting, as shown in the inset Fig. 3(b) as a function of H^2, the $[R(H)-R(0)/R(0) \equiv \Delta R/R(0)]$ are linear up to near 0.14 T at low temperatures of 9–14 K. The magnitude of $\Delta R/R(0)$ showed a minimum value and the sign was changed under the high magnetic field over near 3 T. Increasing the temperature causes a shift towards lower magnetic fields, so that for a temperature near 50 K this minimum lies below 2 T. Recently, many groups report a linear negative MR or a quadratic MR, and especially, it was suggested that a quadratic MR is negative in the case of strong disorder and positive in the case of weak disorder in the weak magnetic-field limit. In our case, the weak magnetic field limit turns out to be about 0.14 T. The ways to affect the magnetic field on the localized states and the hop-

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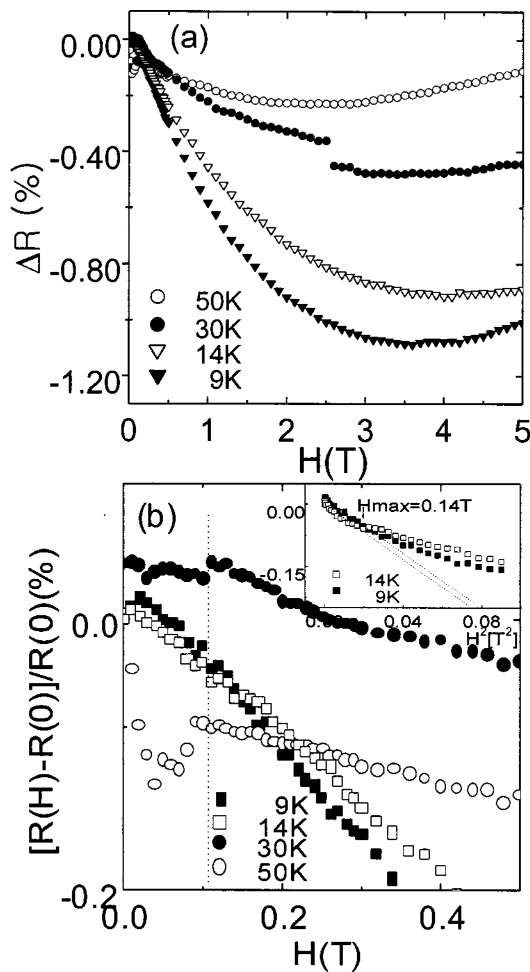

FIG. 3. Change of resistivity as a function of applied magnetic field (a) and magnetoresistance for different temperatures (b). The inset represents the quadractic dependence of resistance on the magnetic field under a weak field limit at 9 and 14 K, respectively.

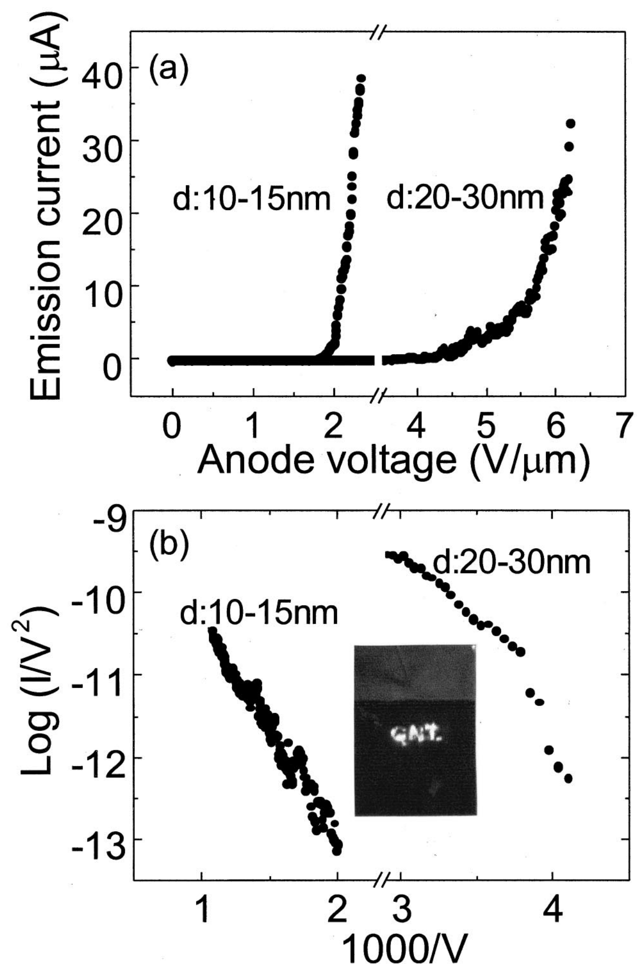

FIG. 4. (a) Emission-current–electric-field characteristics and (b) Fowler–Nordheim plots for the thick-film form MWNT, respectively. Inset shows light emission under the ambient.

ping process are the change of the transmission probability of tunneling between two states due to quantum-interference effects and the change of the energy of the localized states via a Zeeman shift. The electron hopping probability under the magnetic field depends on the relative orientation of the two localized states and increases as they are aligned in the same direction, reducing the probability of antiparallel singly occuppied spin states and resulting in a decrease of the hopping rates. These give rise to the change from negative MR to positive MR.

Finally, field electron-emission properties under a strong electric field were measured on thick-film form MWNTs on a sodalime glass substrate predeposited with Cr lines for the cathode electrodes. The spacing between the ZnO:Zn phosphor coated ITO glass and the MWNT cathode was fixed at 100 μm using glass fiber spacers. Before obtaining field-emission data, we examined the surface of the thick-film form MWNT to check for the occurrence of any cracking areas and stressed several tens of times to stabilize the system. The measurements were performed at a pressure of 2×10^{-6} Torr. The plots of emission current versus electric field for two kinds of thick-film systems with external diameters of 10–15 and 20–30 nm are shown in Fig. 4(a). These characteristics are relatively stable and repeatable without degradation of the background vacuum. The nominal onset fields for an emission current in Fig. 4(a) are 2.0 and 4.5 V/μm, depending on the diameter of the MWNTs, and furthermore, Fig. 4(a) indicates that the lower value of resistivity for the sample with a decrease of diameter was closely related to the lowering onset field of electron emission. The $I-V$ data are plotted according to the typical Fowler–Nowdheim relationship for field emission, as shown in Fig. 4(b).

Our results imply that although thick-film form MWNT films are a nonaligned system mixed with conductive epoxy, the system is successful in bringing out a low turn-on field (1.5–4.5 V/μm) as well as the high emission current required for field-emission displays.

IV. CONCLUSIONS

In this work, the conduction mechanism in a thick-film form MWNT mixed with conductive epoxy was reported. The main focus of this article was to compare the similarity and the difference between an individual MWNT (or sheet form pure MWNT) and a CNT-binder composite system. The behavior of the resistivity of the MWNT for tempera-

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tures of 10–390 K indicates that our system is intrinsically metallic and the main contribution to the conductivity comes from carriers that hop directly between localized states via variable-range hopping. The temperature dependence above 10 K is in good agreement with that of an individual multiwalled carbon nanotube. However, below 10 K, the resistivity is well fit to the Efros $T^{-1/2}$ law, confirming the presence of a Coulomb gap in the system. With the decrease of temperature below 10 K the charge carriers in the system are localized by strong disorder, bringing a nearly insulating state. The behavior on the low-temperature regime can be explained by the ES conduction theory based on a strongly disordered system. Possible sources for the disorder are not confirmed at this moment and, however, it is sufficiently probable that defects such as the residual metallic particles, the entanglement of the CNT system, and the binder effect would have a localization effect on the carriers. The thick-film form MWNTs for large-area display resulted in a highly bright light as well as a very low turn-on field just like individual multiwalled nanotubes at room temperature.

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