Synthesis of Carbon Nanotubes with the EasyTube™ System

ABSTRACT

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DESCRIPTION

Single-walled carbon nanotubes (SWNT's) have unique electronic and mechanical properties and diameters of only a few nanometers. Chemical vapor deposition (CVD) is used to produce SWNT with high quality and purity. The synthesis of the nanotubes is performed using metal particles, such as iron, cobalt and nickel. Multiwall carbon nanotubes (MWNT's) are also synthesized by CVD under different reaction conditions. The EasyTube System is optimized for high quality and reproducible synthesis of carbon nanotubes by catalyzed CVD.

CATALYST AND SUBSTRATES FOR CVD

1. Alumina-supported iron catalyst:
One well-studied catalyst is the alumina-supported iron catalyst solution. This catalyst is reliable and productive. It can produce SWNT with diameters of ~1-3 nm and lengths of several microns to over one hundred microns. The amount of nanotubes grown can be controlled by choice of gases, flow rates and temperature.

First Nano provides this solution catalyst that contains iron oxide particles that are reduced in the growth process to form Fe on an alumina support. This is the catalyst for SWNT. Molybdenum is a growth promoter and raises yields of nanotubes (reduced yield is possible by reducing the amount of Mo). Mo helps with the hydrocarbon deposition – it promotes the growth by increasing the amount of reactive carbon species. The alumina has a very high surface area and is a placeholder for iron particles. It is covered with iron nitrate which eventually form the iron particles. Alumina helps prevent aggregation of iron into particles that are too large for SWNT growth and is the "support" for this type of catalyst. Methanol is used to form the suspension and allow for catalyst deposition. It coats the PMMA resist well without rapidly dissolving it. However, if the suspension is allowed to stay on PMMA /substrate for an extended period, then some of the suspension may dissolve through to the substrate and destroy the patterning and make liftoff more difficult.

Deposition of Fe Solution Catalyst

Technique 1: Spinning

Place substrate (e.g. patterned substrate with PMMA resist) on a spinner with adhesive. Spin at high speeds of greater than 2000 RPM and make sure the chip is attached well.

Use a pipette to place a few drops of catalyst on the substrate. Just 1 or 2 drops can fully cover a 1 cm2 substrate. If you have a pipette, you can apply 20-40 microliters of catalyst. Leave the catalyst on the chip for a few minutes (2-5), then spin off at high speeds.

Bake at ~160 °C in an oven for 5 minutes OR at ~120 °C on a hotplate for 5 minutes. While the substrate is being heated, prepare solvent for liftoff. Dichloroethane (DCE) and acetone work well. DCE is slightly better for liftoff, but acetone alone will also work. Prepare 2 or 3 small beakers with solvent. Our method starts with DCE and alternates between DCE and acetone for clean liftoff. After the heating is complete, place the hot substrate into the first solvent (e.g. DCE) and lightly agitate the solvent for 1-2 minutes. Then place the substrate in fresh solvent and lightly agitate for a few minutes. If possible, let the chip stay in the liftoff solvent for an hour or longer. Several rinses are suggested for complete liftoff. The final step should be an isopropanol rinse (methanol is the alternate) and blow dry with argon or nitrogen. Verify clean liftoff by optical microscopy. It is important to completely remove the PMMA resist, or the synthesis of nanotubes will be affected. Note: Do not overheat the substrate, because high temperatures will cause the resist to be extremely difficult to remove. The catalyst wells orsquares may only form a ring on the edge and not fill the entire square. A ring of catalyst is sufficient.

Technique 2: Drying under inert gas

Place the substrate on a level surface and deposit ~2 drops of catalyst (20 microliters if you have a pipettor). Leave the catalyst on the chip for a few minutes (~2) then dry with a light flow of inert gas (nitrogen or argon) so that the film is uniform, especially over the patterned area.

Bake the substrate as explained above.

The inert gas drying technique usually leaves more catalyst in the lithographically defined patterns. The spinning technique is useful if less catalyst is desired.

Lifetime of catalyst

The catalyst in suspension may have a limited lifetime of a few months. Catalyst on the substrate after liftoff has a much longer lifetime. Do not store catalyst substrates in gel packs or containers that have adhesives that outgas, this can cause the catalyst to become contaminated.

2. Thin film catalyst:

Fe thin film catalyst is used for vertically aligned CNT growth. The film thickness varies from 1 nm to 10 nm. A thinner Fe film will produce a smaller diameter CNT. Fe thin film can be deposited on varies substrate by sputtering or electron beam evaporation. It works well on Si substrate with 200 nm to 600 nm SiO_2 on it. The oxide layer thickness will also affect the growth rate.

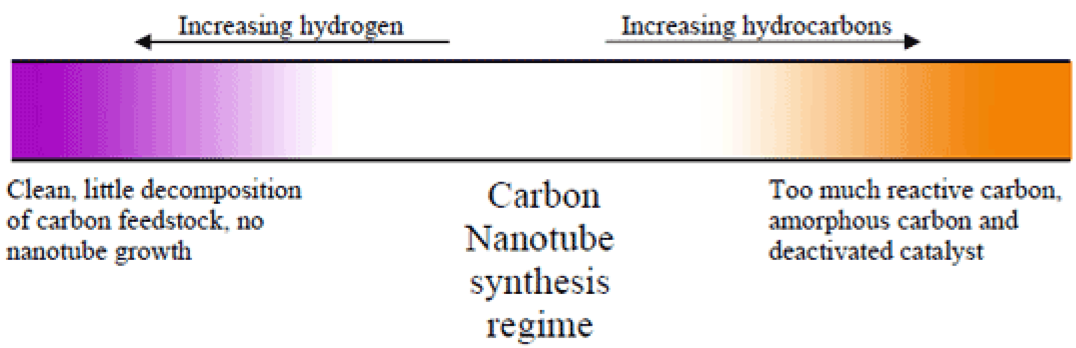
3. Substrate:

Typical substrates for CVD are patterned silicon or silicon oxide substrates. Quartz, silicon nitride, alumina and others have also been shown to work. PMMA is a quality resist for lithographic patterning in nanotube research for several reasons. It allows for wet deposition of the alumina-supported iron catalyst and other nanoparticle catalysts. It can be exposed by electron-beam lithography or DUV photolithography. PMMA is very clean after liftoff and descum processes are not necessary. This is important both for nanotube growth and further use and/or processing with the nanotubes. PMMA also has a long lifetime in ambient and is not exposed by normal lighting. Any masking technique that allows for clean deposition of catalyst without damaging the structure and composition of the catalyst will work for nanotube growth.

Growth Conditions – How to choose gases, flow rates, temperatures and parameters to grow carbon nanotubes

Single-walled carbon nanotubes:

For SWNT growth we aim to balance the amount of reactive carbon for the highest quality nanotube product and the absence of amorphous carbon and other forms of impurities. Methane is chosen as the hydrocarbon gas because it is the most stable and resists self-decomposition, even at the elevated temperatures of growth at 800- 1000 °C. Also, diluted amounts of ethylene (or acetylene) can be added for higher yields. These gases are not as stable as methane against thermal decomposition and need to be heavily diluted or large amounts of carbon deposits will coat the nanotubes, substrates and quartz tube. Hydrogen is a product of the hydrocarbon decomposition. Hydrogen can also be co-flowed to systematically achieve the correct balance for synthesis by neutralizing excess reactive carbon species and opposing the decomposition of the hydrocarbon feedstock. Also, hydrogen makes a cleaner product, with very little amorphous carbon present. The balance necessary for nanotube growth is shown below.

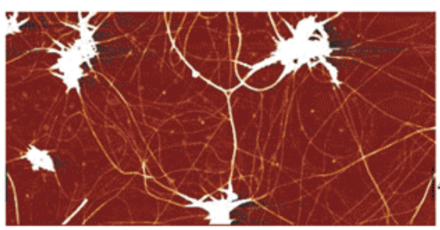


The temperature of 900 °C is used for small diameter SWNT with high degrees of crystallinity and lack of defects. Higher temperatures may produce larger tubes, which is possibly due to aggregation of the metal catalyst particles. Lower temperatures may result in defective SWNT. Therefore, we typically use 800-1000 °C for the highest quality SWNT growth. Figure 1 shows high yields of SWNT synthesized with the High Yield SWNT Recipe and the alumina-supported iron catalyst.

Multi-walled carbon nanotubes:

MWNT's are can also be produced by the EasyTube™ System. Generally CVD for MWNT's uses ethylene or acetylene as the carbon feedstock and temperatures of 550-750 °C. These gases are very reactive and have much higher decomposition rates than methane. MWNT's require more reactive carbon to form. Figure 2 shows MWNT towers synthesized on the EasyTube™ System with 5 nm Fe thin film deposited on a Si substrate with 600 µm thick SiO2 layer.

Figure 1: High Yield of SWNTs with the alumina-supported iron catalyst



4 µm

Figure 2: MWNT towers synthesized with the MWNT recipe and thin films of iron as catalyst