Self-regenerative field emission source

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A self-regenerative field emission source was demonstrated. The emission source (cathode) consisted of carbon nanofibers (CNFs) grown on the tip of conical carbon protrusions on a graphite plate. CNFs were ~25 nm in diameter, 0.3–2.5 μm in length and $\sim 1\times 10^{6}$ mm^{-2} in site density. Initial emission characteristics showed a threshold field of 3.05 V/μm with a current density of 1 μA/cm^2 and a field enhancement factor of 2860 from the Fowler-Nordheim plot assuming the work function of 4.6 eV for graphite. A lifetime test carried out for more than 40 h at a constant applied electric field of 10 V/μm in 10^{-4} Pa region disclosed a stable emission with a current density of $1.7-3.0\times 10^{-4}$ A/cm^2 after a slight initial decrease in the emission current. Detailed morphological observations revealed that a thick layer of newly grown carbon fibers was formed on the cathode surface after the lifetime test which could be responsible for the observed stable and long-sustained emission under a nonultrahigh vacuum condition. Their growth was attributed to the surface diffusion of carbon atoms generated by sputtering of the carbon cathode with ionized residual gas molecules during the field emission process. Thus, the CNF-tipped carbon emitter was believed to be promising as a practical field electron emission source used under low vacuum. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2126152]

Since the discovery of carbon nanotubes (CNTs),[1] much effort has been devoted to the development of field electron emission sources using one-dimensional carbon nanomaterials, e.g., for flat panel displays[2,3] and x-ray tubes,[4–6] because of their fascinating properties of the high aspect ratio, small tip radii of curvature, and high chemical stability. The field emission (FE) current in general decreases with the operation time, mainly due to the damage of emitter tips induced by the bombardment with ionized residual gas molecules. Once tips are damaged, they do not contribute any more to the intense electron emission. This is why UHV, usually lower than 10^{-6} Pa, is required for stable and long-term operation. In their recent publication, for example, Kita *et al.*[7] demonstrated a stable emission from Pd-catalyzed CNTs for 600 h under an extreme UHV condition, 3×10^{-9} Pa. Such an extreme UHV, however, is unrealistic for practical applications. For a wider range of applications, therefore, tough emitters with a long lifetime operating under low vacuum should be developed.

In our previous letters,[8,9] it was demonstrated that Ar^+ ion bombardment onto bulk carbon and carbon coated substrates, even at room temperature, induced the formation of conical protrusions which possess single carbon nanofibers (CNFs), 20–50 nm in diameter and 0.2–10 μm in length, on the tips and that those sputter-induced CNFs showed a good initial property in the field electron emission. The basic growth mechanism of the sputter-induced CNFs is the redeposition of sputter-ejected carbon atoms onto the sidewall of conical protrusions and the excess surface diffusion of the carbon atoms to the tips during Ar^+ sputtering. This may imply that CNFs formed on a carbon cathode will regrow by a supply of carbon atoms generated by sputtering of the carbon cathode with ionized residual gas molecules in a non-UHV emission source during the FE process even if they are once damaged. If it is the case, a long-lifetime emitter operating under low vacuum will be realized. This letter was undertaken to explore a possibility of such a self-regenerative emission source.

A cathode employed was a graphite plate, 20 mm $\times$ 20 mm in size (Tokai Carbon Co., Ltd.). In order to grow CNFs on it, the cathode surface was bombarded with Ar^+ ions at 45° from the normal to the surface using a Kaufman-type ion gun (Iontech. Inc. Ltd., model MPS 3000 FC). The oblique Ar^+ bombardment is known to be suitable for ion-induced CNF growth, compared with sputtering at normal incidence.[8,9] The diameter and energy of ion beam employed were 6 cm and 1 keV, respectively. Sputtering was done at room temperature for 60 min. The basal and working pressures of the CNF-growth chamber were 1.5×10^{-5} Pa and 2×10^{-2} Pa, respectively.

FE characteristics of the cathode thus prepared were measured for an applied voltage range of 0–1200 V under a parallel plate configuration at a typical working pressure of 5.0×10^{-4} Pa in an O-ring-shield glass chamber evacuated

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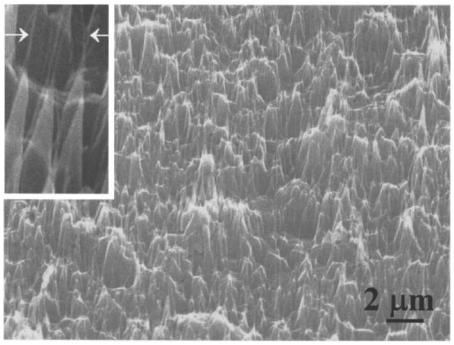

FIG. 1. Overall view of an as-prepared cathode surface. Magnification: ×5000. Inset: Highly magnified SEM image of typical CNFs (arrow-indicated) grown on the tip of conical protrusions.

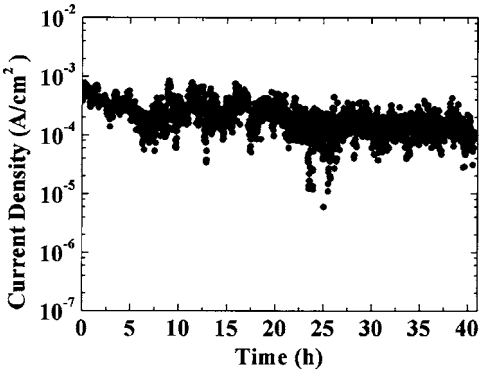

FIG. 3. Time dependence of the emission-current density. Applied voltage and the electric field: 1000 V and 10 V/μm, respectively.

continuously by a turbo molecular pump. For the FE measurements, an indium tin oxide coated glass was used as an anode, which was separated from the CNF-covered cathode by a 100 μm Teflon spacer. The tested emission area was 0.28 cm^2 (6 mm in diameter). The topography of the cathode surface was carefully observed before and after the FE measurements by scanning electron microscope (SEM) (JEOL; JEM-5600).

Figure 1 shows a SEM image of an Ar^+-sputtered graphite surface before the FE measurement, revealing that the whole surface was covered with densely distributed conical projections. It should be noted that single CNFs are grown on almost all of the cone tips (inset of Fig. 1). CNFs ranged from 0.3 to 2.5 μm in length independently of the size of the cone base, whereas they were almost uniform in diameter (25 nm). The numerical density of CNF was $\sim 1\times 10^6$ mm^{-2}. It is well-known that the excess density of emitter tips will lead to the saturation in total FE current, which is due to the so-called "screening effect" of adjacent tips.[10] The CNFs grown on conical bases is advantageous to prevent the excess in emission-site density, and hence, diminish the screening effect.[9]

Figure 2 shows the typical FE characteristics obtained for the CNF-covered graphite cathode. The corresponding Fowler-Nordheim (FN) plot is also shown in the inset of Fig. 2. The current density J was calculated using the anode area (0.28 cm^2). From Fig. 2, the threshold field defined as the field at which J reaches 1 μA/cm^2 was estimated to be 3.05 V/μm. The field enhancement factor (β) calculated from the FN plot was 2860, assuming the work function of 4.6 eV for graphite. These emission characteristics were

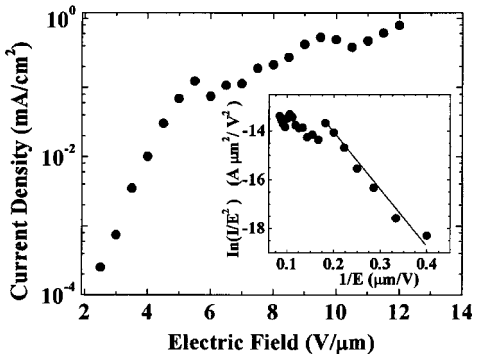

FIG. 2. Initial I–V characteristics attained for the CNF-covered cathode. Inset: Corresponding FN plot.

comparable to those reported for CNTs (Refs. 11–14) prepared by conventional methods at high temperatures, and were much better than those obtained for CNFs grown at low temperatures.[15,16] In order to confirm the reproducibility of the FE characteristics, I–V measurements were performed at several locations. The obtained FE properties were almost independent of the locations, due to the nearly uniform distribution of CNF-tipped cones over the whole sample surface.

After the measurements of the initial I–V characteristics, a lifetime test was carried out for about 40 h at a constant applied electric field of 10 V/μm in non-UHV condition (10^{-4} Pa range). As shown in Fig. 3, the emission-current density gradually decreased with time from $\sim 7\times 10^{-4}$ A/cm^2 to $\sim 1.7\times 10^{-4}$ A/cm^2 at an initial stage (t=0–6h) of the lifetime test, and then strangely increased slightly up to $\sim 3\times 10^{-4}$ A/cm^2. This value was sustained for t=7–20 h. For $t>20$ h, the current density was stable at $\sim 1.7\times 10^{-4}$ A/cm^2. It is surprising that the emitter operated stably for more than 40 h under such a non-UHV condition.

A careful inspection of the cathode surface after the lifetime test with bare eyes revealed that the electron-emitted area, a circular area of 6 mm in diameter, displayed a deeper black color than nonemitted area did, and that a difference in color is more prominent at a peripheral region of the emitted area. This may suggest that a morphological change of the surface of the emitted area, especially at a peripheral region, occurred during the lifetime test. In order to confirm this, a surface morphology of the emitted area was observed by SEM in detail.

Figures 4(a) and 4(b) show SEM images of a central part of the emitted area after the lifetime test for 40 h; Many of the protrusions were rod-like rather than conical and possessed no CNF on the tips [compare the inset in Fig. 1 with the inset in Fig. 4(a)]. The initial decrease in the emission current density for t=0–6 h shown in Fig. 3 may be due to a decrease in number of CNFs on the cathode surface. It should be noted that nonaligned and rather thick carbon fibers (CFs), 0.2–0.5 μm in diameter, were sparsely recognizable on the central part of the emitted area [arrows in Figs. 4(a) and 4(b)].

Figure 4(c) shows a SEM image taken at a peripheral region of the emitted area, disclosing that densely distributed thick CFs newly grew. The thick CFs were nonaligned and measured 220–560 nm (270 nm in average) in diameter. As described earlier, a basic mechanism of Ar^+-ion-induced CNF growth is the redeposition of sputtered carbon atoms

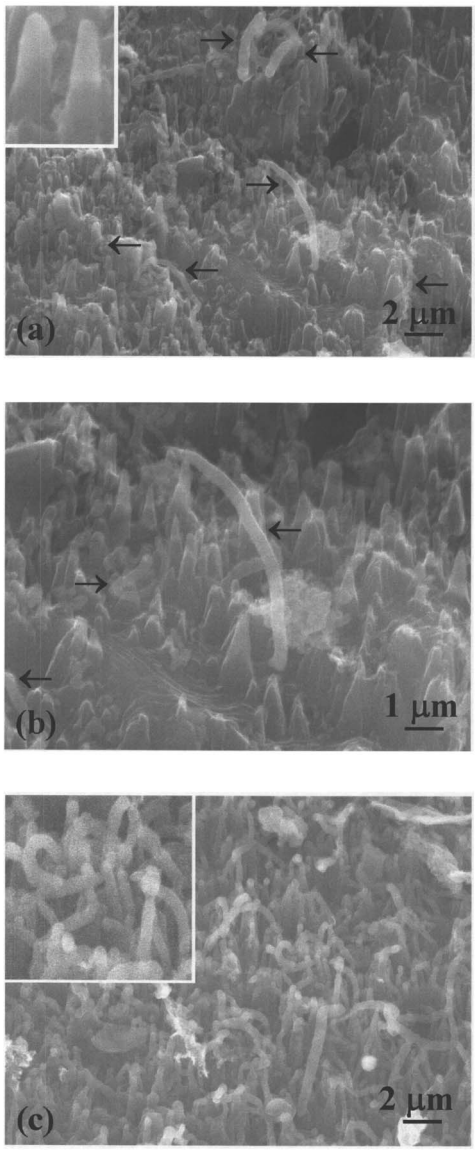

FIG. 4. Typical SEM images of central, (a) and (b), and peripheral regions, (c), of the emission area taken after the lifetime test for 40 h. (b) Enlarged image of (a). Insets in (a) and (c): enlarged images of typical rod-like projections with a round tip and entangled CFs newly grown during the FE process. Magnification: ×5000 for (a) and (c), and ×10 000 for (c).

onto surface conical protrusions and their subsequent diffusion towards the tip of the protrusions. In the present FE source operated under a non-UHV condition, too, the cathode surface would be ceaselessly irradiated with ionized residual gas molecules, and hence, sputter-ejecting carbon atoms from the cathode surface. Those carbon atoms would redeposit onto surface projections and diffuse towards the tips, similarly in the growth process of Ar^+-induced CNFs. In addition, the surface diffusion would be enhanced due to the local resistive heating induced by FE currents. Thus, the thick CFs would grow during the FE process.

In general, the blunter the emitter tips, the weaker the electric field around the tips, thus resulting in the less intense emission. If no CF grew during the FE process, conical tips would be rounded and their apex angles would be larger, due to sputtering with ionized residual gas molecules. Consequently, the emission current would decrease monotonically with the emission time. CFs newly grown during emission, in contrast, were uniform in diameter in their growth direction, implying that the electric field around the tips of CFs were nearly constant throughout the emission process. This may be responsible for the stable and long-sustained emission during the lifetime test. Further optimization of residual gas species in the FE source should lead to a control of the rate and size of growing CFs during the FE process, thus resulting in an ultralong-life FE source operating under non-UHV condition. Experiments along this line are now being undertaken. We believe that the self-regenerative FE source will be promising as an electron source in many practical non-UHV device applications.

In summary, we demonstrated a self-regenerative field emission source operating under non-UHV condition. The stable and long-sustained emission was ascribed to the CF growth during the emission process. The optimization of residual gas species and pressure in the emission source could lead to the development of ultralong-life FE sources operating under non-UHV condition.

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