Sensors and Actuators A 187 (2012) 79–83

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

An overhanging carbon nanotube/parylene core–shell nanoprobe electrode

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ARTICLE INFO

Article history:
Received 27 January 2012
Received in revised form 29 July 2012
Accepted 15 August 2012
Available online 22 August 2012

Keywords:
Carbon nanotube
Assembly
Nanoprobe
Nanoelectrode
Intracellular electrode

ABSTRACT

A nanoprobe electrode based on electrically conductive carbon nanotube (CNT) as the core structure and biocompatible parylene-C as the insulating shell has been demonstrated. The prototype nanoprobe has been fabricated based on a local synthesis and assembly process using micromachined structures to synthesize suspended and both mechanically and electrically connected CNTs in a room temperature chamber. A 1.7-mm-long, overhanging silicon probe has been designed as the carrier for the CNT nanoprobe with typical length of a few micrometers. A conformal deposition of biocompatible parylene-C has been applied as the insulating layer and a local heating process at the distal end has been conducted to break and expose the CNT-tip section to open up the CNT core for possible electrical measurements. Experimental characterizations have shown good electrical interface between the base of the CNT and the growth-side microstructure, while the exposed CNT/parylene tip makes it attractive for applications in nano-scale electrical probing. These core–shell nanoprobe electrodes could find potential biomedical applications in intracellular electrical measurements.

1. Introduction

Micro-scale electrode arrays made by conventional microfabrication technologies have been applied in electrophysiological measurements of biological signals from cells or neurons [1–4]. It is desirable to construct nano-scale electrodes since microelectrodes are capable of measuring extracellular potential but difficult in retrieving intracellular signals due to the micro-scale electrode size. The typical magnitude of recorded extracellular signals is less than 100 μV, which is significantly lower than signals inside a cell of ~100 mV [5]. Other issues associated with micro electrodes are also in favor of nanoprobe developments, including: (1) large size of electrode may cause damage to tissues as well as cell membranes during experiments; (2) signal-to-noise ratio may be too low for meaningful intracellular detections; and (3) recorded signals could originate from several cells instead of a single living cell. These limiting factors might be addressed by next-generation cell recording devices using smaller electrodes such as nano-scale probes.

Previously, advancements in nanotechnology have demonstrated different fabrication processes for cylindrical bioprobe electrodes with diameters of less than 1 μm [6–8]. These and other nanobioprobes have enabled electrodes into cells for direct intracellular potential measurements [9] and DNA/biomolecules deliveries with sub-micro-scale spatial resolution [10]. A recent report has shown the feasibility for cellular probing applications by using a 100 nm in diameter carbon nanotube (CNT) and epoxy fixture for cellular studies [11]. CNT has been chosen in some of these previous studies due to its small diameter, mechanical robustness (large Young's modulus of 1.25 TPa for single walled CNT [12] and ~950 GPa for multiwalled CNT (MWCNT) [13], and high tensile strength [13]) and high electrical conductivity [14]. For the possible applications in electrical cellular probing, it is necessary to encapsulate the conductive-CNT with a biocompatible insulator and expose its tip for the electrical functionality [15]. Here we propose and demonstrate a process to construct such nanoprobe, based on the core–shell nanostructure of CNT/biocompatible parylene-C insulator.

2. Nanoprobe fabrication and assembly

We have demonstrated that suspended MWCNTs can be constructed by direct synthesis and assembly in localized chemical vapor deposition [16–18] and that the number of assembled CNTs can be controlled via real-time electrical feedback control [19,20]. We use this methodology to facilitate a nanobioprobe based on the CNT ("core"), which is subsequently encapsulated with a biological insulator ("shell"), followed by cutting the probe at the distal end to expose CNT-tip (Fig. 1a). Fig. 1(b)–(d) shows the schematic diagram of the fabrication process sequence. The MWCNT is grown

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http://dx.doi.org/10.1016/j.sna.2012.08.025

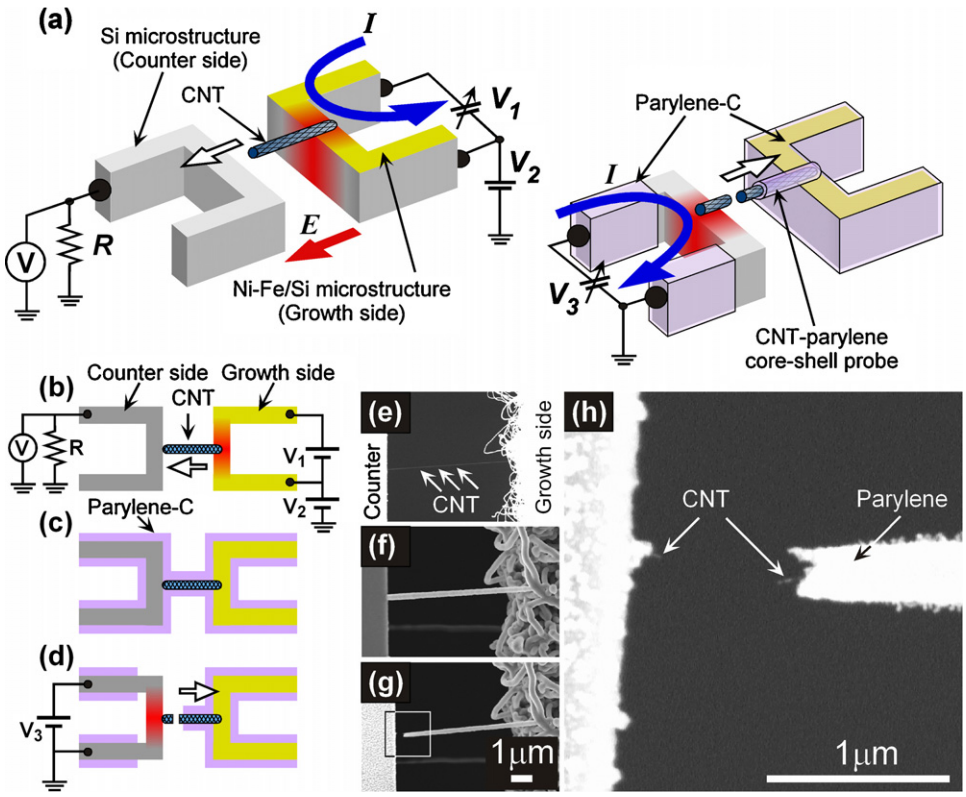

Fig. 1. Fabrication of an individual CNT/parylene core–shell nanoprobe electrode. (a) Schematically illustrated local CNT synthesis (left) and subsequent parylene-C encapsulation processes (right) using two silicon microstructures. (b) Schematic of the top-view of the CNT growth between two silicon structures by local (V_1) and electric-field-assisted (V_2) synthesis. The individual CNT is assembled via real-time electrical feedback control of the counter side (resistor, R and voltage meter, V), which configuration provides voltage signals when a CNT connection is made across the silicon structures. (c) Parylene-C deposition. (d) The simultaneous parylene removal from the CNT-tip and the CNT detachment by heating (V_3) the counter side silicon structure. (e) SEM image of as-grown single CNT between silicon structures (illustrated in schematic (b)), (f) parylene deposition around the CNT (schematic (c)), (g) the tip area exposed by heating of the counter side structure (schematic (d)), and (h) close-up-view of the exposed tip in image (g).

by the local synthesis process from the highly doped p-type silicon growth structure (resistivity of 1×10^{-2} Ωcm), which is coated with a 5-nm-thick nickel (Ni)–iron (Fe) layer as the catalyst. The process requires only a one mask process on a silicon-on-insulator (SOI) wafer. The shape of the microstructures (typically heaters with two contact areas) is defined by photolithography and etched by deep reactive-ion etching (DRIE). The oxide layer underneath the heaters is then removed in a time etching process which will preserve the oxide underneath the contact pad areas. The typical size of the silicon growth structure is 150 μm in length, 5 μm in width and 15 μm in thickness. With the applied voltage V_1 at about 7.5 V, the silicon structure is heated up by Joule heating (850–900 °C) [21]. A voltage V_2 of about 5 V is used for the local electric-field-assisted growth by providing a local electrical field to guide the growth of CNTs, achieving the self-assembly of a CNT between the two silicon structures (Fig. 1b) [19,20]. The synthesis is conducted in a room temperature vacuum chamber of 40 kPa with acetylene (C_2H_2) gas of 50 SCCM (SCCM denotes cubic centimeter per minute at STP). The number of CNTs getting synthesized and assembled across the two microstructures can be monitored and controlled by the electrical signals from the counter side electrode as shown in Fig. 1(b). During the CNT synthesis, once CNTs are made across the silicon microstructures, there are corresponding voltage jumps. By the number of voltage increases, we can determine the number of CNT connections [19,20]; here only one CNT can be assembled by stopping the heater after the first signal detected on the voltmeter V. The sidewall of the assembled CNT should entirely be covered with a good insulating thin layer, in order for potential biological applications including intracellular electrical measurements. Parylene-C is chosen as the insulator and applied in Fig. 1(c), because of its high electrical resistivity (~10^{16} Ωcm), biocompatibility with tissue and the capability of a highly conformal deposition at room temperature [22]. Finally, the parylene at the CNT-tip region is removed by heating the counter side silicon structure by applying the voltage V_3 of about 7.5 V at the counter electrode side as shown in Fig. 1(d), resulting in the evaporation of the parylene to expose the CNT-tip. This also causes the CNT to brake and detach from the silicon counter side due to the thermal contraction of the parylene around the CNT.

3. Experimental results and discussion

3.1. Assembled and tip exposed nanoprobe

Fig. 1(e)–(g) shows scanning electron microscope (SEM) images following the process sequence of Fig. 1(b)–(d) for building a CNT-based nanoprobe of about 7 μm in length as controlled by the gap distance between the two microstructures. Fig. 1(e) is an as-grown bridging CNT between the silicon structures (see Fig. 1b). Fig. 1(f) shows the fabrication result after the parylene deposition as all CNTs are uniformly encapsulated with parylene. Fig. 1(g) illustrates the exposed CNT-tip after heating the counter side silicon structure. It is believed that the detachment of the CNT from the counter side silicon structure is caused by the thermal contraction of the parylene which results in the melting and retraction of the parylene at the distal end of the CNT/parylene nanoprobe. Experimentally, the counter side silicon structure was heated for about 30 min, resulting in exposed CNT tip of about 100 nm in length, as shown in