Field emission microscopy of Al-deposited carbon nanotubes: Emission stability improvement and image of an Al atom cluster

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Aluminum (Al) was deposited on multiwall carbon nanotubes (MWNTs) with mean thicknesses ranging from 1 to 11 nm in vacuum, and the influence of deposited Al on field electron emission was investigated by field emission microscopy (FEM). Al deposition significantly suppressed the fluctuations of emission current after a simple conditioning process. Interestingly, FEM images revealing the atomic detail of an Al cluster with the cubo-octahedron structure were observed. The discussion on the spatial resolution in FEM for MWNTs suggests the probable observation of some atomic structures with a resolution of the order of 0.3 nm. © *2010 American Vacuum Society.*
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I. INTRODUCTION

Field emission of electrons from a multiwall carbon nanotube (MWNT) with a closed cap occurs preferentially from carbon pentagons at the cap, and forms field emission microscopy (FEM) images consisting of bright pentagonal rings,[1] the number of which is usually six though it depends on the cone angle of the cap.[2] However, five carbon atoms forming a pentagon, the nearest neighbor distance of which is 0.144 nm, are not resolved, though a dark region is observed at the center of each pentagonal ring. The pentagonal ring patterns characteristic of capped MWNTs are observed when the surface of a nanotube cap is clean. Adsorption of a gas molecule onto a clean pentagon brings about a change in the FEM images from the pentagonal ring to a bright spot with a sudden increase in emission current.[3] In the case of nitrogen (N_2) and carbon dioxide (CO_2) molecules, dumbbell-shaped images, reflecting their molecular shapes, are observed by FEM.[4,5] In the 1950s, various unusual FEM images from metal tips and whiskers were reported,[6] and the controversy as to whether FEM can reach atomic resolution or not reached its peak. However, the advent of impressive atomic resolution images by helium field ion microscopy (FIM) by Müller and Bahadur[7] in 1956 faded out the controversy, and the question has remained pending ever since. In 1956, Rose[8] proposed a resolution equation for FEM and suggested that atomic resolution in FEM is possible if the tip radius is small enough.

Changes in emission current, i.e., stepwise increase and decrease, in accordance with adsorption and desorption of molecules are clearly observed for carbon nanotube (CNT) field emitters.[3] The random surface phenomenon of molecular adsorption and desorption is considered to be the main cause of emission fluctuation in CNT field emitters, which is required to be reduced for the practical application of CNT emitters to various electron-beam apparatus.

In this work, the effects of aluminum (Al) deposition on MWNT field emitters were studied in viewpoints of the suppression of emission fluctuation and the possibility of observation of a metal cluster deposited on a CNT. The FEM of Al-deposited MWNTs revealed considerable suppression of emission fluctuation and also provided us with an atomically resolved image of an Al cluster with a face-centered structure.

II. EXPERIMENT

Carbon nanotubes employed in the present study were MWNTs produced by arc discharge without a catalytic metal. The diameters of MWNTs ranged from 10 to 20 nm. A bundle of MWNTs was glued on the tip of a "V" shaped filament of tungsten (W) wire (0.15 mm in diameter) by a graphite bond, and the emitter assembly was installed in an ultrahigh vacuum chamber for FEM experiment. Figure 1 shows a schematic of the FEM and metal deposition chamber. When FEM measurements are carried out, the emitter tip is directed to a phosphor screen as indicated by a position A. The distance between the emitter tip and the screen is about 30 mm. When metal is deposited onto MWNTs, the emitter assembly is rotated by 90° to face with a metal evaporator as indicated by a position B. Field emission (FE) measurement of MWNTs before metal deposition was first carried out, and then aluminum (Al) was deposited onto the MWNTs in the FEM chamber without exposing to air. The amount of Al deposited on MWNTs was in a range from ~1 to 11 nm in terms of mean film thickness. Measurements of current (I)-voltage (V) characteristics and FEM of metal-deposited MWNTs were carried out several times using the same emitters. The base pressure of the FEM chamber was 7×10^{-8} Pa.

III. RESULTS AND DISCUSSION

Figure 2 shows I-V curves obtained from a MWNT emitter under different conditions: Fig. 2(a) was obtained prior to Al deposition, Fig. 2(b) was just after Al deposition (i.e., the first I-V measurement after the Al deposition), and Fig. 2(c)

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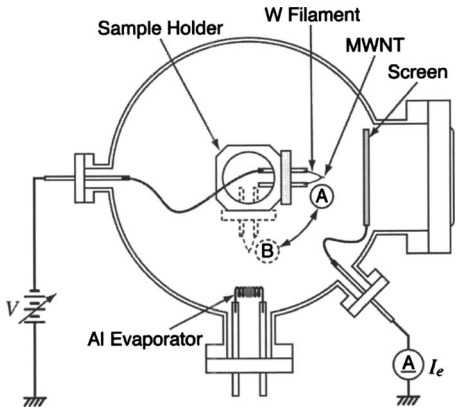

FIG. 1. Schematic of the FEM and metal deposition chamber.

after the first *I-V* measurement (i.e., the second *I-V* measurement after the Al deposition). Figure 2(c) shows that the fluctuation of emission is remarkably reduced and that the *I-V* curves in the upswing and downswing of applied voltage overlap intimately with each other, giving reproducible *I-V* curves. Though the current fluctuation just after the Al deposition was higher than that of the pristine MWNTs without Al deposition, after the first *I-V* measurement both the flickering of bright spots in the FEM and the current fluctuation decreased considerably. The vacuum pressure during FE measurements was raised to about 2×10^{-7} Pa due to the electron-stimulated desorption of gas molecules on the screen and other inner walls of the vacuum chamber. It took about 5 min to record one set of *I-V* curves (upswing and downswing). The time elapsed from the Al deposition to the acquisition of the first [Fig. 2(b)] and the second *I-V* curves [Fig. 2(c)] was approximately 10 and 15 min, respectively.

The reduction in emission fluctuation by Al deposition was accessed in terms of "*I-V* fluctuation degree," which we defined as follows:

$$\frac{1}{N}\sum_{i=1}^{N}\sqrt{\left(\frac{I_{\mathrm{up}}(V_i)-I_{\mathrm{down}}(V_i)}{I_{\max}}\right)^2}\times 100, \tag{1}$$

where $I_{\mathrm{up}}(V_i)$ and $I_{\mathrm{down}}(V_i)$ are emission currents at voltage V_i in the course of its upswing and downswing, respectively, $I_{\max}$ is the maximum current recorded in the *I-V* measurement, and N is the number of sampling points. The values of the fluctuation degree for the three *I-V* curves in Figs. 2(a)–2(c) are 1.88, 4.07, and 0.36%, respectively.

The emission current in field electron sources sensitively depends on changes in surface nanostructures, work functions, and adsorption/desorption of residual gas molecules. The stabilization of emission current observed after the Al deposition is probably due to the reduction of adsorbed gas molecules migrating on an emitter surface. Since Al metal is known to be relatively reactive to form oxide layers on it surfaces, the Al metal on CNT surfaces may trap gas molecules migrating on the surface like a getter. Here, it is worthwhile comparing the amount of Al atoms deposited and the residual gas molecules striking on the MWNT surfaces. For an Al deposit with a typical mean thickness, 2.5 nm, the

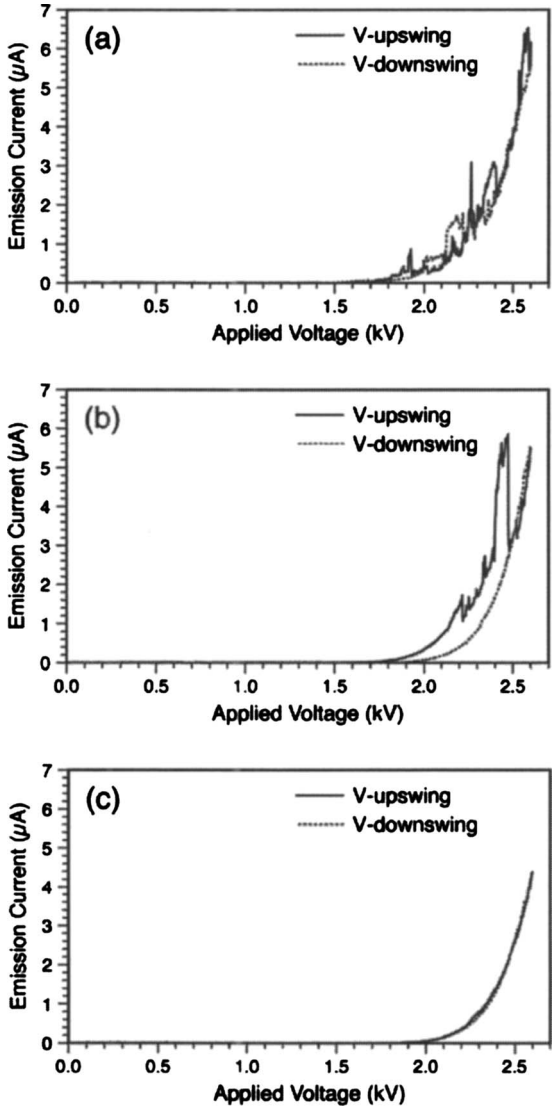

FIG. 2. *I-V* curves: (a) Prior to Al deposition, (b) the first run after Al deposition, and (b) the second run after Al deposition.

number of Al atoms per unit surface is 1.5×10^{20} m^{-2}, while the number of gas molecules striking a unit surface for 10 min (a typical time interval from the Al deposition to FE measurement) at 2×10^{-7} Pa is 4×10^{18} m^{-2}, much smaller than the number of Al atoms on the nanotube surfaces.

Since the work function of Al is 4.3 eV, being lower than that of carbon nanotubes (4.6–4.95 eV) reported so far,[9,10] an enhanced emission current is expected after the Al deposition. In fact, the increase in emission current is observed at the first *I-V* measurement just after Al deposition as observed in the upswing curve of Fig. 2(b), though this enhancement is not so significant except for a momentary increase. At the second *I-V* measurement after Al deposition, emission current was reduced compared with that from the pristine MWNTs. This may be due to the fact that electron emission occurred from the nanotube surface instead of Al after the fluctuation reduction, since the migration of Al clusters on a MWNT and their disappearance from the cap region are observed (vide infra).

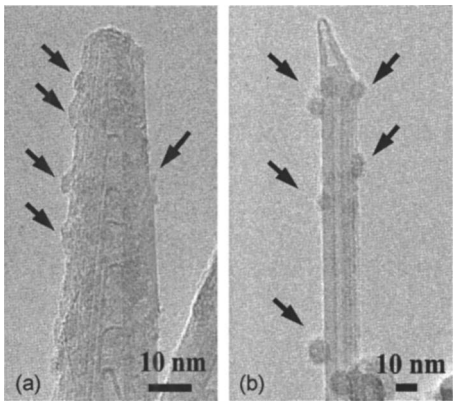

FIG. 3. TEM images of Al-deposited MWNTs (a) before and (b) after field emission. Mean thickness of deposited Al is 2.5 nm. Arrows indicate Al clusters. Different MWNTs are shown in (a) and (b) because we could not find the same MWNT before and after the emission measurement.

Figure 3(a) shows a transmission electron microscope (TEM) picture of Al with a mean thickness of 2.5 nm deposited on MWNTs before the FE experiment. The deposited Al formed a discontinuous film consisting of isolated islands with a diameter of a few nanometers. After the FE experiment, the diameter of Al clusters increased to about 10 nm as revealed by Fig. 3(b).

During the study on the effect of Al deposition by FEM, intriguing FEM images suggestive of an Al cluster with atomic resolution were observed. Figure 4 shows time-sequential FEM images of a MWNT emitter before and after Al deposition. Before the Al deposition, "pentagon" patterns characteristic of clean caps of MWNTs (two MWNTs are visible in this image) are observed, as revealed in Fig. 4(a). Each pentagonal bright ring originates from the pentagon existing on a nanotube cap. By the deposition of Al, as shown in Figs. 4(b) and 4(c), a spotty pattern with a high symmetry (fourfold symmetry in this case) appeared instead

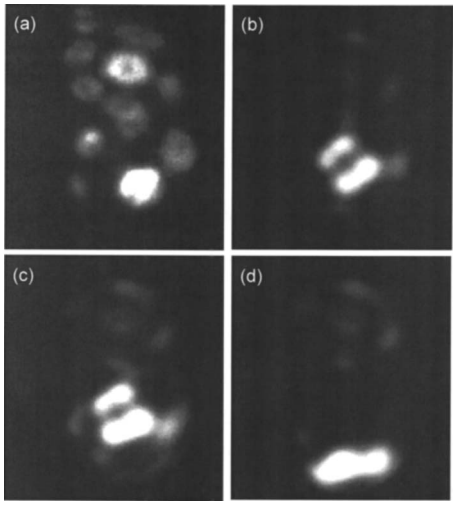

FIG. 4. Time-sequential series of FEM images of a MWNT emitter. (a) Before Al deposition and (b)–(d) after Al deposition. Time elapsed from (b) to (c) is 3.34 s, and that from (c) to (d) is 0.13 s. The voltage applied to the emitter is 1.5 kV.

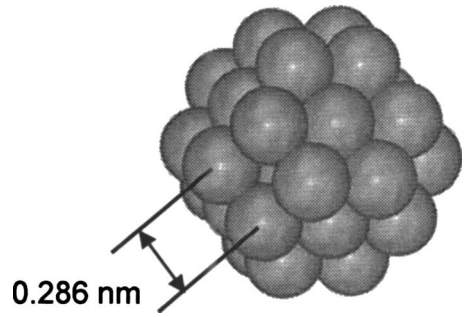

FIG. 5. Cubo-octahedron of an Al_{38} cluster.

of the pentagon pattern. The contrast of the spotty pattern is reminiscent of the structure of an atom cluster with a shape of cubo-octahedron, which is a crystal form characteristic of face-centered cubic metals.[11] A model of the structure consisting of 38 Al atoms is illustrated in Fig. 5. The fourfold symmetry of the Al image suggests that the Al cluster is oriented with its [100] direction normal to the nanotube surface. Four bright spots observed in the central part of the Al image correspond to four corners of the top (100) surface. Four dark regions surrounding the central (100) face correspond to (111) faces, which are outlined by bright edges and corners. Since the electric field concentrates at locally protruding atoms which are located at the corners and the edges, the tunneling probability of electrons at these atoms is significantly high. Therefore, only atoms at the corners and edges are highlighted, which is the same phenomenon observed in FIM of metal emitters.

The distance between neighboring atoms along the edge of the (100) surface is 0.286 nm when the lattice constant of the cluster is the same as that of bulk Al. Using the size of the carbon pentagon (approximately 0.25 nm in diameter) as a measure of magnification of FEM images, under an assumption that the pentagon image originates from five carbon atoms comprising a pentagon, the distance between the bright spots at the corners of the (100) face is estimated in a range from 0.28 to 0.31 nm, in good agreement with the nearest neighbor distance on the Al (100) surface. In the measurement of the Al–Al atomic distance, the following are assumed; (1) the local magnification enhancement of the Al cluster, which originates from a difference in field enhancement at a small protrusion (Al cluster in this case) and at a bare round substrate (nanotube emitter), is neglected, and (2) the size of the image of a carbon pentagon is assumed to be the geometrical size of five carbon atoms forming the pentagon (i.e., 0.25 nm across). According to the discussion on the magnification enhancement by Rose,[8] the enhancement factor is estimated to be approximately 3.5 for an Al cluster of 0.5 nm in radius situated on a MWNT tip with 5 nm in radius. When we postulated the distance between the bright spots of the Al cluster correspond to the nearest-neighbor distance between Al atoms, the magnification enhancement factor suggests that the pentagon image originates from a larger area (about 0.9 nm in diameter) than that of an isolated

single carbon pentagon, i.e., the area exhibiting the pentagon image includes hexagons surrounding the pentagon.

Metal clusters or nanoparticles often exhibit atomic structures different from crystal structures in bulk, e.g., icosahedral or multiply twinned structures for elements which form fcc structures in bulk. For Al, however, icosahedral structures have never been observed ever for small particles by electron microscopy.[11] Theoretical calculations also suggest that the structural transition from the fcc to the icosahedron structures lies in a range between 13- and 55-atom clusters.[12] The present Al cluster falls in this transition range in size. Thus, it is highly probable that the Al cluster exhibits the same structure with the bulk.

The polyhedral Al cluster [Figs. 4(b) and 4(c)], exhibiting rotation and migration, disappeared in several seconds from the field of view after its appearance, as shown in Fig. 4(d). The migration and diffusion of Al clusters on MWNTs are responsible for the increased diameter of Al clusters observed by TEM after the FE experiment, as shown in Fig. 3(b).

In 1956, Rose[8] gave the equation of FEM resolution δ, which consists of the two principal components, namely, the momentum uncertainty and the effect of the transverse velocities of the electrons near the top of the Fermi level in the emitter:

$$\delta = \left(\frac{2\hbar\tau}{mM}\right)^{1/2}\left(1+\frac{2m\tau\nu_0^2}{\hbar M}\right)^{1/2}, \tag{2}$$

where M is the magnification, τ is the time of flight of an electron from emission tip to screen, ν_0 is the average transverse velocity, $\hbar$ is Planck's constant/2π, and m is the electron mass. When M/τ is large enough to assume $2m\tau\nu_0^2/\hbar M << 1$, the term containing ν_0 become negligible and the resolution is limited by the uncertainty principle. Under such a condition, say $M/\tau \approx 2.5\times10^{15}$, he suggested that small protrusions on the surface of the tip can provide resolution of the order of 0.3 nm so that some of their atomic detail should be observable. M is always reduced by a factor β from that expected for a spherically symmetric geometry, where the tip and screen are assumed to be concentric spheres of radii R and z, i.e.,

$$M = z/\beta R. \tag{3}$$

Using the approximation $\beta \approx 1.9$, $\tau \approx z(2eV/m)^{-1/2}$ and $\nu_0 \approx 2\times10^5$ m/s(=0.11 eV), the following practical form of resolution equation[8,13] is obtained:

$$\delta = 0.860(R/\sqrt{V})^{1/2}(1+2.22R/\sqrt{V})^{1/2}, \tag{4}$$

where δ is in the nanometer, R is the tip radius in nanometers, and V is the applied potential in volts between the tip and screen.

From Eq. (4), we see that atomic resolution is attainable for $R/\sqrt{V} < 1$. In the present experiment, R and V are the tip radius of a MWNT of about 5 nm and the applied voltage of 1.5 kV, respectively. These parameters give a resolution of the order of 0.3 nm, indicating that some of the atomic detail is observable in the present experimental condition.

IV. CONCLUSION

Field electron emission from Al-deposited MWNTs was studied by field emission microscopy. Though the fluctuation of emission current became larger just after the deposition of Al, a significant reduction of the fluctuation was observed after the first current-voltage measurement. This stabilization of emission current may be due to the gettering action of Al clusters deposited on MWNTs, i.e., Al clusters trap gas molecules migrating on MWNT surfaces. A FEM image of an Al cluster showing atomic detail was observed, and the possibility of atomic imaging of protruding structures on nanotube tips by FEM was discussed.

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