

Deposition of Optical Thin Films of Nanotubes

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One of the current problems with studying nanotubes is the difficulty in creating thin films of them, which can be studied on a macro scale. We have developed a way to homogeneously deposit nanotubes on optically transparent substrates. We have also done this in such a way as to allow us control over the films thickness. The method we have sublimates the solvent to leave the nanotubes deposited on the substrate. This avoids the problems associated with depositing the nanotubes out of a liquid solution.

Single walled carbon nanotubes are a new form of carbon discovered less than 10 years ago by Sumio Iijima [1]. Due to their relatively new appearance on the stage, there is still a great deal of work to be done on basic characterization. The work that has been done so far has shown that nanotubes are quite an amazing new material.

Single walled nanotubes are long tubes made entirely out of carbon. They can be

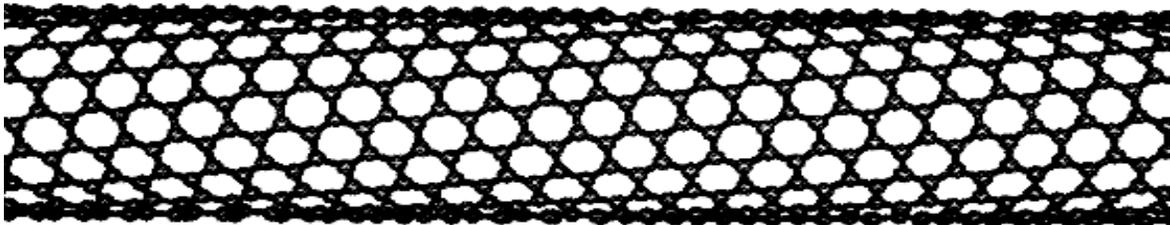


Figure 1. A nanotube midsection

thought of as a planar sheet of graphite, a hexagonal planar carbon network (see Figure 1). This sheet is wrapped into a seamless tube, which is nanometers in diameter and microns in length. They can be capped at either or both ends with half a spheroidal Fullerene, or they can be left open-ended (depending on the method of synthesis and post-synthesis

processing). The nanotubes are characterized by what is referred to as a roll up vector (the direction in which the flat graphite sheet would be rolled up to form the tube), which specifies the so-called helicity of the nanotube. Depending on its helicity, a nanotube can be either semiconducting or metallic in its electronic transport characteristics (for a good overview see Ref. 2 and references therein).

The novel physical and electrical structure of nanotubes provides an interesting system to study. In particular we are interested in studying the non-linear optical properties of the tubes. However, a problem arises in trying to make optical measurements of the nanotubes. This problem is the inability to form uniform films of the nanotubes. In the past optical measurements have been done on tubes in solution or on tubes in poorly deposited inhomogeneous films. Both of these deposition techniques lead to problems. When doing optical measurements in a solution, the background signal of the solution must be subtracted, which decreases the resolution of the measurement. Also, if the background signal is large enough, it may mask the signal of the tubes, thus providing misleading data. In a solution the tubes also have the ability to move, which can lead to problems when the tubes are hit with the high-intensity field of the probe beam. This field may be strong enough to align the tubes in solution, which, due to the nanotubes' highly 1D character, may give us data that are not truly representative of a randomly oriented sample of nanotubes.

In order to solve these problems, it is necessary to remove the tubes from solution. However, the method by which this is done may cause other problems that also have to be overcome. These problems depend largely on the method by which the nanotubes are deposited on a substrate. There are several ways in which the tubes can be deposited.

The simplest method is drop drying. Here a drop of solution containing nanotubes is placed on a substrate and then the solvent is allowed to evaporate off. This method has several problems. One problem is that during the evaporation process the nanotubes have time to settle in the solution and tend to flock together, which leads to them being deposited in inhomogeneous clumps. Another problem is that as the drop dries, a form of capillary flow tends to pull material towards the outer edge of the drop, forming a sort of nanotube “coffee stain” [3]. Moreover, because liquids have a surface tension, they tend to pull small objects into clumps as the last drops evaporate. Finally, any impurities in the solution are deposited on the surface along with the nanotube.

An alternative deposition method relies on the fact that the nanotubes tend to pick up negative charge in solutions. An electric potential applied between the substrate and another electrode in the solution causes the tubes to be driven to the positive electrode (electrophoresis). When the nanotubes hit the positively charged substrate they lose their charge and stick to it. The electro-deposition method has the advantage that tubes can be deposited without the evaporation of the solution. However this method can only be used for a very dilute solution of the tubes where complete coverage of the substrate is not

desired. If thicker or more complete films are made with this method, flocculation tends to occur. It also requires an electrically conducting substrate, which even for very thin metal films would interfere with the optical measurements.

What is needed for optical measurements is a well-dispersed nanotube film, a film that we can control the thickness of. To make such a film, we will employ technique called freeze drying. One of my several nanotube related projects this summer was to construct a freeze drier.

In freeze drying, the nanotubes are placed in solution and well dispersed with the aid of an ultrasonic bath. The solution is then quickly frozen to avoid any flocking. The sample is then cooled to slightly below its freezing point and placed in a vacuum. This procedure provides conditions under which sublimation of the solvent can occur. In sublimation the sample goes from the solid phase to the gas phase directly, skipping the liquid phase and avoiding any problems that are encountered therein. This technique should result in a film of nanotubes that are non-flocculated. Also this method should allow us to accurately control the thickness of these films. The nanotubes we used were produced by the pulsed laser vaporization method [4]. This results in a diameter distribution for the nanotubes that is peaked around 1.4 nm. The tubes then undergo an acid purification step in order to remove any amorphous carbons that are mixed in with the tubes. The solvent we use to suspend the nanotubes in is N,N-dimethylformamide (DMF). This solvent, while it provides a very good suspension of nanotubes, has several

drawbacks when used. Its vapor pressure is not very high, which causes it to evaporate very slowly at atmospheric pressure. It has a rather high boiling point of 426.2 K and a rather low freezing point of 212.85 K [5, 6]. DMF also starts to decompose above about 340 K causing all sorts of junk to be left behind. DMF is also known as a “super solvent,” which means that it essentially dissolves anything, including any impurities in the air. These impurities that dissolve in the DMF also tend to be left behind after the DMF is evaporated, contaminating the sample.

The major problem with DMF for freeze drying is its low freezing point. This is well below the range that can be easily reached with thermoelectric coolers, which required that we build a gas flow freeze drier. In this case we are using cooled nitrogen gas. The system we built is illustrated in figure 2. In this system the gas is flow is

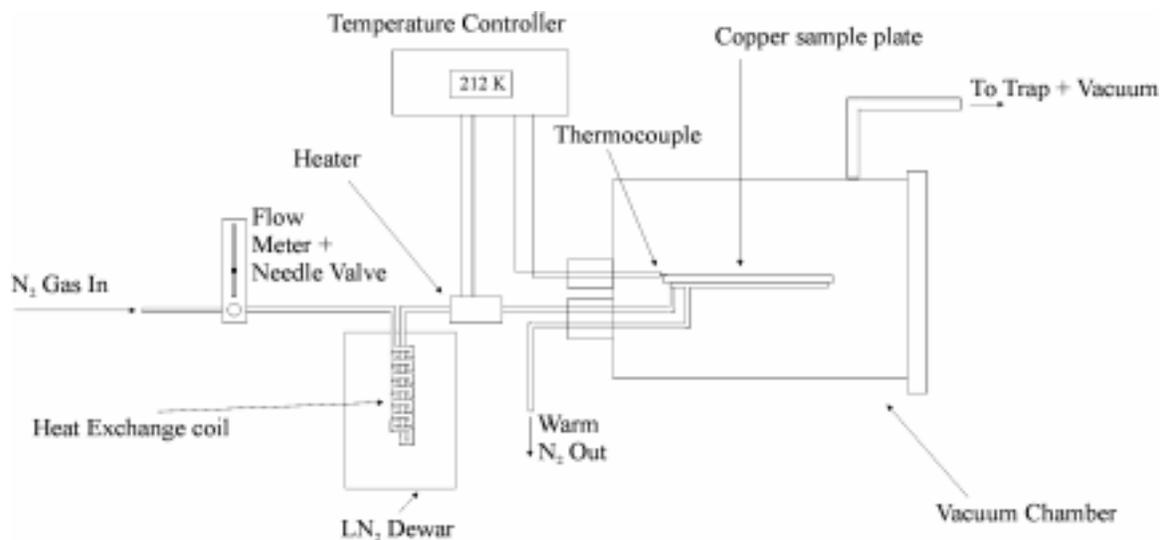


Figure 2. The Freeze Drying System

controlled by a needle valve and monitored by a flow meter. The stream of N₂ gas is passed through a heat exchanger in a liquid nitrogen (LN₂) filled Dewar, and then through a section of pipe that is wrapped with resistive heater wire. The nitrogen gas then flows via a vacuum feed-through into a copper cold plate inside a vacuum chamber and then via another feed-through back out to be expelled into the atmosphere. A copper cold plate supports the sample. A thermocouple attached to the copper plate, monitors the temperature of the cold plate and provides feedback to a temperature controller. The controller regulates the temperature of the gas providing the appropriate current to the heater coil. The entire vacuum chamber is wrapped in insulation and pumped down to approximately 10 millitorr. The pump line must pass through a LN₂ vacuum trap before it enters the pump. This vacuum trap ensures that DMF does not enter the pump, causing harm to it.

In order to prevent flocking the sample will quickly be frozen with LN₂ before being placed on the precooled cold plate in the chamber. Because the sublimation rate is maximized when the temperature is regulated to be just below the freezing point of the solvent, the temperature will be maintained as close to, but just below this temperature.

We have not fully completed the freeze drier due a delay in the acquisition from the manufacture of the two LN₂ Dewars necessary for the vacuum trap and for the heat exchanger. Once these arrive we will complete the freeze drier and iron out any bugs in the system. Over the following months we will study the optical and microwave

absorption properties and the nonlinear optical properties of the nanotube films in collaboration with Prof. Tanner's and Prof. Reitze's groups.

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