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Fabrication of CNT microarray for biosensor applications

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Abstract

Microarray technology has become one of the indispensable tools which can be used to identification of bio-molecules in cells, tissues, and disease, such as disease diagnosis, prediction, prevention, and drug discovery. The major advantages of the microarray biosensor are their ability of the simultaneous analysis of thousands parameters on a single platform and minimal sample consumption. Furthermore, carbon nanotubes (CNTs) with their outstanding properties are potential material for many applications including biosensors. To increase the fluorescence detection, the microarray will be established within the three-dimensional (3D) structure. The advantage of the 3D structure CNT for microarray platform is the enhancement of active surface area without sacrificing the size of the device. For instance, the external surface area of one CNT spot is roughly ~3.14×10^{-5} mm^2. As arrays of 100 mm^2 of CNT platform with 50 μm spacing, it can contain as many as 1.82×10^8 spots that is high-density microarrays. This high-density microarray is powerful tools for the screening of pharmaceuticals, investigation of biomolecule interactions and patient diagnostics. In this paper, the CNT is fabricated in microarray configuration to realize biochip sensor design. The CNT microarray was fabricated by using electron beam lithography for patterning microarray on silicon substrate, RF sputtering for deposit catalyst, and thermal plasma chemical vapor deposition (CVD) for growing vertically aligned CNT.

Keywords

APPJ; plasma functionalization; CNT; 3D microarray; biosensor applications

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1. Introduction

Carbon nanotubes (CNTs) are nanomaterial carbon allotropes with a high surface-area-to-weight ratio (~300 m^2g^{-1}) (J. N. Wohlstadter et al., 2003; L. Dong et al., 1996) and excellent material properties such as electrical conductivities and mechanical strength (M. S. Dresselhaus & P. Avouris, 2001; P. M. Ajayan, 1999). CNTs are attracting much attention due to their outstanding properties, with promising applications in numerous areas such as field-effect transistor (S. J. Tans, et al., 1998), fuel cell (Wang, et al., 2004), lithium-ion battery (C. de las Casas & W. Li, 2012), transparent conductive film (Wu, et al., 2004), including biosensors (F. Lu et al., 2009).

Biosensor based on CNTs compose of three associated elements: (1) bioreceptor; (2) interface (functionalized CNT); and (3) transducer. Bioreceptor is a sensitive biological element (such as enzyme, DNA probe, or antibody) for recognizing the analyte (such as complementary DNA and antigen). To work as biosensor, the CNTs have to functionalize as interface layer because the CNTs structure is remarkably stable so that it is insoluble in most solvents. As a result, functionalization of CNT is necessary to allow a better processing of CNT toward the development of biosensors, and improve the solubility and the selectivity of biomolecules recognition (T. Abuzairi et al., 2015, 2016). The transducer converts the biological event to other measurable signals, such as currents, absorbance, mass or acoustic variables.

In this work, the CNT is fabricated in microarray configuration to realize biochip sensor design. The CNT microarray was fabricated by using electron beam lithography for patterning microarray on silicon substrate, RF sputtering for deposit catalyst, and thermal plasma chemical vapor deposition (CVD) for growing vertically aligned CNT (T. Matsuda, et al., 2009; T. Matsuda, et al., 2008).

2. Experimental

Initially, a silicon substrate 10×10-mm^2 was cleaned by piranha solution (40 mL sulfuric acid and 10 mL hydrogen peroxide) for 3 minutes, and rinsed by a mixture of 47.5 mL distilled ionized (DI) water and 2.5 mL hydrofluoric acid (HF) for 1 minute. The Si substrate was then coated with hexamethyldisilazane (HMDS) as pre-resist coating and ZEP-520A as positive electron-beam photoresist by automatic spin coating Suss Delta 80 Gyrset. After that, the Si substrate was baked at 180°C for 2 minutes. The photoresist layer was patterned by electron beam lithography ELS-7700K with acceleration volatage 80 kV, beam current 1.5×10^{-9} A, and dose time 0.2 μs. To remove pattern photoresist, the substrate was developed by O-Xylen at 23°C for 2 minutes and 2-propanol for 40 seconds. The pattern result was shown in **Fig. 1(a)**.

The substrate was then deposited by chromium (Cr) thin film as a diffusion barrier layer for 20 seconds and nickel (Ni) film as a catalyst for 60 seconds by a RF magnetron sputtering SVC-700RF in argon gas ambient as illustrated in **Fig.1(b)**. A lift-off process was conducted to remove the positive photoresist film by remover ZDMAC and left behind the array catalyst on the substrate after one day as depicted in **Fig. 1(c)**. Finally, the growth of CNT array was carried out in the plasma thermal CVD at a substrate temperature of 700 °C for 5 min pre-treatment with NH_3 (150 sccm) followed by 15 min

post-treatment with a mixture of NH_3:C_2H_2 (3:1) and an applied dc bias voltage of -550 V to the substrate stage.

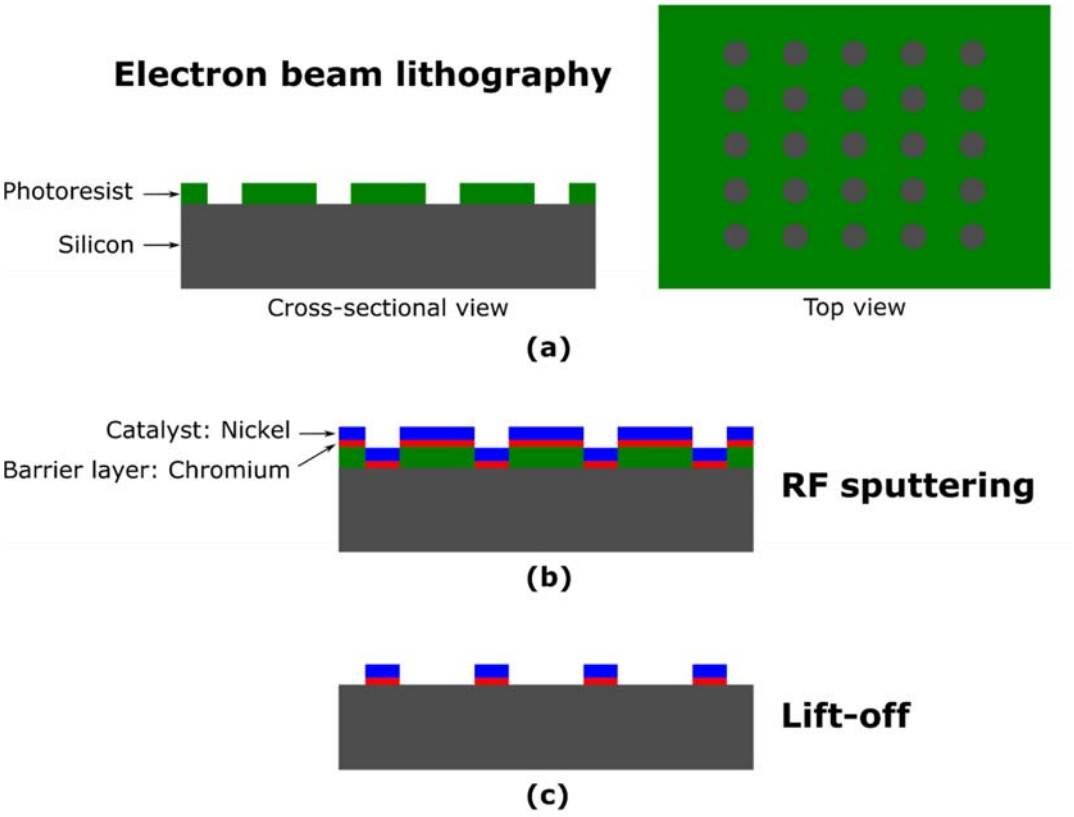

Figure 1. Fabrication of carbon nanotube microarray. (a) Electron beam lithography. (b) RF sputtering. (c) Lift-off process.

3. Results and Discussion

The CNT were fabricated by using electron beam lithography for patterning microarray, RF sputtering for deposit nickel catalyst, and thermal plasma chemical vapor deposition for growing vertically aligned CNT on the silicon substrate (T. Matsuda et al., 2008). **Fig. 2** depicts an FE-SEM image of the CNT microarray with 50 μm spacing and 5 μm dot size, and magnified image of bundle structure of vertically aligned CNT in cross-section and top views. Each dot consisted of a bundle of multi-walled CNT having a typical length of ~2 μm and diameter of about 100 nm. The vertically aligned CNT were fabricated in microarray form to realize the development of biosensor (Kricka, 2001), which has a comparable size of the microarrays biosensor fabricated by other methods, for example photolithography (Malainou, et al., 2012), physical masking (Lee et al., 2010), laser printing method (Duocastella, et al., 2010), micromachine (Bhatnagar, 2007), or microcantilivers processing (Belaubre et al., 2003).

Each CNT spot is comprised of a bundle of multiwall carbon nanotube having a typical length of about 2 μm and a diameter of about 100 nm. The primary advantage of

the 3D structure CNT for biosensor platform is the enhancement of active surface area without sacrificing the size of the device. For instance, the external surface area of one CNT spot is roughly ~3.14×10^{-5} mm^2, calculated from the diameter and length of the CNT (5 µm diameter and 2 µm length) (A. Peigney, et al., 2001). As arrays of 100 mm^2 of CNT platform with 50 µm spacing, it can contain as many as 1.82×10^8 spots that is high-density biochip microarrays. This high-density microarray is powerful tools for the screening of pharmaceuticals, investigation of biomolecule interactions and patient diagnostics (C. Wingren & C. A. Borrebaeck, 2007; J. Clausmeyer, et al., 2014).

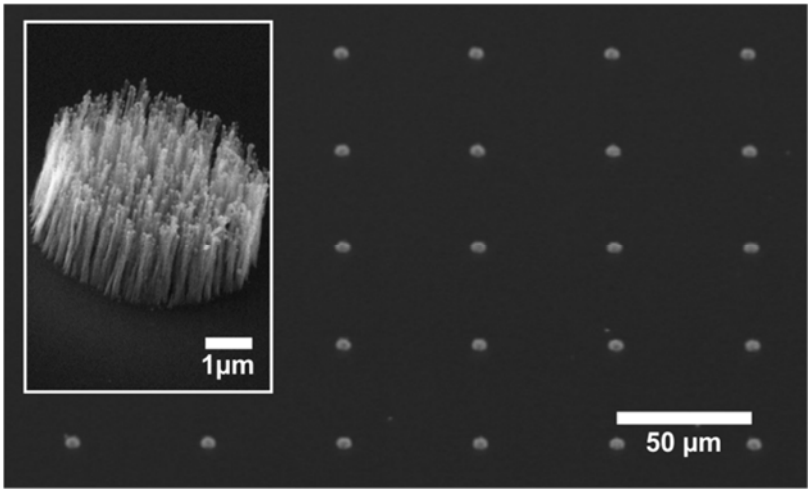

Figure 2. FE-SEM images of the CNT biochip sensor platform and a magnified image of one spot CNT is shown inset (T. Abuzairi et al., 2016)**.**

Additionally, based on the calculation of the CNT surface area, the total surface area of one platform is estimated as ~5715 mm^2. Therefore, the 3D structure of CNT will enhance surface area as ~57 times compared with the 2D structure platform of 100 mm^2. From this point of view, CNT materials are great potential for miniaturization the biochip device, which may allow for the detection of currently undetectable disease markers (C. Wingren & C. A. Borrebaeck, 2007; J. W. Silzel, et al., 1998).

4. Conclusion

The vertically aligned CNT is successfully fabricated by using electron beam lithography for patterning microarray, RF sputtering for deposit nickel catalyst, and thermal plasma chemical vapor deposition (CVD) on the silicon substrate. The 3D structure of vertically aligned CNTs can enhance the active surface area without sacrificing the size of the device. Therefore, CNT materials are great potential for miniaturization the microarray biosensor, which may allow for the detection of currently undetectable disease markers.

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