Chemical Physics Letters 583 (2013) 87–91

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Thin micropatterned multi-walled carbon nanotube films for electrodes

Niina Halonen [a], Jani Mäklin [a], Anne-Riikka Rautio [a], Jarmo Kukkola [a], Antti Uusimäki [a], Geza Toth [a], Leela Mohana Reddy [b], Robert Vajtai [b], Pulickel M. Ajayan [b], Krisztian Kordas [a,*]

[a] Microelectronics and Materials Physics Laboratories, Department of Electrical Engineering, University of Oulu, P.O. Box 4500, FI-90014 Oulu, Finland
[b] Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005, USA

ARTICLE INFO

Article history:
Received 15 June 2013
In final form 20 July 2013
Available online 25 July 2013

ABSTRACT

Micropatterned electrodes based on thin multi-walled carbon nanotube films are grown by catalytic chemical vapour deposition on lithographically defined quartz and Inconel alloy substrates. The electrical contact at the interface between the root of the nanotube arrays and the thin Ti hardmask layer on the quartz surface is found to be poor disabling proper capacitive characteristics. On the other hand, nanotube-Inconel electrodes show low series resistance and good electric double layer capacitor operation close to that of ideal devices. Patterning of the electrodes enhances both specific capacitance and power in reference to non-patterned bulk carbon nanotube film electrodes.

1. Introduction

Carbon nanotubes are considered as promising materials in electronics [1,2] and in devices related to renewable energy solutions such as dye solar cells [3–8] and supercapacitors [9–12]. However, exploiting the unique properties of CNTs (electrical conductivity, porous structure, flexibility, etc.) requires their immobilization on various substrates in a controlled manner either by deposition [13–15], transfer [16–21] or by direct synthesis [22–24] with well-defined structure and geometry. In electrical applications, the contact resistance at the substrate-CNT interface [2,17,25], mechanical robustness and integrity [17,26] as well as charging/discharging behavior of the devices [9–12] are among the most important parameters to be taken into account.

Catalytic chemical vapor deposition (CCVD) is an appealing growth method due to scalability, high yield, purity, good control on nanotube dimensions and also because of its compatibility with lithography techniques [27–29]. A further advantage of CCVD is a relatively simple control of CNT film thickness. Fine tuning of growth time and synthesis temperature allows the selection of any expected film thickness (from a few micrometers up to a few centimeters) thus no post-processing such as chemical mechanical polishing [25] is needed e.g. to obtain planar structures in multilayer devices. Nanotubes directly synthesized on conductive surfaces are probably the most attractive solutions for electrode applications in solar and fuel cells, capacitors as well as in chemical and biochemical sensors. Bulk MWCNT forests grown on Inconel [10], Inconel/Al [11] and Cu [30] surfaces were demonstrated earlier as feasible structures particularly in supercapacitor devices with corresponding specific capacitances in the range of ~20–80 F/g. However, electrodes made on insulating substrates might be also interesting from the point of view of integration and packaging in electrical devices. In such a case, the challenge is to make electrical interfacing between the insulating substrate and the conductive electrode material.

Here, we report a simple method for controlled and selective growth of short MWCNT forests on micropatterned Inconel and quartz sheets with titanium hardmask by combining photolithography and CCVD processes. The contact resistance and specific capacitance of the films are evaluated, and the advantages as well as limitations of the structures to be used in electrode applications for electric double layer capacitors are discussed.

2. Experimental section

Nickel–chromium–iron alloy foils (Inconel® 600, thickness of 75 μm and composition of Ni 72%, Cr 16% and Fe 8% from Goodfellow) and double side polished single crystal quartz wafers (thickness of 500 μm, obtained from Silicon Quest Int. Inc.) were used as substrates. A thin, ~50 nm Ti film was deposited on both types of substrates by RF sputtering (210 W, deposition rate ~1 Å/s) and micropatterned with lift-off (photoresist LOR2A, Microchem Corp., and AZ1512HS, Microchemicals GmbH) resulting in a grid of Ti hardmask. The as-made wafers and foils were then laser cut to smaller pieces having size of 20 × 16 mm^2. The grid structure itself has 100 × 100 μm^2 openings with 50 μm spacing over total area of 14 × 6 mm^2 on each patterned sample.

The substrates were washed with acetone in ultrasonic bath prior the nanotube growth and then placed in a horizontal tube reactor which was pumped down to ~1 Torr and heated up to 770 °C. The Ar carrier gas flow rate was set to 40 mL/min and the

* Corresponding author. Fax: +358 8 553 2728.
E-mail address: lapy@ee.oulu.fi (K. Kordas).

0009-2614/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cplett.2013.07.047

ferrocene-xylene precursor (20 g ferrocene in 1000 mL xylene) was introduced to the reactor with a rate of 0.1 mL/min [29]. The reaction times were 4, 6, 8, 10 and 12 min for the quartz and 10, 15 and 17 min for the Inconel samples.

The quality of the films and selectivity of growth were evaluated by field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus), transmission electron microscopy (EFTEM, Leo 912 Omega) and by Raman spectroscopy (Horiba Jobin–Yvon LabRAM HR800 UV–vis μ-Raman at $\lambda = 488$ nm). Thickness of the films (and thus the approximate length of CNTs) was determined from electron and optical micrographs (latter ones by an Olympus BX51 instrument).

To estimate the total series resistance of the MWCNT-Inconel and MWCNT-quartz electrodes a sandwiched structure was constructed by placing a piece of blank Inconel sheet on top of the grown MWCNT electrode structure and pressing it with the probe needle with an average force of ~50 mN. The compressive force produced by the probe needle was measured in parallel experiments by probing the structures on the tray of a balance. The contact resistance between the growth substrates and the probe needle was evaluated by measuring resistance vs. conductor length on narrow (2 mm) substrate pieces using a Keithley 2636A System SourceMeter driven by a LabView code. The measured probe contact resistance values were 0.7 Ω, 0.6 Ω and 210 Ω for the Inconel, Inconel-Ti and quartz-Ti substrates, respectively.

Electrochemical capacitors were built from MWCNT-Inconel as well as from MWCNT-quartz electrodes by applying a bulk MWCNT forest (grown on Inconel) as counter electrode and 3 layers of filter papers (Whatman 1, Cat No 1001-047) as spacers. For electrolyte, a mixture of aqueous KOH (6 mol/L) and isopropyl alcohol (volume ratio of 4:1) was used. The role of isopropanol was to improve wetting of the nanotube electrodes. Finally, the cell was fixed with a clamp. To determine the capacitance, cyclic voltammetry measurements were carried out with voltage sweep rates of 0.05, 0.1, 0.25, 0.5 and 1.0 V/s using a potentiostat (Princeton Applied Research VersaSTAT 3). Transient current measurements were performed by powering the capacitor devices and a 3 Ω value resistor connected in series using a signal generator (Agilent 33120A), while measuring the potential drop on the resistor by an oscilloscope (Tektronix TPS 2024B).

3. Results and discussion

Raman and TEM analyses of the samples show that well graphitized nanotubes were grown on both types of substrates (Figure 1). The relatively high Raman intensities of the in-plane sp^2 carbon vibrations (at ~1586 cm^{-1}) compared to the intensities caused by sp^3 hybridized carbons (at ~1360 cm^{-1}) indicate low defect densities in the lattice. TEM micrographs of the samples show hollow tubular structures that are rather straight (grown on quartz) or slightly curved (grown on Inconel). The diameters of the nanotubes are between ~20 and ~100 nm.

As the surface roughness of the substrates has a considerable effect on the alignment of the nanotubes [31], the differences in the alignment between the nanotube films grown on the very smooth polished quartz and the rough Inconel surfaces are reasonable (Figure 2). In fact, the nanotubes grown on Inconel are somewhat curly and tangled, which explains why the thickness values of films on quartz are larger under similar growth conditions. In addition, dissolution and diffusion of iron catalyst into the metal substrate (in contrast to quartz, which is typically used as a diffusion barrier) [28,32,33] can have also influence on the CNT growth rate. The selectivity of growth compared to the substrates and the Ti hardmasks are excellent. This is due to the catalyst poisoning effect of titanium, in which Fe can diffuse very efficiently at 770 °C while intermetallic compounds and solid solutions of Fe and Ti form [34–37]. Titanium is a convenient and practical choice as hardmask since it is relatively cheap, its thin films are commonly applied in Si fabrication (as adhesion promoter), and has high corrosion resistance, which is important in applications using various electrolytes [38].

The total series resistances measured for the Inconel and quartz based electrodes are of very different magnitudes and show different trends as a function of synthesis times. Although the current–voltage characteristics of each measured sample show ohmic behavior, the total electrode resistance for the MWCNT-quartz structures (in the kΩ range) decreases as the nanotube film thickness increases; meanwhile for the MWCNT-Inconel electrodes, the total resistance is quite low (in scale of ~20 Ω) and appears to be independent on the film thickness (Figure 3).

The unexpected dependencies of the total series resistances are obviously related to the contacts between the nanotubes and substrates, and somewhat to the entanglement and percolation of the nanotubes themselves, as there are three different kinds of electrical contact areas between the nanotubes and metals. (*i*) On quartz, the conduction path is represented by the titanium grid and nanotubes growing from the openings leaving the only effective contact area on the perimeter of the opening areas of the hardmask. (*ii*) On Inconel, the electrical contact comes from the titanium grid as in the case of quartz but in addition also from the bottom of the MWCNT square since it directly grows on a metal surface. The considerably low resistance values measured for these samples indicate that this latter path is playing the main role in conduction. (*iii*) The top electrode or counter electrode contact is similar for both quartz and Inconel (blank Inconel placed on the top of the CNTs) thus should have no influence on the results or at least is not expected to cause any differences among different samples.

A plausible reason for the decreasing tendency of total resistance with increasing growth time for the MWCNT-quartz electrode is the increasing density of forests. Films that are densely populated with nanotubes have inherently more nanotube-nanotube and nanotube-Ti contacts thus better conduction. In the case of Inconel-MWCNT electrodes, the low total resistance and its independence on the film thickness suggests an excellent contact

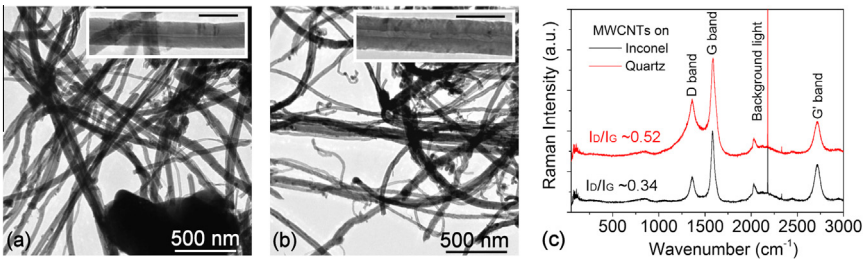

Figure 1. TEM images of MWCNTs grown on (a) quartz and (b) Inconel. The scale bars in insets denote 100 nm. (c) Raman spectra of corresponding samples. Note, the peaks at ~2080 and 2130 cm^{-1} are artifacts caused by stray light in the laboratory.