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Field emitter arrays with multiwall carbon nanotubes (CNTs) grown inside their gated holes were fabricated on glass substrates. The Fe–Ni–Co alloy catalyst dots on which the CNTs would be grown were deposited into the gated holes by a self-aligned method to maintain a constant distance between CNT emitters and gate electrodes. The CNTs were synthesized by thermal chemical vapor deposition using a gas mixture of CO and H_2 at 500 °C. The CNT lengths were controlled by changing ratios of CO to H_2. Field emission currents and images were monitored as a function of gate and anode voltages. It was shown that the CNT emitters grown just up to the gate electrode height operated best in a triode mode. © *2002 American Institute of Physics.*
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It has been a hot issue for about last ten years to explore new materials for the field emitters which can easily emit electrons, from metals having high electron densities near the Fermi level to wide band gap materials having negative electron affinity.[1–3] Since the discovery of carbon nanotubes (CNTs), they have attracted much attention due to their excellent field emission characteristics for vacuum microelectronics. The CNTs possess inherent geometry of high aspect ratios (small diameter and large length) such that many scientists have investigated their field emission properties, reporting lower electric fields for electron emission than any other materials.[4–6] Beyond such scientific interest, the efforts to apply the CNTs to vacuum microelectronics have been intensively made, among which gated CNT field emitter arrays (FEAs), in particular, for the display applications, are most interesting.

Two methods have been developed to put CNTs into the gated holes so far. One is to squeeze the CNT mixtures[7,8] (in most cases with organic vehicles) into the holes, and the other is to directly grow the CNTs inside the holes by chemical vapor deposition (CVD).[9–12] The former approach has already demonstrated color moving pictures with the gated CNT FEAs.[8] This has shown a strong potential of application of the CNTs to the field emission displays, but seems to be limited to large area and low resolution displays. Thus, to achieve high-resolution displays with extremely low operation voltages requires direct growth of CNTs inside of the gated holes and precise control of gate-to-CNT emitter distances. Several groups[9–12] have fabricated and operated the gated FEAs with the CNTs directly grown by CVD, however, those were of primitive cells and moreover fabricated at high temperatures over 600 °C. Higher temperatures than 500 °C are usually not allowable to field emission displays based on glass substrates. One of the requirements to develop the gated CNT FEAs is controllability of their dimensional parameters such as gate hole diameters, CNT lengths, CNT-to-gate electrode distances, etc. Here we developed a self-aligned growth method of CNTs inside the gated holes to easily keep a designed distance between CNT emitters and gate electrodes. The CNTs were deposited into the gated holes as low as 500 °C by thermal CVD on the gated FEAs of glass.

The gated FEA templates with the 2.5 in. diagonal were fabricated by photolithography processes, as illustrated in Fig. 1. The larger gate holes in diameter than expected by photoresist (PR) are defined by overetching. The SiO_2 insulator is wet-etched through the gate holes as well as the PR holes. Thereafter, the Invar alloy (Fe:Ni:Co=52:42:6) is deposited to be catalyst for the CNT synthesis by electron

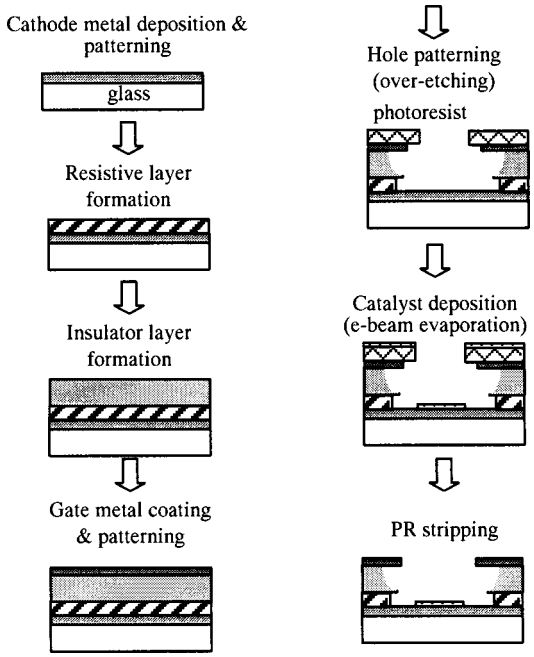

FIG. 1. Schematics of fabrication processes of FEA templates.

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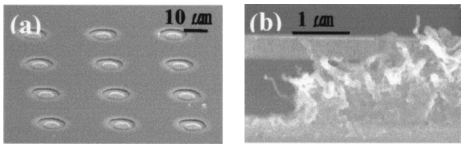

FIG. 2. (a) SEM image of an FEA with the CNT dots grown inside gate holes at the CO/H_2 flow rates of 80/1270 sccm and (b) cross-sectional SEM image of CNTs in a dot.

beam evaporation using the PR layer as a mask to define the catalyst dots inside the gate holes. The subsequent PR stripping produces the gated FEA template. The electron beam deposition that supplies evaporated metal beams in the vertical direction, forms inside the gate holes the catalyst dots with the same diameter with that of the PR holes. This process results in concentric, circular catalyst dots self-aligned with each gate holes. No contamination by catalyst on the sidewall surfaces of insulator holes prevents electrical leakage between the cathode and gate electrodes. The self-aligned formation of catalyst dots provides an easiness of fabrication by reducing the processing steps. The diameters of catalyst dots, gate holes, and insulator holes at the bottom are 9, 13, and 15 μm, respectively in this experiment. The as-fabricated FEA template was characteristic of a resolution of 120 lines$\times$40 lines$\times$3 (red, green, blue colors) with totally 1 800 000 gate holes for an active area of 3.96 cm (gate electrodes)$\times$5.28 cm (cathode electrodes). The gated FEA template was loaded into a vacuum chamber to grow CNTs. After evacuating the chamber down to 1×10^{-2} Torr, a CO and H_2 gas mixture was introduced up to an atmospheric pressure with the total flow rate of 1350 sccm. Then, the substrate was heated up to 500 °C by an infrared light radiation. The peak temperature of 500 °C was kept for 20 min for CNT growth and thereafter ramped down to room temperature. The substrate temperatures were monitored by a thermocouple located just underneath the substrate, which was well calibrated by a CNT-coated thermocouple in contact with the topmost surface of the substrate. CNT deposition method and system were described in a previous report.[13]

Figure 2(a) shows scanning electron microscopy (SEM) images of a resultant CNT FEA. Hemispherical dots of CNTs are selectively grown only on the catalyst areas. The CNT dots are kept uniformly apart from the gate hole edges by the designed distance of 2 μm so that the electrical insulation is maintained between the cathode and gate electrodes. As shown in Fig. 2(b), the hemispherical CNT dots are composed of an inner amorphous carbon layer enclosed by an outer CNT layer. The CNTs are randomly oriented. The amorphous carbon and CNT layers are about 0.8 and 0.2 μm thick, respectively. It seems that the inner amorphous carbon forms because infrared light heating is not enough to synthesize CNTs at the initial stage of growth. Insufficient decomposition of CO and H_2 on the catalyst due to low thermal energies would result in an amorphous phase of carbon. As the amorphous carbon layer forms, the Invar alloy catalyst dots undergo the color change from shiny metallic to black. Such color change enables them to absorb more energy from an infrared light, consequently giving rise to a temperature increase of the substrate. In our observation, the color change

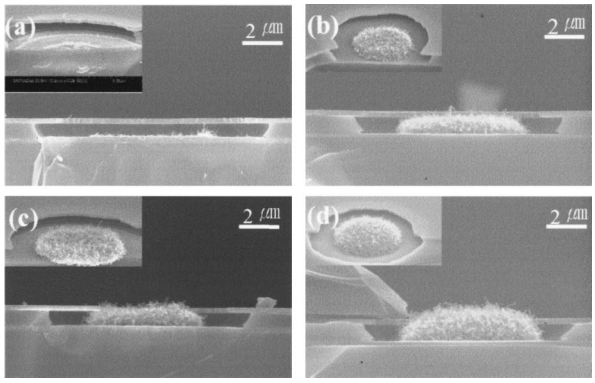

FIG. 3. Cross-sectional SEM images of the CNT dots grown inside gate holes with the CO/H_2 flow rates of (a) 50/1300, (b) 80/1270, (c) 100/1250, and (d) 150/1300 sccm, where the insets are their tilted images.

of substrate from metallic to black started to occur at 350 °C and CNTs were not grown during ramp up to 500 °C. Conclusively, the amorphous carbon starts to form at 350 °C where the color change increases the substrate temperature by absorbing more energies. The amorphous carbon deposition continues until CNTs start to grow at 500 °C, finally leading to the configuration of the CNT layer enclosing the amorphous carbon layer. A transmission electron microscopy investigation of CNTs shows the herringbone, multiwalled structure.

Figure 3 shows cross-sectional and tilted SEM images of the CNT dots grown inside the gated holes with different flow rates of CO while keeping the same total gas flow rate of 1350 sccm. The CNT dot heights become larger with an increase of the CO flow rates from 50 to 150 sccm. At 50 sccm, a small amount of CNTs, probably including the amorphous carbon, are deposited at the bottom of the gate hole [Fig. 3(a)]. At 80 sccm, the CNTs are grown to just fit the gate electrode height [Fig. 3(b)], whereas the CNTs are overgrown slightly above the gate electrode at 100 sccm [Fig. 3(c)]. It is observed that the CNTs are more uniformly grown

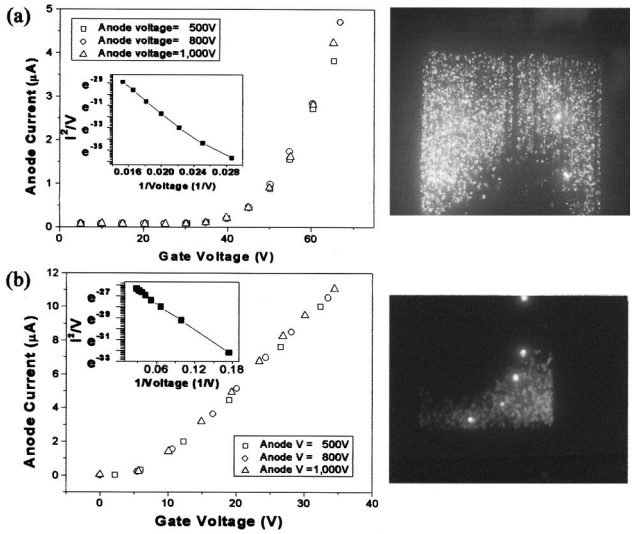

FIG. 4. Field emission currents measured at anode electrodes as a function of gate voltages for constant anode biases of 500, 800, 1000 V from the CNT FEAs with the CO/H_2 flow rates of (a) 80/1270 and (b) 100/1250 sccm, where the insets show their Fowler–Nordheim plots. The corresponding emission images were observed at the gate voltages of (a) 60 and (b) 30 V for the anode voltage of 800 V.

at 80 sccm than 100 sccm. When the CO flow rate increases to 150 sccm, the CNT dot as high as 1.7 μm occurs [Fig. 3(d)]. The growth rates of CNTs (as well as amorphous carbon) strongly depend on the supplied carbon quantities.

Emission characteristics of our gated CNT FEAs were measured for the cathode-to-anode gap of 1.1 mm. Measurement conditions are descried previously.[8] Figures 4(a) and 4(b) gives anode currents from the 2.5 in. diagonal FEAs with the CNTs grown with the CO gas flow rates of 80 and 100 sccm [Figs. 3(b) and 3(c)], respectively, with gate biases for constant anode voltages of 500, 800, and 1000 V while the cathode electrodes were grounded. Sufficient electron emission was not observed from the 50 sccm CO grown sample, probably due to the low CNT dot height. The sample grown with 150 sccm CO has too low electrical resistance between the cathode and gate electrodes to measure field emission properties. It seems that the low resistance comes from carbonaceous deposit formed on the sidewall surface of the insulator holes at the high CO concentration. It is already reported that high carbon concentrations give rise to lower cathode-gate resistances in the CNT FEAs made by CVD.[14] The FEAs with the CNTs reaching the gate electrode height of approximately 1 μm show a successful operation in a triode mode. As shown in Fig. 4(a), the sample grown with 80 sccm CO turns on at the gate voltage of around 40 V, and shows a linearity in the Fowler–Nordheim plot, representing that measured anode currents occur by field emission. The phosphor emission image shows a quite good uniform emission over a diagonal 2.5 in. area. When the flow rate increases to 100 sccm, the turn-on gate voltage drops to 7 V, but several bright spots are observed in an emission image. It is considered that most emission currents are contributed from these bright spots, giving rise to such a low turn-on gate voltage. An appearance of the bright spots would result from shorter distances between the CNT dots and gate electrodes in the corresponding gate holes. This seems to agree with the nonuniform growth of CNTs in a hole, as shown in Fig. 3(c). It is noted that emission currents do not significantly change with anode voltages from 500 to 1000 V for the cathode-to-anode gap of 1.1 mm. This implies that electron emissions from the CNTs are controlled only by gate voltages without any diode electron emission by anode biases.

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