Single-walled carbon nanotubes with small diameter, controlled density and defined locations produced from catalyst-containing polymer films

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ABSTRACT

We report CVD growth of single-walled carbon nanotubes (CNTs) using catalyst nanoparticles derived from the catalyst-containing polymers PMGI, PS-b-PVP, and PS-b-PFEEMS. Polymeric materials have in general two main advantages in this application: the number of catalyst atoms incorporated in the polymers can be well controlled, and the polymers serve as carriers to distribute the catalyst nanoparticles uniformly across a wafer during spin-coating. CNTs grown from these catalyst nanoparticles are uniformly distributed on the macroscopic scale and have very high quality with a small number of defects and dangling bonds. The typical diameters of these CNTs are less than 2 nm. In some polymers, inorganic elements may be added so that the resultant catalyst nanoparticles are matrixed in an inorganic nanostructure. CNTs grown in this case have diameters of 1 nm or less. Subtractive and additive patterning schemes have been developed to lithographically pattern catalyst-containing polymer films. The catalysts produced from the patterned catalyst-containing polymer film allow spatially selective growth of CNTs at the micron and submicron scale. Utilizing the excellent film-forming capability of a polymer material, the catalyst particles can be uniformly distributed across a wafer by conventional spin-coating. As a result, CNT networks with uniform density have been produced. The simultaneous control of catalyst particles at the nano, micro, and macro levels enables the growth of CNTs with great control in diameter, locations, and density.

Keywords: carbon nanotube, carbon nanotube network, catalyst-containing polymer, nanocatalyst, block copolymer, biosensor, CNTFET, solid-state self-assembly

1 INTRODUCTION

CNTs offer great technological promise due to their remarkable electrical, thermal, and mechanical properties. A lot of researches have been devoted to understand their fundamental properties and develop products that utilize their novel attributes. For example, CNTs are being exploited as field-emitter tips in displays, as transistors, as interconnect and memory elements in integrated circuits, as scan tips for atomic force microscopy, and as sensor elements for chemical and biological sensing. A major obstacle to commercialization is the lack of a manufacturable fabrication method to produce CNTs with controlled diameter and density at predefined locations.

In this paper, we report catalysts derived from polymeric precursors that offer great potential for controlling size and placement of CNTs at nano-, micro-, and macroscales. In these polymer-based approaches, we use a catalyst-containing polymer chain to control the number of catalyst atoms incorporated in each catalyst cluster, thus controlling the catalyst particle size. The non-metal-containing segment in a diblock copolymer determines the spacing between catalyst clusters, while the distance between catalysts in a random polymer can be tailored by dilution, thus enabling the nanoscale control of the size and the spacing of the resultant catalyst particles. We have developed both subtractive and additive schemes to lithographically pattern catalyst-containing polymer films. The catalysts produced from the patterned catalyst-containing polymer film allow spatially selective growth of CNTs at the micron and submicron scale. Utilizing the excellent film-forming capability of a polymer material, the catalyst particles can be uniformly distributed across a wafer by conventional spin-coating. As a result, CNT networks with uniform density have been produced. The simultaneous control of catalyst particles at the nano, micro, and macro levels enables the growth of CNTs with great control in diameter, locations, and density.

Preliminary MALDI-MS (Matrix Assisted Laser Desorption Ionization-Mass Spectrometry) studies on uniformly distributed CNT surfaces indicate that we can positively identify bovine serum albumin (BSA) at 500 attomoles. Patterned CNT patches with controlled and reproducible density make the fabrication of CNT-based biological sensors with multiplexed detection capability possible. The combination of patterning capability of the catalyst-containing polymer films and the ability to control catalyst size and density provide a practical way to manufacture CNT-based electronic devices.

2. EXPERIMENTS AND RESULTS

In this study, we employed both random and diblock copolymers as templates to control the number of catalysts incorporated onto polymer chains. Spin-coating
was used to distribute catalyst-containing polymer chains evenly on silicon substrates coated with 500 nm thermal silicon oxides. Either thermal or solvent vapor anneal was used to induce the order and to generate catalyst nanoparticles or catalyst-containing silicon nanostructures with controlled size and spacing. When solvent vapor anneal was used, additional thermal treatment was applied to remove the solvent. Chemical vapor deposition was used to grow CNTs selectively on catalyst locations as described previously.7 The substrates with and without patterning were heated to 900°C under H₂. Subsequently either a mixture of CH₄ and C₂H₄ or pure CH₄ was added to the gas flow to initiate CNT growth. The growth time was 10 min for unpatterned film and 5 min for patterned film.

2.1. IRON-COMPLEXED POLYMER

The random polymer polymethylglutarimide (PMGI) has multiple ligand sites on its polymer chain. Transition metals such as iron have energetically accessible d orbitals. This partially filled outer electronic orbital structure provides a number of reaction pathways. To satisfy the 18 electron or inert gas rule, electron rich ligands complex with the empty orbitals of iron. The proposed coordination reaction product with iron species is shown in Figure 1a. In our studies, we use iron nitrate as the iron source, which is complexed with PMGI. After spin-coating and thermal annealing of the iron-complexed polymer, UV-ozone was used to remove all the organic components. Figure 1a depicts the AFM image of iron oxide nanoparticles showing a range of diameters between 1.5nm and 2.5nm and a mean diameter of 1.8 nm.

![AFM image of iron oxide particles (2um by 2um scan); 1b, SEM image of CNTs](image)

Figure 1b. Raman analysis at the radial breathing mode (RBM) and AFM height measurements indicate that the majority of tubes have diameters between 1.2 nm and 1.8 nm. Raman analysis at the high-frequency mode indicates that the numbers of defects are minimal. Iron-complexed PMGI is soluble in aqueous base solutions used to develop photoresist. Employing a bilayer structure where iron-complexed PMGI is the underlayer and photoresist is the top layer, patterned PMGI has been produced in a single lithography step by overdevelopment to remove the iron-complexed PMGI in the exposed area. As a result, CNT patterns have been readily generated as demonstrated in Figure 2.

![SEM images of CNTs grown on lithographically defined catalyst derived from iron-complexed PMGI](image)

2.2. DIBLOCK COPOLYMER APPROACH

In the iron-complexed PMGI system, the distance between catalyst particles is related to dilution. Therefore, there is no mechanism to achieve periodic spacing between catalyst nanoparticles. The main attraction of a diblock copolymer system is that both size and spacing of catalysts can be simultaneously controlled. Diblock copolymers are comprised of two covalently linked, immiscible polymer segments that undergo self-assembly in the solid-state to afford well-defined arrays of nanostructures dictated by the polymer architecture and molecular weight. When the minority segment of a diblock copolymer contains metal such as iron that is used to catalyze CNT growth, a periodically ordered catalyst-containing polymeric thin film can be formed. After removal of all organic components, a periodic array of catalyst nanostructures is thus formed.
2.2.1 COMPLEXATION OF CATALYST COMPOUNDS WITH THE MINORITY SEGMENT

The empty d orbitals of transition metals such as iron, cobalt and molybdenum can be complexed with electron-rich pyridine units of polystyrene-b-polyvinylpyridine (PS-b-PVP). The proposed coordination reaction is shown in Figure 3. Annealing spin-coated thin films followed by UV-ozonation yields catalysts such as Fe, FeMo, Co, CoMo with controlled size and spacing. Figure 3 shows a representative AFM image of iron oxide nanoparticles with an average size of 2.3 nm. The inserted 2D Fourier Transform analysis clearly indicates a high degree of order of the nanoparticles. This demonstrates that periodic spacing of catalytic nanoparticles has been achieved. Based on Raman and AFM analysis, the majority of CNTs produced from the iron catalysts derived from this system have diameters around 1.6 nm while the majority of tubes grown from the cobalt catalysts are around 1.0 nm in diameter. Figure 4 is the Raman spectrum of a CNT mat produced from the iron catalyst. The high ratios of G/D and D*/D indicate that the CNTs have high quality with a minimal amount of amorphous carbon and very small number of defects.

Figure 3. AFM image (and its 2D Fourier Transform) of iron oxide nanoparticles derived from PS-b-PVP.

Cobalt-complexed PS-b-PVP was also investigated for patterned CNT growth. Cobalt-complexed PS-b-PVP solution was spin-coated on a pre-patterned substrate. Catalyst islands were obtained by removing the sacrificial pattern material by a lift-off process. Optical inspection of three-inch wafers show that the lift-off process is effective, leaving only the catalytic islands behind. The SEM image in Figure 5 depicts arrays of CNTs grown from lithographically defined 1.0 μm catalytic islands over a large surface area. There is no evidence of CNT growth initiated in the regions between the catalytic islands indicating that this additive patterning scheme is effective in generating patterned catalyst substrates.

Figure 5. SEM image of large-scale patterned CNTs using cobalt catalysts produced from Co-complexed PS-b-PVP.

2.2.2 DIRECT SYNTHESIS OF A CATALYST-CONTAINING DIBLOCK POLYMER

In the previous approach, the level of metal complexation may not be identical for all polymer chains and thus catalyst size control by this method is somewhat limited. To further improve the control of catalyst size, a sequential living polymerization was used to polymerize nonmetal-containing styrene monomers followed by the catalyst-containing ferrocenylethylmethylsilane to form polystyrene-b-poly(ferrocenylethylmethylsilane)(PS-b-PFEMS). The chemical structure is shown in Figure 6. After spin-coating, the polymer film was annealed to induce self-assembled periodic nanostructures within the thin film. During UV-ozonation and thermolysis at 700 °C in air, the PFEMS blocks mineralize to form iron-containing silicon oxide nanostructures. The AFM image and 2D Fourier Transform analysis shown in Figure 6 indicate the formation of iron-containing silicon nanostructures with highly uniform size and spacing. The size of iron nanoparticles in this system can be potentially predefined at the atomic level.

Figure 6. AFM image (and its 2D Fourier Transform) of Fe/Si nanostructures derived from PS-b-PFEMS.
Furthermore, silicon in the PFEMS segments was mineralized to form silicon oxide during thermolysis. The SiO₂ reduces the iron nanoparticle agglomeration, allowing growth of CNTs with diameters of 1nm or less. Figure 7 shows the SEM image of patterned arrays of CNTs grown from lithographically defined catalyst islands prepared using the additive approach described above. The Raman and AFM analyses shown in Figure 7 prove that the majority of tubes had diameters around or less than 1nm.

![Figure 7. SEM and AFM images of patterned CNTs grown on Fe/Si catalysts nanostructures and Raman spectrum of RBM](image)

### 3. APPLICATIONS

#### 3.1 CNT MAT FOR MALDI-MS

The ability of this polymer-based approach to generate uniformly distributed CNTs in a reproducible and manufacturable manner offers great potential for developing and commercializing both functionalized and non-functionalized CNT devices. The CNT surfaces produced from iron-complexed diblock copolymer systems have been investigated as MALDI targets. The preliminary result indicates that CNT-based targets show improved MS sensitivity. Most spectra obtained from TiN MALDI targets failed to identify BSA at 500 attomoles. Positive identification was repeatedly obtained from the CNT surfaces. Figure 8 shows the representative mass spectra of BSA at 500 attomoles using a TiN and a CNT MALDI target. As can be seen, the CNT target provides a very definitive spectrum with positive identification.

![Figure 8. Mass Spectra of a TiN (left) and a CNT (right) coated MALDI surface](image)

#### 3.2 PROPOSED BIOSENSORS AND ELECTRONIC DEVICES

CNT mats can be used as electronic transducers for biological and chemical sensing. Since the electronic signals are determined by the average properties of the individual CNTs, the difficulties in precise control of positioning and diameter are circumvented in this application as long as the density of CNTs can be controlled. The polymer-based catalyst precursor makes it easy to generate arrays of mats with controlled density. By functionalizing each patch with different antigens, a CNT-based biosensor with real-time multiplexed biosensing capability can be fabricated. Figure 9a is the schematic drawing of a CNT-based biosensor.

![Figure 9. Drawing of CNT-based sensor array(a) and transistor(b)](image)

The difficulty of placing nanotubes in prescribed locations hinders their use in electronic devices. The polymer-based catalyst precursor shows great promise in manufacturing CNT-based electronic devices using standard semiconductor industry methodologies. Polymer-based catalyst precursors enable the fabrication of CNT field effect transistors where the number of CNTs and the locations of CNTs are controlled in a predictable and reproducible fashion. In our design, a lithographically defined catalyst island shown in blue in Figure 9b contains a number of catalytically active sites. CNTs are grown radially from the catalyst islands that minimize the possibility that CNTs will cross. The circular shape of the source maximizes the number of CNTs with uniform chain length between source and drain. High tube density, few crossovers, and uniform length will all increase the drive current and transconductance of the resulting RF devices.

### REFERENCES