Integrating vertically aligned carbon nanotubes on micromechanical structures

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We present preliminary results on a microfabrication approach to enable the integration of high yield, uniform, and preferential growth of vertically aligned carbon nanotubes (VACNTs) on low-stress micromechanical structures using a combination of “electron-beam crosslinked” poly(methylmethacrylate) surface nanomachining and direct current plasma enhanced chemical vapor deposition of electric-field-aligned carbon nanotubes. In this article, selective placement of high yield and uniform VACNTs on a partially suspended Ni/SiO$_2$/Ti microstructure has been demonstrated. © 2003 American Vacuum Society. [DOI: 10.1116/1.1591743]

I. INTRODUCTION

It is desirable to incorporate carbon nanotubes (CNTs) into microelectromechanical systems (MEMS)/nanoelectromechanical systems (NEMS) for various fundamental research and potentially technological applications. The coupling of the micron-scale mechanical component, which typically exhibit nanometer-scale translational precision with the remarkable structural, electrical, and mechanical properties of CNTs will greatly enhance the performance of MEMS as sensors in mechanical, electrochemical, biological, or electronic applications.\textsuperscript{1}

Since the discovery\textsuperscript{2} that vertically aligned CNTs (VACNTs) could be grown using plasma enhanced chemical vapor deposition (PECVD), CNTs have emerged as highly promising field emitters in applications such as scanning probes, displays, microwave amplifiers, and parallel electron-beam lithography.\textsuperscript{3} Attempts to integrate CNTs into electronic devices and electromechanical systems include patterned growth of CNTs to bridge predefined molybdenum electrodes,\textsuperscript{4} placement of a CNT onto a MEMS structure using a hybrid atomic force microscope/scanning electron microscope (SEM) system,\textsuperscript{1} demonstration of wafer scale production of CNT scanning probe tips by selectively placing catalysts on prefabricated Si tips,\textsuperscript{5} and recently, the fabrication of an on-chip vacuum microtube using CNT field emitters employing MEMS design and fabrication principles.\textsuperscript{6} Clearly, a reliable, high yield, and precise fabrication process is needed to realize the integration of MEMS and CNTs, which offers exceptional flexibility in designing sophisticated electromechanical devices.

In this article, we demonstrate how the combination of crosslinked poly(methylmethacrylate) (PMMA) surface nanomachining,\textsuperscript{7} and the selective post-MEMS processing growth of high yield and uniform arrays of VACNTs\textsuperscript{3,8,9} using direct current-PECVD (dc-PECVD), can be used to integrate CNTs with low-stress micromechanical components. With the appropriate ratio of deposition gas acetylene (C$_2$H$_2$) to etching gas ammonia (NH$_3$) and other parameters including the Ni catalyst layer thickness, bias voltage, deposition temperature, and pressure during the VACNTs growth process, a partially free-standing structure with integrated uniform and high yield VACNTs is demonstrated. This approach affords VACNT micromechanical devices without any postgrowth processing, which may cause damage to the nanotubes during microfabrication, and will find applications in NEMS.

II. EXPERIMENT AND DISCUSSION

The crosslinked PMMA surface nanomachining technique [Figs. 1(a)–1(e)], which exploits the quantifiable relationship between electron-beam irradiation levels and the solubility of PMMA in acetone, is used in fabricating the sacrificial layer, upon which the structural layer would be laid. The crosslinking process to define the sacrificial layers can be performed in the same process step with the electron-beam lithography of the mechanical structures. In other words, by controlling the amount of electron dose that the exposed regions of the PMMA receive, one can use the PMMA resist as a positive or negative resist in a single run. We can also choose to define the sacrificial layers first with electron-beam lithography, and subsequently use optical lithography to define other patterns. We have previously demonstrated the modulation of the thickness of the remaining crosslinked PMMA resist as a function of electron dose by changing the spatial extent in which the energy from the electrons is absorbed by the resist.\textsuperscript{7} Linearly graded edges of the sacrificial layer can be patterned by electron beam by exposing different doses at the edge of the sacrificial layer, followed by reflow [Fig. 1(e)].
This enables the thermally evaporated (nonconformal deposition) microstructures to easily climb over the sacrificial layers [Fig. 2].

The process schematic for the fabrication of VACNTs on our suspended Ni/SiO₂/Ti cross structures are shown in Fig. 1. We start with a (100) antimony doped n⁺⁺-Si wafer substrate (cleaned with hydrofluoric acid) with nominal resistivities measuring between 3–10 ohm cm. After cleaning, two layers of PMMA are spun on one after the other, both at 6000 rpm for 50s. The first spun-on layer is baked for 10 min at the curing temperature of 150 °C, and the subsequent one for 30 min immediately after. We then selectively crosslink an array of 50 μm × 50 μm squares onto the bilayer PMMA by electron lithography with a 25 kV accelerating voltage, a current of 300 pA, and a dose of 120 C/m² using a modified Hitachi S800 SEM [Fig. 1(a)]. After dissolving the unexposed PMMA in acetone, crosslinked PMMA square grids remain behind [Fig. 1(b)]. The high dose causes the PMMA molecules to crosslink with each other to form a network of larger molecules and is, therefore, resistant to acetone. After exposure, the thickness of the PMMA reduces by around 50%, possibly due to the evaporation of low volatile products which are formed during irradiation. After exposure, the thickness of the PMMA reduces by around 50%, possibly due to the evaporation of low volatile products which are formed during irradiation. The substrate is then loaded into the CNT deposition chamber and evacuated

ment of 30 min at 60 °C and 5 min at 150 °C is performed [Fig. 1(c)]. Reflowing reduces the thickness further by 5–8 nm. We then proceed with the subsequent patterning of the cross structures using optical lithography, which is aligned over the crosslinked PMMA sacrificial layers. The transparent nature of the thin PMMA sacrificial layers allow the alignment during the optical lithography step to be more easily performed. A 180 nm thick layer of Ti is thermally evaporated followed by magnetron sputter-deposited 8 nm SiO₂ film and 3.5 nm Ni film with vacuum breaking in between the Ti and SiO₂ steps. Standard lift off in acetone follows with the resulting structure shown in Fig. 1(d). In the final step before CNT deposition, the Ni/SiO₂/Ti structures are dry released using an isotropic oxygen plasma for 55 s as depicted in Fig. 1(e). This is done using a microwave plasma stripper with O₂ gas flow at 100 sccm.

In short, Figs. 1(a)–1(e) show the schematic of the crosslinked PMMA surface nanomachining method used for the fabrication of the floating cross structure while Fig. 1(f) shows the schematic for the deposition of the VACNTs. Figure 2 shows SEM micrographs of the cross structure, which is suspended about 200 nm above the substrate upon dry release. The crosslinked PMMA appears like a dark rectangle because, being an insulating material, it will therefore have a low emission of secondary electrons. This is in contrast to conducting materials, which appear bright. The substrate is then loaded into the CNT deposition chamber and evacuated...
to a base pressure of $5 \times 10^{-2}$ mbar using a rotary pump. The substrate is heated up to 650 °C in NH$_3$ and the plasma initiated by applying a dc bias of $-600$ V to the cathode. The dc discharge between the cathode (sample) and the anode (grounded gas inlet 1/4-in.-diam steel pipe) was initiated using an AE MDX 1 kW supply with the anode–cathode distance around 3 cm. After that, C$_2$H$_2$ is introduced to form a 25% C$_2$H$_2$ in NH$_3$ mixture and the deposition is performed for 15 min at a total pressure of 4 mbar. The depositions were carried out in a stable discharge. At this temperature (650 °C), the thin Ni film catalyst coalesced into nanoclusters [Fig. 1(f)], which then seeded the growth of the CNTs via a weak-catalyst–support interaction (tip-growth mechanism). The carbonaceous gas decomposes on the surface of the catalyst particle, the carbon diffuses across the particle under an activity gradient, and the carbon then precipitates out on the opposite side. The thin SiO$_2$ film serves as a diffusion barrier to prevent Ni from alloying with Ti, which would result in lesser Ni catalytic material. Also, Ti is selected as the main structural material to prevent excessive diffusion of amorphous carbon into the Ni during the deposition of VACNTs, which causes undesirable volume expansion. The electric field in the plasma sheath guides the nanotubes vertically during growth. A conducting substrate (highly doped Si) is chosen to prevent arcing between the substrate and the Ti cross structure during the generation of the plasma. A more detailed description of the deposition process of VACNTs can be found in Refs. 8 and 9.

After growth, the sample is observed with a Philips XL30 SEM and we find the Ti structure partially free standing. Only this time, it is covered with a dense and uniform “forest” of VACNTs [Figs. 3(a) and 3(b)], highly selective to areas which contained the catalyst. However, we notice a slight buckle in the middle of the cross structure [Fig. 3(a)] suggesting reduced support at the edges. Further investigations reveal discontinuous tears at the edge of the supports, particularly at the corners. This may result from differential stress generated between the substrate and the Ti structure due to the high temperatures (650 °C) incurred during VACNTs deposition. The shear forces resulting from this mismatch are the most likely cause of the tears at the edges. The support films are thinnest at the step-up edges due to the nature of thermal evaporation.

Using the transmission electron microscope, a Ni catalyst was observed at the tip of the tubular and mostly hollow VACNT, which contained 20–40 well crystallized graphene walls parallel to its axis (multiwalled VACNTs), suggesting...
excellent conductivity [inset of Fig. 3(b)]. The fact that the catalyst particle remains at the tip of the growing tube suggests the basic tip-growth mechanism described earlier. The structures produced using the crosslinked PMMA surface nanomachining method had remarkably low stress and are not significantly affected by the high sintering temperatures even up to 650 °C [Fig. 3(b)]. This has been observed previously up to 450 °C for 30 min for a surface nanomachined 150 nm thick Ni/Au cantilever. Because of the extremely low Young’s modulus of crosslinked PMMA (nominal PMMA has a modulus of around 5 GPa) as compared to other sacrificial materials, such as SiO2 or metals, it absorbs most of the stress in the deposited mechanical structures by deforming.

III. CONCLUSION

In conclusion, we demonstrate the feasibility of integrating VACNTs selectively on low-stress post-MEMS processed microstructures. Further work is necessary to solve issues of reliability in this integration process, primarily due to differential stress generated during the growth of high-temperature VACNTs. Advances in high reliability and high yield and selective placement of CNTs on MEMS will surely facilitate the combination of the flexibility in MEMS design with the unique properties of CNTs, thus adding more functionality to devices incorporating nanotube architectures.

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