Growth of carbon nanotubes on metal substrate for electronic devices

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Abstract

We developed a novel growth method of CNTs on metal substrate for device applications, deposited by a triode direct current plasma enhanced chemical vapor deposition (dc-PECVD). With resist-assisted patterning (RAP) method, we had grown CNTs on metal substrate, which were strongly bonded with metal substrate.

1. Introduction

The remarkable properties of carbon nanotubes (CNTs) make them attractive for nanoelectronic applications [1], especially for electron emitter. CNTs have several superior characteristics, such as high aspect ratio, high thermal conductivity, and low chemical reactivity [2]. These characteristics are suitable for production of X-ray tubes [3] and electron gun[4]. For device applications, we need the selectively grown CNTs on metal substrate.

Growth of CNTs have been considered on various substrates for electronic devices. For example, growth of self-aligned CNTs on glass substrates using plasma-enhanced chemical vapor deposition (PECVD) [5] and the synthesis of massive arrays of mono-dispersed CNTs on patterned porous silicon [6] were already reported. The synthesis of carbon materials on metal surfaces [7] showed different features compared with that of the conventional CNTs grown on silicon wafers or on glass. The growth of CNTs on large area, low-cost substrate such as metal

substrate is important for practical applications. But, it is not easy to grow good CNTs on metal substrate directly due to the difficulty in forming fine-grain seeds for CNTs growth and cracking of surface during the thermal treatment.

Previously, we reported the growth of CNTs by using a resist-assisted patterning (RAP) process without a diffusion barrier [8-10]. The electron-emitter array was made with simple island patterning on the silicon wafer by using the RAP process [11]. After the catalyst etching, the substrate was formed under vacuum at high-temperature 600 ℃ condition. The RAP process is a very simple and less expensive for the fabrication of CNT electron-emitter arrays.

TABLE 1. The comparison between conventional method and RAP method

	Conventional	RAP
Structure		
Advantage of RAP	· Good adhesion between CNT and substrate · Simple process and not necessary to use barrier metal · Easy to control the emitter shape	

In the present work, CNTs were grown on metal substrate with a-Si ballistic layer. We have grown patterned CNTs with RAP by direct current plasma enhanced chemical vapor deposition (DC-PECVD). The morphology and structure of the CNTs were examined using a field emission scanning electron microscope (FESEM, Hitachi 4700), transmission electron microscope (TEM, FEI-tecnai G2) and Raman spectroscopy.

2. Experimental

Fig. 1 shows the process flow of patterned CNTs using the resist-assisted patterning process. The ballistic layer, a-Si of 15 nm thickness was deposited onto the metal substrate by ICP-CVD using SiH_4.

The Ni catalyst of thicknesses 30 nm was deposited by a reactive sputtering and then patterning with photo patternable resist. After the patterning, the Ni catalysts were etched by Ni etchant and then, the forming procss was carried out for 60 min at 600 ℃ prior to CNTs growth. During the forming process, the resist react with catalysts and make nucleation seed for CNTs growth.

(a) Substrate (Ni/a-Si/substrate)

(b) Coating of resist layer

(c) Pattering of resist layer

(d) Forming of substrate at 600 ℃
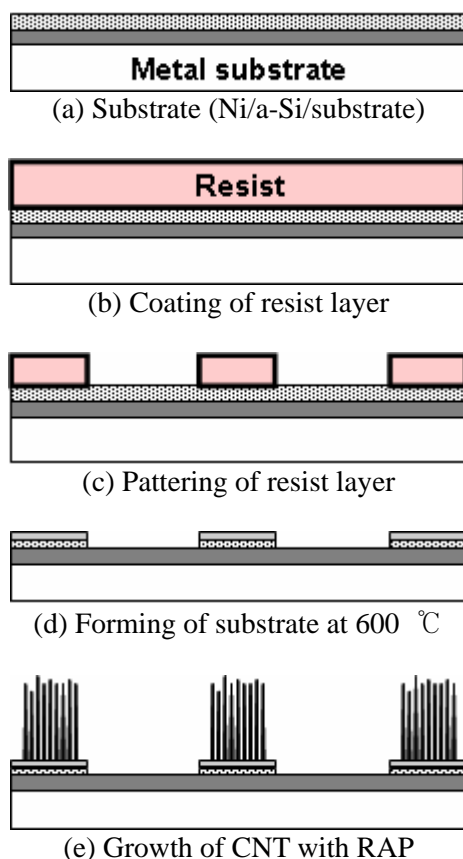
(e) Growth of CNT with RAP

Fig. 1. Novel process flow of CNTs growth with RAP process

After forming, the CNTs were grown using a triode dc-PECVD, with a mesh grid being placed 10 mm above the substrate holder electrode with + 300 V bias. The substrate electrode was maintained at –600 V with the top electrode grounded, and the spacing between the two electrodes was fixed as 30 mm. The ammonia (NH_3) plasma pretreatment was done for 3 min for the granulation of the Ni catalyst layer prior to CNT growth. C_2H_2 and NH_3 gases were used for CNT growth, with the acetylene flow rate ratio of 40 %. The total gas pressure during the growth was kept as 2 Torr and the CNT growth time was 20 min. The growth temperature was maintained at 580 ℃.

3. Results and discussion

Fig. 2 (a) shows the SEM image of CNTs grown with line patterns on metal substrate. The line width and pitch are measured as 50 μm and 200 μm, respectively.
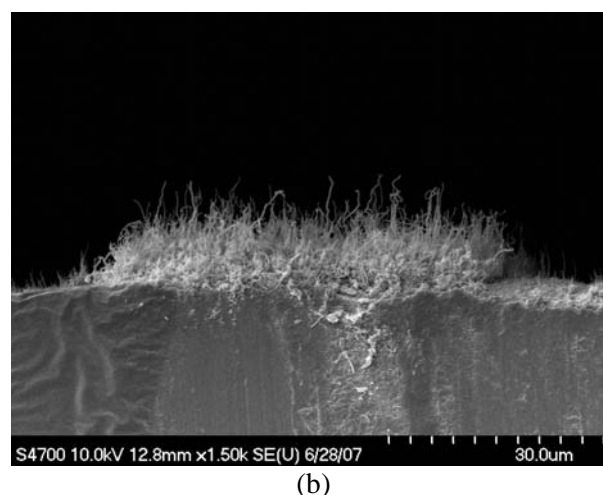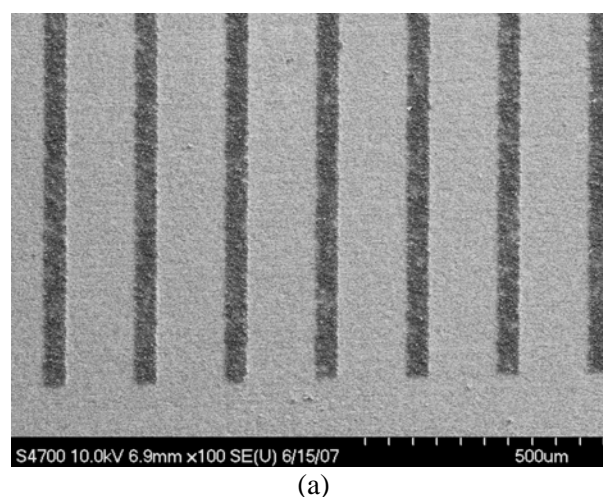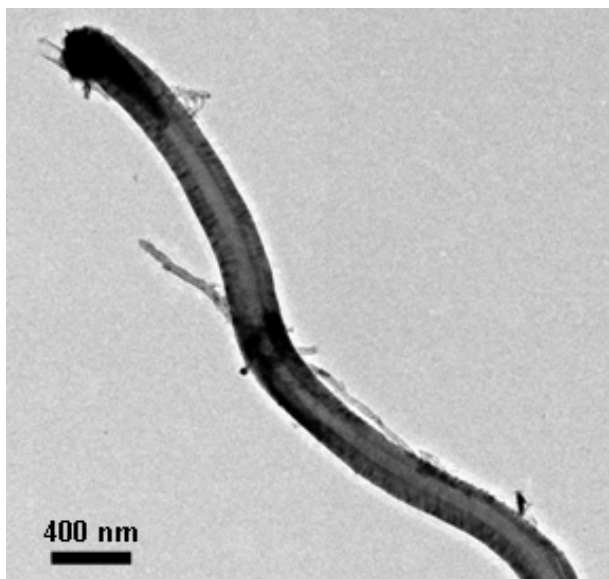

(a)

(b)

Fig. 2. SEM images of (a) line shape emitter array and (b) magnified image of (a).

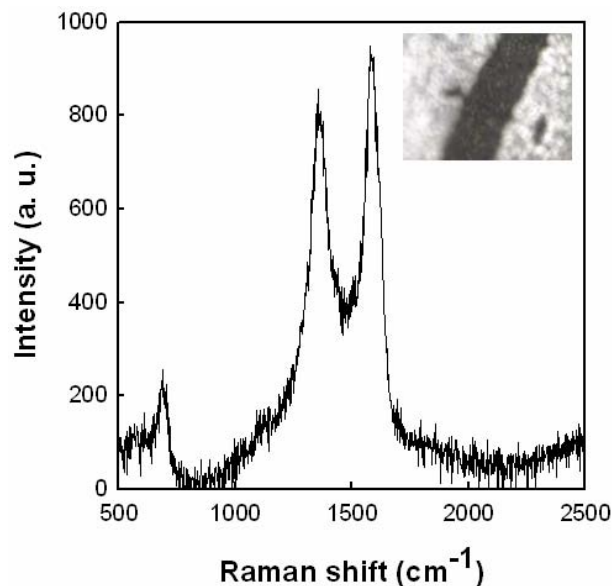**Fig. 3. TEM image of the grown CNT on metal substrate with RAP**

Fig. 4. Raman spectrum of the grown CNT on metal substrate.

From the SEM image of the grown CNTs [Fig. 2 (b)], the average length of CNTs was measured as ~ 20 μm on metal substrate. The line patterns in the figure show very good selectivity. Further, the shape of CNTs seems to be slightly different from that of CNTs grown on Si or glass. The grown CNTs on Si are normally well-aligned features, whereas the CNTs on metal have non-aligned features.

The TEM image of the CNTs is shown in Fig. 3. The TEM image was obtained by placing the grown CNTs on a copper grid. The presence of Ni particle on the tube tip is identified and the inner hole is clearly seen from the analysis. Moreover, the TEM analysis further confirmed a multiwalled tubular structure of average diameter ~200 nm.

Fig. 4 shows Raman spectrum of patterned CNTs and the inset represents the optical image of the measured line pattern. The excitation laser of wavelength 514.532 nm (Ar-ion laser) was used in the present experiment. The multiwall structure of CNTs is confirmed by the presence of G-peak at 1571.84 cm^{-1}. The D-peak at 1350 cm^{-1} corresponds to the amorphous or carbonaceous particles.
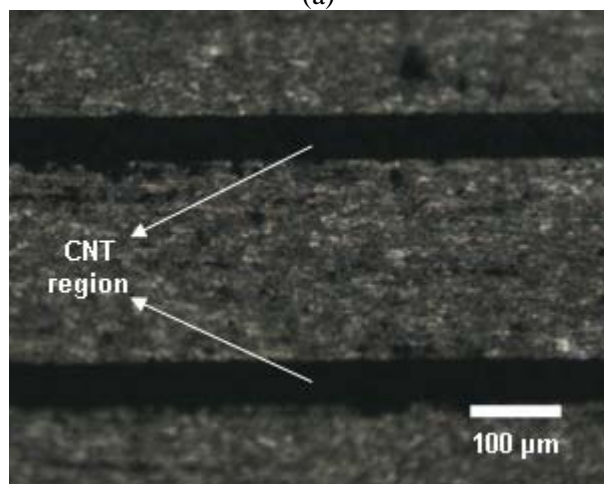
Fig. 5 shows the optical images of bended metal substrate after bending ten times at 90°. More interestingly, it is observed that during such a test, the cracking of surface does not exists. This analysis clearly indicates the good adhesion between CNT-emitter region and the metal substrate.

(a)

(b)

Fig. 5. Optical image of (a) the patterned CNT on metal substrate recorded after bending ten times at 45° and (b) magnified image of (a)

It is known that the, growth of CNTs on metal substrate is difficult due to cracking of surface. However, no crack was observed with this RAP process on metal substrate. This suggest the potential application for field emission on metal substrate. Further, the area of electron source can be controlled using patterned CNTs on metal substrate with RAP process. The grown CNTs on metal can be used for LCD backlight and electron source for X-ray system.

4. Summary

A novel process has been developed for CNT growth on metal surface using a DC-PECVD. The structural and morphology of the grown CNTs were characterized by SEM, TEM analyses and Raman spectroscopy. The RAP process can be extendable to fabricate electron emitter arrays for vacuum nanodevices. Following the same process, one can easily control the emission area with various patterns and size with improved adhesion to the substrate.

5. ACKNOWLEDGEMENT

6. References

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