INTRODUCTION

Carbon nanotubes (CNTs) are long molecules having exceptional properties: several times the strength of steel at one-fifth the density, at least five times the thermal conductivity of copper, and high current-carrying capacity with short-range ballistic conductance \[1\]. These fundamental properties, along with application-oriented characteristics such as high surface area, diverse capabilities for chemical modification and functionalization, and strong interactions with polymers and composite host materials, are generating broad demand for control of CNT growth as a manufacturing process spanning from the nano- to macro-scales.

In the widely-developed method of catalytic chemical vapor deposition (CVD), CNTs form by organization of carbon on a nanoscale metal catalyst particle in a high-temperature hydrocarbon atmosphere (Fig. 1). The carbon dissociates from the source compound and adds to the CNT through surface and/or bulk diffusion at the catalyst. When the catalyst particles are arranged on a substrate, CNT-CNT or CNT-substrate interactions in addition to the arrangement and activity of the catalytic sites determine if CNTs grow in an isolated, tangled, or aligned configuration. For example, isolated SWNTs can be grown to several millimeters or centimeters when suspended during growth by a gas flow; however, the density of catalytic sites must be very low to prevent entanglement between CNTs. At a high catalyst density and CNT growth rate, a vertically aligned (VA) growth mode is typical whereby the CNTs self-orient perpendicular to the substrate surface due to initial crowding and continue to grow upward in this direction.

At all stages of CNT growth, chemical and mechanical interactions are highly coupled. These interactions must be managed in order control the position and orientation of CNTs growing on substrates, from single-CNT applications such as emitters and transistors, to many-CNT applications such as films, microstructures, and filters.

Here, we present a suite of techniques for making CNT assemblies with hierarchical two-dimensional and three-dimensional organization: conformal films of tangled single-walled CNTs are grown on silicon microstructures, millimeter-thick films and microstructures of aligned multi-wall CNTs (MWNTs) are grown on flat silicon substrates, large-area CNT micropatterns are fabricated by post-growth dry embossing of aligned CNT films, and 3D forms of CNTs are directly grown to take the shape of microfabricated template. These growth processes use catalyst thin-films deposited by electron beam evaporation and atmospheric-pressure thermal CVD, which is scalable from academic-level prototyping to industrial-level manufacturing.

MATERIALS AND METHODS

To enable growth of CNTs on silicon substrates, a supported catalyst film is first deposited by electron beam evaporation on bare 6” wafers (100-orientation, Silicon Quest International). The catalyst metal (Mo/Fe for SWNTs and Fe for MWNTs, details in later sections) is supported on a thin layer of Al2O3 (10-20 nm) which significantly enhances the yield and quality of CNT growth from the metal catalyst, owing to strong dispersion effects which limit agglomeration of Fe clusters on the Al2O3 surface \[2\], the nature of metal–support interactions in promoting electron transfer between the catalyst and the support \[3\], and other factors. The film topography evolves and the metal coarsens into nanoparticles when the substrate is heated to the growth temperature.

CNT growth is performed in a single-zone atmospheric pressure quartz tube furnace (Lindberg), having a tube inside diameter of 22 mm and a 30 cm long heated zone \[4\]. Flows of argon (Ar, 99.999%, Airgas), methane (CH4, 99.995%, BOC), ethylene (C2H4, 99.5%, Airgas), and hydrogen (H2, 99.999%, BOC) are metered using manual needle valve rotameters (Matheson Tri-Gas and Gilmont Instruments). After loading the sample in the tube, the furnace is flushed to displace atmospheric air. Next, the furnace temperature is ramped linearly to the setpoint temperature for 10-30 min, stabilized for 10 min, and then the reactant gases are intro-
duced for the growth period. Afterwards, the carrier gas is maintained for 10 min to displace the growth gases from the tube and then the flow is reduced to a trickle while the furnace cools.

CONFORMAL CNT FILMS GROWN DIRECTLY ON BULK MICROSTRUCTURES

Films of high-quality tangled SWNTs are grown from Mo/Fe/Al₂O₃ catalyst layer which is directly deposited on flat silicon substrates and various bulk-micromachined topographies. Typically, the furnace is heated while maintaining Ar atmosphere inside the tube, and then a mixture of 320/80 sccm CH₄/H₂ is introduced for a growth period of 15 minutes (although it was later found that growth completes within the first minute of reaction).

Despite oblique-angle effects on the thickness of the catalyst layer induced by directionality of electron beam evaporation, we achieve conformal and uniform growth of CNT films (Fig. 2) on vertical sidewalls of silicon posts fabricated by deep-reactive ion etching and on slanted surfaces fabricated by etching in aqueous potassium hydroxide (KOH) [5]. Film characterization by resonant Raman spectroscopy quantitatively demonstrates that the highest yield is obtained at a reaction temperature of 825 °C, and that the CNTs have a high “quality” factor as indicated by a G/D peak intensity ratio exceeding 20. Although uniform, CNT growth on the DRIE-etched vertical walls is less dense than on slanted surfaces. Topography-driven effects on particle size, and therefore on catalytic activity, will vary widely among different catalyst and CVD methods. Further, we demonstrate growth of aligned carbon nanofibres (CNFs) by plasma-enhanced CVD on silicon “micrograss”, using a colloidal solution of Co nanoparticles as the catalyst [6].

We expect that this process can be extended to grow a wide variety of nanostructures on microstructures having arbitrary three-dimensional topography, extending the fabrication capability for hierarchically microstructured and nanostructured substrates, for applications such as super-hydrophobic surfaces and cell growth. For example, leaves of lotus and rice plants are superhydrophobic because of the combined effect of microscale and nanoscale roughness [7].

Fig.2 Conformal films of tangled SWNTs on (a) vertical sidewall of DRIE-etched silicon post; (b) sloped sidewall of KOH-etched silicon pyramid inside microchannel.

MILLIMETER-LONG SELF-ALIGNED CNTS

Using ethylene (C₂H₄), a higher-activity carbon source, and a catalyst film of 1 nm Fe supported on 10 nm Al₂O₃, vertically-aligned CNTs (VA-CNTs) grow to millimeter-scale length (film thickness) while the catalyst particles remain rooted at the substrate [8]. In this process, the tube furnace is typically heated to a reaction temperature of 750 °C under a flow of 500/100 sccm H₂/Ar or H₂/He, and then 100 sccm C₂H₄ is added to the flow. High-resolution TEM examination indicates that these CNTs typically have 5-7 concentric and parallel walls (MWNTs), with an outer diameter of ≈10 nm.

Full-coverage “forests” grow from a uniform catalyst film, while microstructures of aligned CNTs are grown by lithographically patterning the catalyst film by lift-off of image-reversal photoresist (Fig. 3). The lithographic patterning defines the 2D cross-section and the CNTs grow upward to “extrude” this shape. Cross-sectional dimensions ranging from 3 µm to millimeters and aspect ratios up to 100 are achieved, and the growth rate depends on the local areal density of catalyst, which is analogous to loading effects in plasma etching processes [9].

In the tube furnace, a forest typically grows to 1 mm thickness in 15 minutes, with an areal density of approximately 1.5 × 10¹⁰ CNTs/cm². Further, growth on a resistively-heated silicon substrate enables independent control of thermal activation of the reactant, and we have tuned this technique to...
grow films to 4 mm thickness in 30 minutes [10,11]. We are using this new apparatus to optically monitor the reaction progress, seeking to understand the limiting aspects of VA-CNT film nucleation and growth.

Owing to poor adhesion to the growth substrate, the films and microstructures can be physically or chemically delaminated and transferred to other substrates including metal foils and plastics, enabling mechanically robust post-growth interconnection with thermal and electrical contact to large numbers of CNTs in parallel [12].

**DRY EMBOSSING OF CNT FORESTS INTO MICROPATTERNS**

The VA-CNT films can be embossed into micropatterns by compressing the film using a silicon “stamp” after growth. The stamp is fabricated by DRIE, and the CNT structures are embossed by placing the CNT film in contact with the silicon mold and compressing the sandwich in an Instron loading machine equipped with a load cell and force-feedback control. The target force is approached by specifying a displacement rate of 5 μm/s (of the mold relative to the CNT substrate). The force is removed as soon as the target force is reached. Based on a 10% areal density of embossing features on the stamp, the estimated embossing pressure is 0.2-0.5 MPa.

![Silicon stamp](image)

**Silicon stamp**

**VA-MWNT forest**

**Silicon substrate**

![0.2–0.5 MPa](image)

**Fig.4 Process for dry embossing of VA-CNT films: (a) align stamp in proximity to CNT substrate; (b) emboss film, applying effective average pressure of 0.2-0.5 MPa to feature areas; (c) remove stamp, leaving features embossed in CNT film.**

A range of embossed pattern sizes, arrangements, and depths have been fabricated during our initial experiments (Fig. 5), including channel-like indentations with 100 μm width and pitch, and arrays of cylindrical indentations with 10 μm diameter and pitch. A stamp having a slightly tapered sidewall gives a smooth sidewall profile in the embossed film. Further work is studying the mechanical and electrical properties of the embossed films, where the CNTs are locally compressed into high-density arrangements.

**“GROW-MOLDING”: DIRECT GROWTH OF CNTS INTO 3D MICROSTRUCTURED FORMS**

Finally, in addition to the post-growth embossing technique, we directly grow 3D-shaped CNT microstructures by mechanical confinement during growth [13]. This process was motivated after we demonstrated that CNT growth can exert a significant force; and control of this force controls the growth rate of the film while degrading the film microstructure and the structural quality of the CNTs.

Here, the catalyst-coated substrate is clamped against a microfabricated silicon template using a quartz fixture, and the assembly is preloaded using Al₂O₃ bolts and high-temperature spring washers and placed in the center of the tube furnace. The template pattern is etched on the non-polished side of the wafer to prevent bonding of the template to the growth substrate during the shape transfer process. After the growth and cooling sequence, the fixture is disassembled and the template is cleanly removed from the growth substrate, leaving free-standing structures (Fig. 6).
Fig. 6  “Grow-molding” of 3D CNT microstructures: (a) fabrication sequence where template is cleanly delaminated after growth; (b) 100 μm wide CNT mesas; (c) cross-section of CNT mesa having trapezoidal cross-section, where top region is aligned and bottom region is disordered indicating mechanically-driven evolution of structure during growth.

This new technique is a catalytic analogue to micromolding of polymer and metal microstructures. It surpasses traditional methods for growing CNT microstructures using two-dimensional catalyst patterns on substrates, allowing fabrication of arbitrary shapes having sloped and/or curved surfaces and nonorthogonal corners, and does not require patterning of the catalyst.

In our initial experiments, concave corners of the microform (convex corners of the template) are sharper than convex corners and yet are rounded to 5-10 μm. The finest replication we have attempted so far is a 5 μm wide KOH-etched microchannel with triangular cross-section, and the apex of such a microform is rounded to ≈2 μm. The accuracy and resolution of shape replication depend on the density of CNTs growing from the substrate and on the gas flow through the template. With appropriate and uniform gas flow, such as by using a porous template, these structures could be fabricated over large substrate areas. Further, application of an electric field between the growth substrate and template may help guide the CNTs into especially narrow template features and sharp corners, achieving shape transfer at a significantly higher resolution than demonstrated here.

ACKNOWLEDGEMENTS
This work was funded by the National Science Foundation (DMI-0521985) and the MIT Deshpande Center for Technological Innovation. AJH is grateful for the support of a graduate fellowship from the Fannie and John Hertz Foundation. Thanks to Y.-M. Chiang of the MIT Department of Materials Science and Engineering for sharing his laboratory space for our CNT growth facilities, and to Matthew Dirckx of the MIT Laboratory for Manufacturing and Productivity for assistance with embossing.

REFERENCES