Electron Emission Properties of CNT Arrays Grown with MIcro Molding In Capillary (MIMIC) Assisted Process

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Abstract

Carbon nanotube arrays were fabricated using micro molding in capillary (MIMIC) process. Patterns remained on the surface in the pattern complementary to that present in the mold. CNTs were selectively grown on the MIMIC patterned sites with a triode PECVD. And turn on field for10 μA/cm^2 electron emission current was 2.2 V/μm turn on field.

1. Introduction

Photo lithography patterning process requires high cost equipment and complicated fabrication process. Many research groups are studied to replace conventional photo lithography to non-photolithographic process. Among many non-photolithographic techniques demonstrated, a soft lithography is a promising technique for low cost and simple process [1]. A key element for soft lithography is an elastomeric stamp or mold with the desired pattern [2]. Micro contact printing (μ-CP) and micro molding in capillary (MIMIC) are simple way to pattern on a solid surface [3]. Typically, stamp of μ-CP and MIMIC are made of polydimethylsiloxane (PDMS).

The MIMIC method has a versatile process for forming microstructure. It is based on the spontaneous filling of capillaries formed between two surfaces in conformal contact. But, MIMIC needs to form appropriate networks of micrometer-scale channel having surface properties that promote capillary filling. In this paper, we fabricated CNTs emitters using MIMIC process. The electron emitter array was made with simple island patterning by using the MIMIC process and electron emission properties were studied.

2. Experimental

Figure 1 shows the PDMS stamp for MIMIC process is made by master pattern of line shape. For this experiment, the height of pattern was varied for resist thickness control. Typically, the height of mold pattern is 1 μm and width between pattern to pattern is 80 μm.

Figure 2 shows the process flow of selective growth of CNT using MIMIC process. PDMS stamp having relief features in its surface was placed on a Ni deposited Si wafer at room temperature. After conformal contact, various resist materials (UV type resist, positive PR, Novolak resist diluted PGMEA, and so on.) were dropped on the substrate to fill channels by capillary action. After spontaneously capillary action and curing, the PDMS stamp was detached from substrate. The microstructures remained on the surface in the pattern complementary to that present in the PDMS stamp. After the patterning, Ni catalysts were etched by Ni etchant [4].

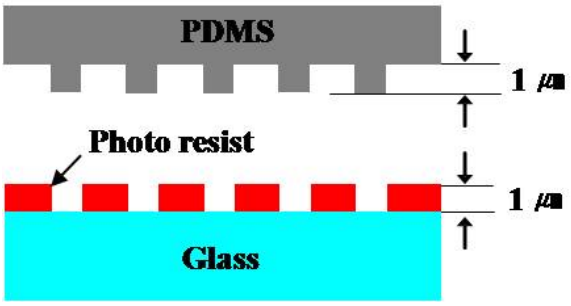

Fig. 1. Fabrication of a PDMS mold with protrusion line shape using master mold.

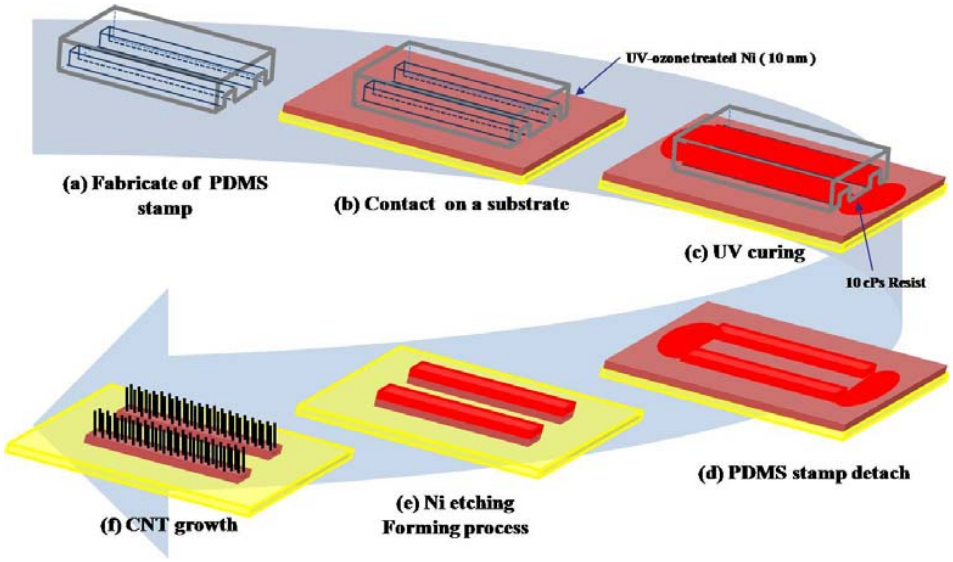

Fig. 2. Process flow of the CNT growth using MIMIC process; fabrication of PDMS stamp (a), place on a support to form micro-channels (b), place a drop of a UV-type resist to fill channels by capillary action and UV curing (c), remove of PDMS stamp (d), Ni etching and forming, and CNT growth(f)

Then the substrate was put in high temperature furnace. During forming process, the resist react with catalysts and make nucleation seed for CNTs growth.

After forming the sample, the CNTs were grown in a triode dc-PECVD, with a mesh grid of 10 mm above the substrate holder electrode with 300 V of positive bias. The substrate electrode was maintained at – 600 V with the top electrode ground, and the spacing between the two electrodes was 30 mm. NH_3 plasma pretreatment was done on the sample for 3 minutes for the granulation of the Ni catalyst layer prior to CNT growth. Acetylene (C_2H_2) and ammonia (NH_3) gases were used for CNT growth with the acetylene flow rate ratio of 50 %. CNT growth was performed for 20 minutes with gas pressure of 2 Torr at 580 ℃ [5]. The triode dc-PECVD method allows controlling growth parameters to control growth rate, density and diameter respectively. [6]

The morphology and structure of the CNTs were examined using a field emission scanning electron microscope (FESEM, Hitachi 4700) and Raman spectroscopy.

3. Results and discussion

Figure 3 shows the optical images of PDMS stamp with protrusion line shape produced by the master (a), resist line pattern on Ni coated wafer substrate (b), line pattern after Ni etching (c), and line pattern after forming (d).

The width of line pattern is 10 μm and pitch between lines is 80 μm. Line patterns on Ni coated Si wafer substrate are made by using PDMS stamp and shown Fig. 3 (b). Line patterns just after Ni etching and after forming are shown as Fig. 3 (c) and (d), respectively.

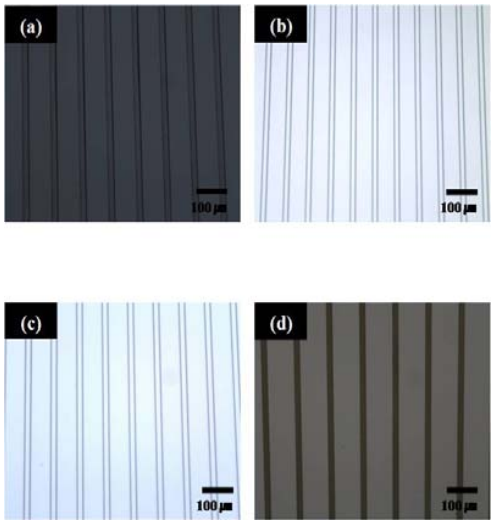

Fig. 3. Optical images of PDMS stamp with protrusion line shape produced by the master (a), resist line pattern on Ni coated wafer substrate (b), line pattern after Ni etching (c), and line pattern after forming (d).

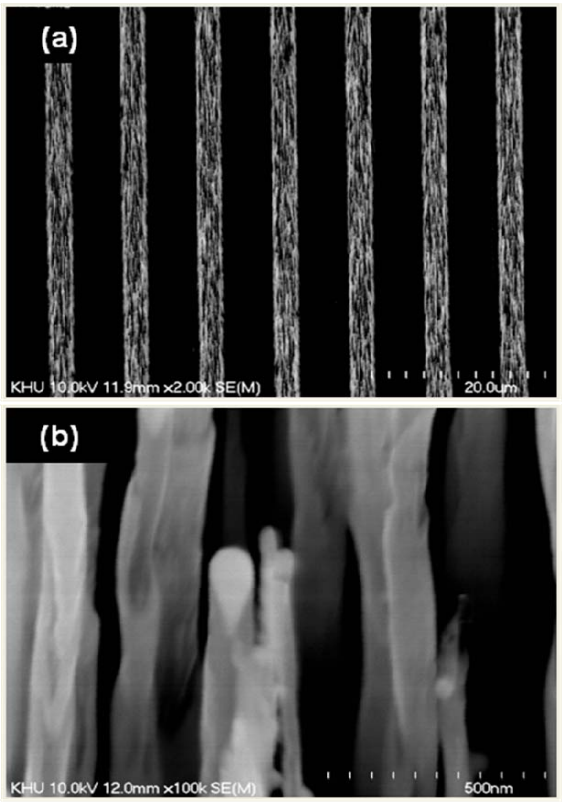

Fig. 4. Aligned CNTs grown on Ni deposited Si wafer. SEM images of CNTs grown on line patterns (a) and its magnified image (b)

After forming, photo resist is not removed because Ni catalyst recombined with resist at high temperature [6]. Scanning electron microscopy (SEM) images of grown CNT on the patterned Si wafer by the MIMIC process is shown in Figure 4. Selective growth and uniformity of each line is examined using a SEM. Fig. 4 (a) shows that CNTs are clearly patterned and grown. Figure 4 (b) is a magnified SEM image. We can found Ni catalyst at the tip of carbon nanotube and diameter of around 100 nm.

Figure 5 shows the Raman spectra of carbon nanotubes. This peak consists of D-band (~1350 cm^{-1}) and G-band (~1590 cm^{-1}) peaks. From the deconvolution of the Raman peak, we can find new peak in 1472 cm^{-1}, the origin is not clear yet. However, one possibility of the peak is related to nitrogen. Nitrogen doped carbon nanotube show strong peak in ~ 1470 cm^{-1} [7]. It needs to study for the origin of the peak. The I_D/I_G ratio is of CNTs is 1.1.

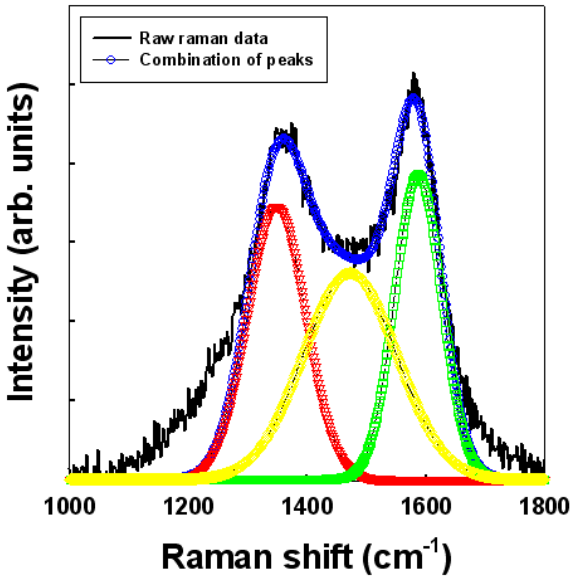

Fig. 5 Raman analysis of CNTs grown by MIMIC process grown by MIMIC process

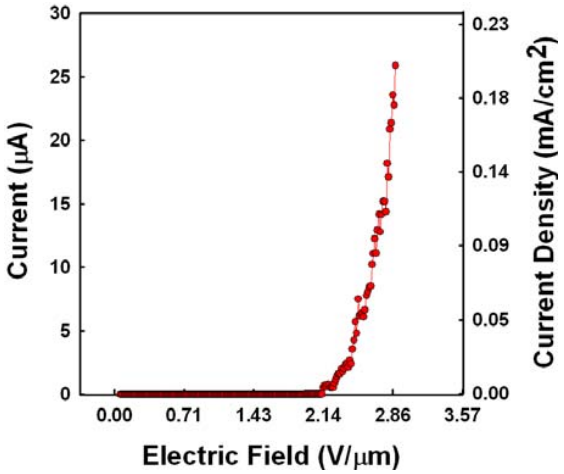

Fig. 6 Field emission characteristic of carbon nanotubes

Figure 6 shows the electron emission characteristics of the CNTs. The field emission property of the CNT emitters was measured using a diode type electron emission measurement system in a high vacuum (< 1 x 10^{-7} Torr). Turn-on field which is required electric field for field emission current of 10 μA/cm^2 is 2.2 V/μm. This value is lower than previous works done by RAP process on Si wafer. [5]

4. Summary

Selective positioning of CNTs is one of the key techniques for FED application. The positioning and size of the CNT stripe could be controlled by resist layer patterning and forming. We introduced a low cost lithography technique using micro molding in capillary (MIMIC) process. Patterns for growth sites remained on the surface in the pattern complementary to that present in the mold. CNTs were grown on the MIMIC pattered sites by various resist materials with a triode PECVD. We can obtain well aligned CNT with selectivity. Electron emission properties of the emitter array shows turn-on field of 2.2 V/μm for 10 $\mu A/cm^2$ current density.

5. References

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