Selective Growth of Multi-walled Carbon Nanotubes by Thermal Chemical Vapor Deposition and Their Field Emission Characteristics

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Abstract
Multi-walled carbon nanotubes (CNTs) grown on catalyst dots by thermal chemical vapor deposition were vertically aligned with a high population density. Such densely populated CNTs showed poor field emission characteristics due to the electrical screening effect. We reduced the number density of CNTs using an adhesive tape treatment. For dot-patterned CNTs, the tape treatment decreased the CNT density by three orders of magnitude, drastically improved the turn-on electric field from 4.8 to 1.8 V/μm, and changed the emission image from spotty to uniform luminescence. We also report long-term emission stability of dot-patterned CNTs by measuring the emission currents with time at different duty ratios.

1. Objectives and Background
Since their discovery, carbon nanotubes (CNTs) have been considered to be one of the most promising materials for field emitters, because of their inherent nature.[1] Many factors of CNTs govern their field emission (FE) characteristics, such as the aspect ratio (ratio of the length to the diameter), population density, crystallinity, electrical conductivity, chemical inertness, adsorbed gases on surface, etc. The population density among them, in particular, seems to be the most important physical parameter to be controlled in the fabrication of field emitter arrays. Nilsson et al.[2] have reported that the maximum emission current occurs at an intertube distance of ~2 times the CNT height. Since the CNTs grown by using chemical vapor deposition (CVD) occur, in many cases, as a forest consisting of numerous closely packed ones, they have poor FE properties. Several methods have been tried to tune the density of CVD-grown CNTs, including lithography[3,4], catalyst site density using catalyst diffusion through the barrier[5], catalyst etching[6,7], dispersion of a catalyst solution[8], electrochemical deposition of a catalyst[9], or laser irradiation to as-grown (AG) CNTs.[10] However, easiness of density control, application over a large area, and cost are still problems met in some approaches. Here we report a novel density control method, the tape treatment, which greatly reduces the CNT density while maintaining their vertical alignment, thereby remarkably improving the FE characteristics.[11] This study fabricated diode-type CNT emitters where CNT dots were patterned to have the same geometry as those of the triode-type emitters. We also investigated an emission stability of the dot-patterned CNTs by measuring the emission currents with time under pulse voltages at different duty ratios.

2. Experimental
A 150 nm-thick Mo layer deposited by electron beam evaporation served as a cathode electrode on glass. A photoresist was patterned by an UV exposure and a subsequent development, followed by coating a 10 nm-thick Al and a 1 nm-thick Invar alloy (52%Fe-42%Ni-6%Co). Lift-off processing of the photoresist produced an array of Al and Invar dots with a diameter of 3 μm and a pitch of 11 μm. Here the Invar acts as a catalyst for CNT synthesis. During heating up to the growth temperature of 650°C for 5 min in Ar, Al was oxidized by residual oxygen to result in the formation of Al oxide nanoparticles on whose surface smaller-diameter Invar nanoparticles occurred.[12] CNTs were grown for 10 min at 1.6 torr of C_2H_2 (200 sccm) and Ar (500 sccm) using thermal CVD equipped with a 4-in-diameter quartz tube reactor surrounded 24 infrared lamps. CNTs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. FE characteristics of CNT emitters were measured in a diode configuration in a pressure lower than ~3×10^{-8} torr. An indium tin oxide glass coated with ZnS:Cu,Al phosphor and a 5 mm-thick stainless plate were used as an anode. The cathode-to-anode gap of 1.1 mm was kept by glass spacers.

3. Results and discussion

Fig. 1 shows an array of CNT dots having the diameter and length of 3 μm and 4-4.5 μm, respectively, where CNTs with the diameter of 10-15 nm are vertically aligned. An employment of the Al layer underneath the catalyst layer greatly reduced the diameter of CNTs from 30-50 nm. It was observed that CNTs were grown out from catalyst nanoparticles on the surface of round-shaped Al oxide.[12] The Al layer seems to effectively prohibit catalyst particles from agglomerating. Otherwise, thick-diameter CNTs would be resulted. CVD synthesis produced highly populated CNTs with the density of ~7.5x10^{11}/cm^2 in a dot. Such a highly crowded population of CNTs would result in the electric field screening between them upon application of electric field. Thus, we attempted to reduce the number density of CNTs in a dot by using an adhesive tape. The tape was rolled down in direct contact with the as-grown CNT surface and then removed. The adhesive tape treatment decreased the number density of CNTs by three orders of magnitude, down to 9.6x10^8/cm^2, while the CNT length was also reduced to 1-2 μm. This process thinned out the full-grown CNTs, leaving the under-grown CNTs on the surface.

Fig. 2 shows FE I-V characteristics of an array of CNT dots before and after the tape treatment. The turn-on electric fields drastically improve from 4.8 to 1.8 V/μm. From the Fowler-Nordheim plots[16], we estimate the field enhancement factor β and the effective emission area α in the low-field region. β is defined as E= $\beta V/d$, where E is the local electric field at the tips, V the applied voltage, and d the cathode-to-anode gap. The β value, in principle, depends only on the geometrical shape of the emitters for a given work function. For the work function of the CNTs assumed to be the same as that of graphite, 5.0 eV, the β values are calculated to be 954 and 4073 and the α values to be 3.0×10^{-3} and 4.7×$10^{-3}$$cm^2$ before and after the treatment, respectively. The taping-off process increased α and β values at the same time, expectedly improving the emission uniformity as well as FE I-V properties. The tape treatment seems to relieve the electric field screening effect by reducing the density of CNTs. The treatment makes the CNTs shorter, but provides a much larger number of CNTs to work as emitters. Such FE properties of CNTs will be collectively reflected in phosphor images, as in Fig. 3. The images were observed at the same electric field before and after taping-off. The as-grown CNTs show a spotty pattern, but the tape-treated CNTs demonstrate quite a uniform emission over a 1x1-cm^2

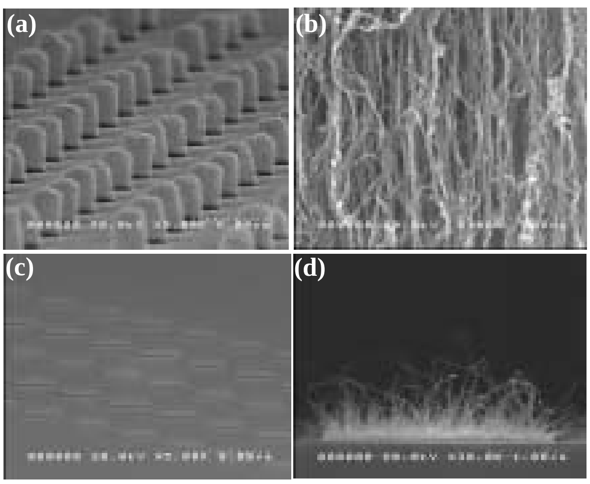


Fig. 1 SEM images showing an array of CNT dots (a), (b) before and (c), (d) after an adhesive tape treatment.

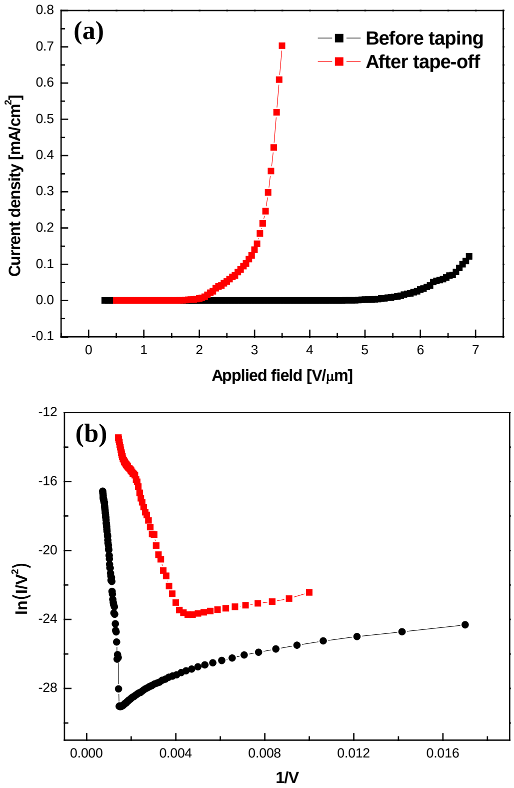
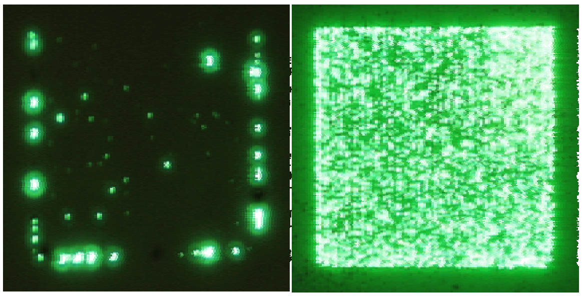


Fig. 2 (a) FE I-V curves from an array of CNT dots before and after the tape treatment and (b) their Fowler-Nordheim plots.



(a) (b)

Fig. 3 Phosphor emission images from an array of CNT dots (a) before and (b) after the tape treatment.

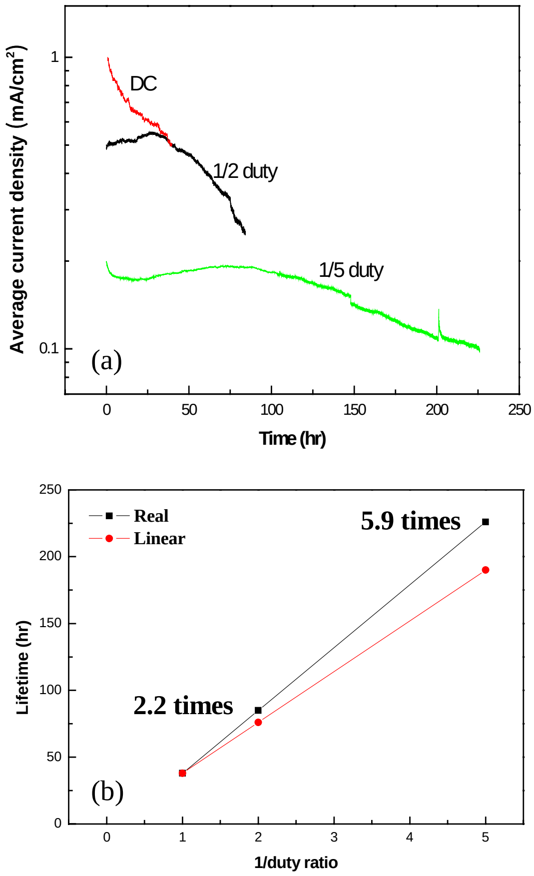


Fig. 4 (a) FE lifetimes measured at the duty ratios of dc, 1/2, and 1/5 and (b) lifetimes plotted as a function of 1/duty ratios. Here a lifetime of the emitters is defined as the time for the current density to be reduced to half of the initial value. The initial peak current density is set to ~1 mA/cm^2 for all measurements.

area. We estimate that 63% of the pixels work in Fig. 3(b).

We also measured the long-term emission stability of dot-patterned CNTs by measuring the emission currents with time at different duty ratios. Our diode-type field emitter arrays were fabricated based on QVGA-resolution, 5-in-diagonal panels. The real devices would be operated with a duty ratio of 1/240, but our diode-type emitters were measured by applying square-pulse voltages having dc, 1/2, and 1/5 duty ratios, because a very long time would be taken at lower duty ratios. We measured the lifetimes of the emitters, defined as the time for the current density to be reduced to half of the initial value. The initial peak current density was set to ~1 mA/cm^2 for all cases. Currently, the lifetime of our devices are ~38, 85, and 226 hr at the dc, 1/2, and 1/5 duty ratios, respectively, as shown in Fig. 3(a). The lifetimes are plotted again as a function of 1/duty ratios in Fig. 3(b). When the duty ratio is lowered from dc to 1/2 and 1/5, the lifetimes increase by 2.2 and 5.9 times, respectively. A reference line from dc to the duty ratio 1/5, which is a simple linear relationship of lifetimes with 1/duty ratios, indicates that more deviation would occur at lower duty ratios. For the 1/240 duty, a linear extrapolation suggests the lifetime of ~ 11,000 hr, but a much longer lifetime is expected in a real operation due to more rapidly increasing nature of lifetimes with 1/duty ratios. Lifetimes at the duty ratios of 1/10 and lower are now under measurement.

4. Conclusions

We grew vertically aligned CNTs with their outer diameters as thin as 10-15 nm by adopting an Al layer underneath the catalyst layer, but with a very high population density. The tape treatment decreased the density of CNTs by three orders of magnitude, resultantly improving the FE characteristics measured from an array of CNT dots. Their turn-on fields and emission uniformity were considerably enhanced such that α and β values increased at the same time. Lifetimes of our emitters measured under accelerated duty conditions showed a more rapid increase than a simple linearity. A linear extrapolation suggested the lifetime of ~ 11,000 hr for the 1/240 duty ratio, but a much longer lifetime was expected in a real operation.

5. References

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