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Selective growth and field emission of vertically well-aligned carbon nanotubes on hole-patterned silicon substrates

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Abstract

We have achieved selective growth of high-purity carbon nanotubes (CNTs) on iron-deposited hole-patterns by thermal chemical vapor deposition (CVD) of acetylene gas. The vertically well-aligned CNTs were uniformly synthesized with good selectivity on hole-patterned silicon substrates. The CNTs indicated multiwalled and bamboo-like structure. The turn-on gate voltage at the CNT-based triode structure was about 55 V and emission current density was 2.0 μA at the applied gate voltage of 100 V.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], many researchers have studied the synthesis of high-quality CNTs using various methods such as arc discharge [2], laser vaporization [3], pyrolysis [4,5], plasma-enhanced [6] or thermal chemical vapor deposition (CVD) [7,8]. CNTs have also attracted much interest because of many potential applications due to their unique physical and chemical properties. One of the most potential applications of CNTs is a field electron emitter at relatively low voltages [9,10].

For application of the field emission display (FED), a triode type FED has some advantages such as stable emission property, effective emission, and high-quality screen, in comparison with a diode type FED. In order to realize a CNT-based triode type FED having gate electrode structure, selective growth of CNTs onto hole-patterned substrates was considered as a key technology. There were many reports for field emission from aligned CNTs on flat substrate [11–15] and selectively grown CNTs on a catalyst patterned substrates [16–20]. Recently, the field emission from selectively grown CNTs on the hole-patterns has been studied [21–24]. They reported field emission

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properties from CNTs grown on hole-patterns but the CNTs were not vertically well-aligned on the substrate. Moreover, there was no information for structure and crystallinity of the CNTs in their results. Sohn and Lee [25] announced the selective growth of CNTs on hole-patterns with various shapes and sizes, but did not evaluate field emission properties from the CNTs.

In this Letter, we demonstrated the selective growth of vertically well-aligned CNTs on Fe-deposited hole-patterns using thermal CVD and investigated structure and crystallinity of the CNTs. We also evaluated field emission from the CNT-based triode structure, which was fabricated on hole-patterned silicon substrates.

2. Experimental

Fe-deposited hole-patterns were prepared on silicon substrates in order to grow CNTs selectively at hole inside. Hole-patterns with various shapes and sizes were fabricated on the silicon substrates by a conventional lithography method. After making the hole-patterns, Fe film was deposited by sputtering method followed by lift-off process. A 30-nm thick Fe film was only remained at the bottom of a hole. To synthesize CNTs on the bottom of the hole-patterns, the hole-patterned substrate was mounted into a quartz tube of thermal CVD system, and the quartz tube was then heated up to the growth temperature in the range of 750–850 °C, with Ar flow of 500 sccm. After arriving at the growth temperature, Ar gas was switched to NH_3 gas with the flow rate of 100 sccm for 20 min. Generally, NH_3 gas etches Fe film at a high temperature, resulting in nanosized Fe particles which serve as a catalyst for CNT synthesis. For the synthesis of CNTs, the NH_3 gas flow was replaced by C_2H_2 gas with the flow rate of 30 sccm for 5 min at the same temperature. After the reaction, the quartz tube was cooled to room temperature with Ar ambient.

Scanning electron microscope (SEM; Hitachi, S-4700) was used to investigate the CNT growth on the hole-patterns and transmission electron microscope (TEM; JEOL, JEM 2000 EX) was used to investigate structure and crystallinity of the CNTs. In addition, crystallinity of CNTs was characterized by Raman spectroscope (Renishaw, Micro-Raman 2000). Field electron emission measurement was performed in a high vacuum chamber at 10^{-6} Torr. The cathode was contacted through the backside of the silicon substrate and a copper plate was applied as the anode, which was positioned about 1 mm above the CNT-based triode structure.

3. Results and discussion

It is well known that the synthesis of well-aligned CNTs on hole-patterns is very difficult due to turbulence of the reaction gas flow in hole inside. To realize the selective growth of aligned CNTs on the hole-patterns, it is necessary to optimize reaction conditions cautiously. Fig. 1 shows that CNTs are selectively synthesized on the hole-patterns at 850 °C. Fig. 1a indicates good selectivity of CNTs with pillar shape on a large area substrate. Fig. 1b shows the magnified SEM image of the vertically well-aligned CNTs grown on the hole-patterns. The inset shows that the CNT pillars have no carbonaceous particles on the surface. The CNTs have diameters in the range of 50–60 nm. Fig. 1c represents the cross-sectional SEM image, showing that the well-aligned CNTs are attached on the bottom of hole-patterns.

Fig. 1d shows the SEM image of the CNTs grown on the hole-patterns with different shape and size from Fig. 1b. The length of CNTs grown at the edge area of the hole-patterns are longer than those at the center area, indicating that carbon molecules can effectively be supplied at the edge area compared with the center area [20].

The vertical alignment of the CNTs on the substrate is important for practical applications of CNTs as field emitters [11]. Generally, the CNTs grown on hole-patterns have some merits for the vertical alignment because the direction of CNT growth must be confined by the hole-patterns. The well-aligned CNTs grown on the hole-patterns can promise to fabricate the triode type FED.

We tried to fabricate the CNT-based triode structure on the hole-patterns. The schematic diagram for the CNT-based triode structure is

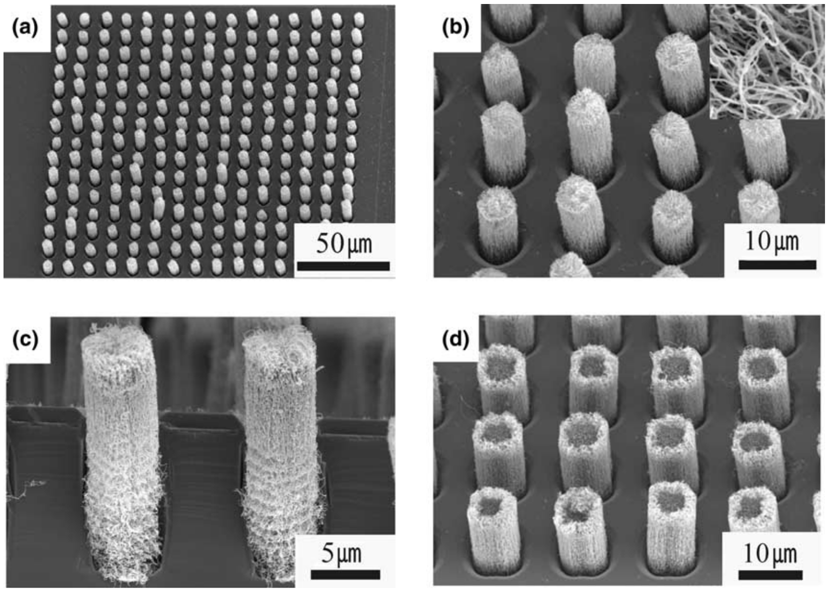

Fig. 1. SEM images of CNTs grown on hole-patterns at 850 °C. (a) Low-magnification SEM image of the CNTs grown on a large area substrate. (b) High-magnification SEM image of the CNTs. The inset shows that the CNT pillars have no carbonaceous particles on the surface. (c) Cross-sectional SEM image of the CNTs. (d) SEM image of the CNTs grown on the hole-patterns with different shape and size. The CNTs grown at the edge area of the hole-pattern are longer than those at the center area.

shown in Fig. 2a. The fabricated hole-pattern has a depth of 12 μm and a width of 8 μm in the silicon substrate. A 100-nm thick Cr film was used to the gate electrode and the thickness of top SiO_2 and spacer SiO_2 layers were 300 and 70 nm, respectively. The CNTs were selectively grown on the hole-patterns with the optimized condition. In order to maximize field emission controlled by the gate electrode, it is necessary to grow the CNTs just up to the bottom of the gate as shown in Fig. 2b. It is well known that the growth rate of CNTs can be controlled by growth parameters such as temperature, time, and gas flow rate. As shown in Fig. 2c, the just growth of well-aligned CNTs was realized on the hole-patterns at 750 °C.

Fig. 3a shows the TEM image of a typical CNT selectively grown on the hole-patterns, in which the CNT has multiwalled graphene layers and bamboo-like structure. HRTEM observation is useful technique to investigate the structure and crystallinity at a specific area. In HRTEM image (Fig. 3b), the CNT has high-crystalline graphene layers at the inner wall while it has amorphous graphene layers (about 1.8 nm) at the outer wall. The graphene layers of the CNT have tilted angle about 10° toward a growth direction, resulting

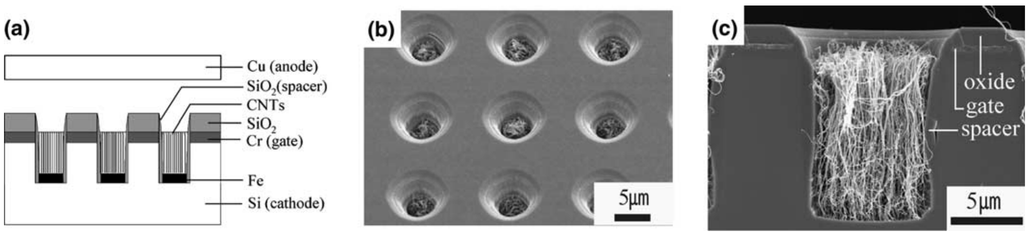

Fig. 2. (a) The schematic diagram for the CNT-based triode structure. (b) SEM image of the CNTs-based triode structure. (c) Cross-sectional SEM image of the CNT-based triode structure.

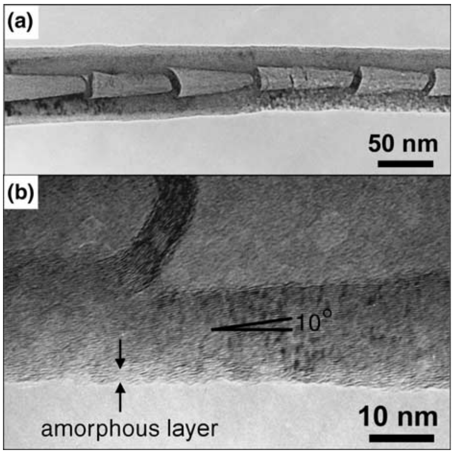

Fig. 3. TEM images of a typical CNT. (a) TEM image of a MWNT having bamboo-like structure. (b) HRTEM image of a typical MWNT.

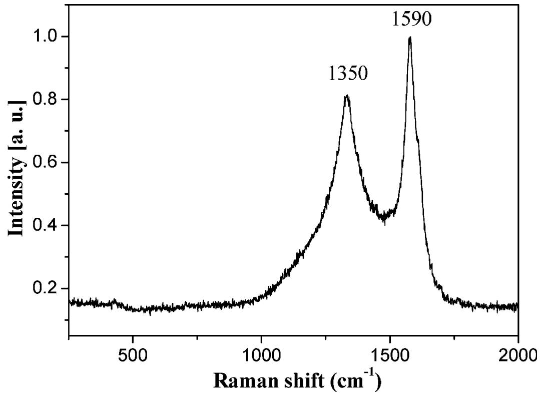

Fig. 4. Raman spectrum of the CNTs grown on the hole-patterns.

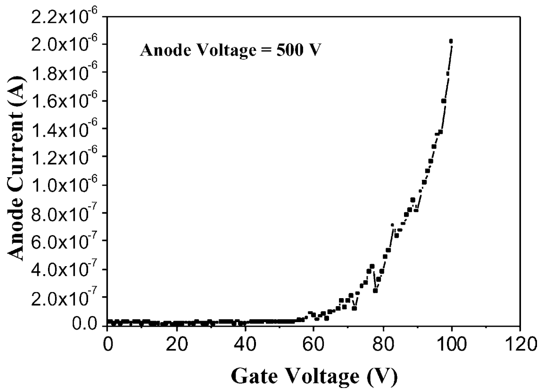

Fig. 5. Field emission properties from the CNT-based triode structure under the anode voltage of 500 V.

from the shape of catalyst particles during the synthesis of CNTs [26].

Fig. 4 shows a typical Raman spectrum of the CNTs by using the 514.5 nm Ar excitation. Raman spectrum shows overall crystallinity of whole CNT film. The spectrum presents two peaks of the graphitic structure at approximately 1350 and 1590 cm^{-1}, respectively. The strong G-line peak at 1590 cm^{-1} indicates high-crystalline graphene layers, while the broad D-line peak at 1350 cm^{-1} indicates the existence of defective graphene layers such as amorphous carbon layers [27]. If graphene layers had waving structure or buckled structure, the intensity of G-line would become weak. We consider that overall crystallinity of the CNTs is good from Raman spectrum analysis even though there is partly defective graphite structure.

Fig. 5 indicates field emission properties from the CNT-based triode structure on the hole-patterns as shown in Fig. 2. Field emission property was measured at an area of 100×100 μm^2. To measure current–voltage characteristics, a constant voltage of 500 V was applied to the anode plate, and the gate voltage was swept positively from 0 to 100 V. The experimental data was averaged by five measurements. The CNT-based triode structure, which is operated by the gate voltage, indicates stable operation mode even though there are some fluctuations in emission current. The turn-on gate voltage is about 55 V. A large emission current of 2.0 μA is achieved as the gate voltage is applied to 100 V. Other groups reported that the turn-on voltage in the triode structure was about 40 V, and emission current was in the range of 1.2–3.1 μA at applied gate voltage of 40 V [21–24]. We consider that emission current from our triode structure is similar to their results and enough high to be applicable to FED. In general, there were some reports that turn-on voltage and emission current from CNTs were degraded after high current loading because CNT tips demonstrate outer shell wear out under high current annealing. Actually we could find some degradation of CNT tips after high current annealing in many field emission experiments. But in this work, there are a lot of CNTs at the hole-patterns, which can contribute electron emission. Therefore, field emission from CNTs at hole-patterns may maintain constant value even though high current annealing degrades some CNT tips. We could obtain considerably stable and reproducible field emission from CNTs at hole-patterns. It is considered that the CNT-based triode structure fabricated by our experiment can be applicable to FED.

In summary, we demonstrated the selective growth of the CNTs on hole-patterned silicon substrate using thermal CVD method. The vertically well-aligned CNTs were grown on the hole-patterns and the just growth of CNTs was suitably controlled by optimized growth conditions on the hole-patterns. The CNTs have bamboo-like structure and tilted graphene layers about 10° toward a growth direction. The CNTs have high-crystalline graphene layers at the inner wall but amorphous graphene layers at the outer wall. The CNT-based triode structure indicated stable operation according to the gate bias. The turn-on gate voltage was about 55 V, and the emission current was 2.0 μA at the gate voltage of 100 V. It is suggested that the CNT-based triode structure fabricated by our method can promise application to FED.

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