Transparent Conductors Based on Single-Walled Carbon Nanotubes

Introduction

Many optoelectronic applications require transparent conductors for at least one electrode. The most common of these transparent conductors, indium tin-doped oxide (ITO), is used extensively in displays, LEDs, and solar cells. ITO has good transparency at visible wavelengths, and shows very low resistance even in thin-film form. The disadvantages of ITO are that it contains lots of indium, which is costly and rare, and that it is made by a high-energy sputtering process, which is only compatible with inorganic substrates like glass. In addition, ITO films themselves are brittle, so when they are produced on a plastic substrate, they often crack when the film is flexed. This is a major problem when large-area low-cost substrates are desired. Thus, while ITO and its relatives (e.g., fluorine-doped tin oxide (FTO)) are currently the transparent conductors of choice, they have limited applicability for flexible (plastic) electronics, large area, and long-term availability.

For flexible, all-plastic systems, people often employ doped polyanaline (PANI), although the strong color of PANI sometimes limits its applicability. In this lab, we explore a new type of material—interconnected networks of single-walled carbon nanotubes (SWNTs) for applications as transparent conductors.\textsuperscript{1–3} Nanotubes have the advantage of solution processing, good mechanical properties, and high conductivity. They have the disadvantage of having some absorption in the visible, although production of thin films can mediate this problem.

Single-walled carbon nanotubes are rolled up sheets of graphite. Depending on the helicity and size of the tube, they can be either semiconductors or metals. While all tubes show good electron mobility, only the metallic tubes have a finite density of states at the Fermi level, and so only these metallic tubes conduct significantly at room temperature. In a randomly produced sample of nanotubes, only $1/3$ of the tubes will be metallic, while $2/3$ will be semiconducting. While methods have now been developed to separate metallic and semiconducting nanotubes, these methods are somewhat laborious, and so we will employ a random mixture of tubes. To produce a high quality conductor, a complete interconnected network made up of metallic tubes is needed. Additionally, in general, a thicker film is better for conductivity but also is more absorptive.

Another option is to induce conductivity in the semiconducting tubes through doping. In this lab, you will thus produce films of carbon nanotubes of different thicknesses and on different substrates. You will then examine the conductivity of these films to determine the optimal trade-off between optical clarity and low resistance. Finally, you will dope the films with various reagents to examine the changes in conductivity.
Chem 285 Lab 7  Transparent Conductors Based on Single-Walled Carbon Nanotubes

Procedure

Overview

Day 1 Clean substrates and coat them with APTES. Make nanotube/SDS solution.
Day 2 Make CNT films of various thickness. Measure optical density of films on glass. Start electrical measurements.
Day 3 Finish electrical measurements. Examine the response of the films to dopants.

Preparation of Nanotube Films

Make 25 ml of a 1-mg·ml⁻¹ aqueous solution of SWCNT. Add 0.25 g sodium dodecyl sulfate (or 1 wt% of SDS relative to water) to the solution. Sonicate the solution in order to disperse the tubes in the solvent using the probe sonicator. It should only take pulses for about 5 minutes to allow for all of the nanotubes to disperse.

Cut two microscope slides into three squares each. Thoroughly clean six glass substrates. Do not touch them with your bare fingers at any time, even by the edges (edges are OK with gloves). Handle them only with tweezers and gloves, and do not use a Brillo pad when cleaning, as this will scratch it.

Use a Kimwipe with DI water + Alconox detergent to scrub your substrates. Once scrubbed, place the wafers and the glass slide onto the bottom of a crystallizing dish with about 1/2” deionized (DI) water and about 1 teaspoon of Alconox detergent. Cover the dish with a watch glass and place it in the sonicator and agitate for ten minutes. In the meantime, turn on the vacuum oven and set the temperature to 120°C.

Drain the soapy water and rinse well with DI water. Then refill dish with plain DI water, cover with watch glass, and sonicate for five minutes. If you do not rinse off all the soap, your device will not work well, so do this carefully. After the pure DI sonication, place the substrates on the watch glass and place in the vacuum oven with the empty dish so to dry all. Turn on the vacuum, and dry the glassware/samples for ten minutes.

Once dry, put in 1/2” of acetone. Sonicate for five minutes. When finished, take your samples out and blow them off with compressed air from one of the tanks near the furnaces. Since it is acetone, they will dry quickly. Also, dispose of the acetone in your dish.

Finally, put in 1/2” of alcohol (ethanol or isopropanol). Sonicate for five minutes. Then drain the alcohol and put the wafers and the glass slide into the preheated vacuum oven, turn on the vacuum, and dry the wafers for ten minutes. After this step, you should try to keep your substrates in a covered container so to avoid dust particles gathering.

At this point, if at all possible, you should use a UV-ozone or ozone plasma cleaner to do the final cleaning of your substrates. The lab may or may not have such an instrument, and if not and you know...
someone who does have one, try to use theirs. The ozone reacts with organic compounds and “ashes” them away, leaving an ultra-clean and very hydrophilic surface.

Make 50 ml of 1-wt% aminopropyltriethoxysilane (APTES) solution; use dry ethanol for this step only and place thoroughly cleaned glass substrates in the APTES solution for at least an hour. Do not leave the glass substrates in the APTES solution for longer than a class period. Rinse several times with ethanol.

Transfer the SWCNT solution to the spray-coating container. Make sure it is filled such that when the container is turned to its side, you can still spray. Adjust spray-coater head to provide a large spray area. Use the temperature controlled plate from OLED experiment; cover the plate with aluminum foil. Place APTES-coated glass on 180°C heating plate. Turn spray-coater on its side and point spray-coater head directly at substrate. Spray a continuous film by sweeping head from left to right, all over the slide and off the sides so that there is a uniform thickness on the glass square. It would be advisable to practice with just water before using your nanotubes solution in the spray gun. Thickness of film is determined by the number of sprays. The films should vary in transparency from light to dark. (For example, to get different shades you can spray 5, 10, 20, and 30, but it may vary depending on the conditions you use to spray and the concentration of your solution.) Make sure the film is dry before each spray. Before spraying your substrates, be sure to practice on a paper towel or glass slides until you can make a uniform film. Check that your films are conductive before moving to the next step.

Optical and Electronic Characterization of the Films

Once the films are on glass slides, they can be used for optical absorption measurements. Measure the transmission through the films throughout the visible and near-IR regions. Note that we have a film holder for this instrument. Be sure to record the transmission at multiple positions on your film and report an average.

Please review the difference between resistance, sheet resistance, and resistivity. The best way to determine a film’s sheet resistance is to use the van der Pauw approach. For more details on this method, see Ref 5.

To do this measurement, you will need to break off a roughly square piece of glass (exact geometry is not important) from your microscope slide and scratch a small line between the corners with a razor blade (see Figure 1a), leaving the middle of the film untouched. Next, using a Keithley 2400,* contact the sample like that shown in Figures 2a and 1b by dabbing silver paste on the corners and connecting/wiring accordingly—make sure that the red terminals are adjacent and each corresponding black terminal is adjacent to its red terminal (NO kitty-cornering)!

*If all GPIB computers/cables are in use, you can always use the serial port to connect the Keithley to a computer—just make sure that the correct VISA Resource Name is selected in the .vi program.
Figure 1: (a) Schematic of sample before/after scratching lines. Note that in theory the sample geometry is irrelevant. However, it is nicer to measure if it is roughly square. (b) Overall schematic of the measurement that is realized in Figure 2.

Figure 2: The van der Pauw measurement setup. (a) One of two configurations needed to measure the sheet resistance. (b) The same configuration on the sample but with the terminal contacts rotated by 90°. Note that you can start the measurement in either configuration (a or b); it doesn’t matter as long as you rotate to the other configuration when the program commands.
Now you will source a current and measure a voltage in two different configurations rotated 90° from each other, like in Figure 1b. To do this, open the program titled van der Pauw Ke2400 located on the desktop or in Labview Programs/Van der Pauw Ke2400 Sweep/Van der Pauw Ke2400_v2.0.vi. Choose sourcing power option and supply 1–5 mW as needed. Hit run and, when prompted, rotate by hand the terminal plugs by 90° —like that shown in Figure 2b—then click Ok and save if desired. Repeat for all samples of interest, and note that the contact rotation can start or finish in either orientation shown in Figure 2a or b.

Finally, select two or three glass films of different thicknesses for doping experiments. Make sure you use one of your lighter samples, even if this sample gave you an overload value when you measured its resistance in the as-synthesized form. Here you can also use one of your van der Pauw samples, but connected in a kitty-corner orientation (i.e., this is a simple resistance measurement and not a van der Pauw measurement). You will now also need to switch to a Keithley 2000, and use the program titled Ke2000 Resistance vs Time.vi located in the Labview Programs folder. This part of the lab will use a jar like the PANI nanowire sensor jar. Attach the electrical clips to the film and hold it carefully above the jar. Once everything is well attached, activate the fan, and start collecting data every few seconds using the LabView program. After you’ve obtained ~30 seconds of stable “sensor in the normal air” data, very carefully and slowly lift the lid of the jar straight up and add a piece of solid NH₄CO₃. Seal it—keep collecting data, but note the time when you added the carbonate. When the doped reading stabilizes, take the lid off the jar (but keep collecting data). Stop when you stabilize, or after a few minutes. When you are done, remove the solid NH₄CO₃ and flush the jar with N₂. Repeat the same experiment with solid I₂ and repeat the experiment for films with different thicknesses. Note: it is important to do the doping experiments in this order (ammonium carbonate then iodine).

Some Thought Questions

1. What inherent properties of the nanotubes inhibit their conductivity?
2. What advantages do nanotube networks have over standard inorganic conductors?
3. Why do NH₄CO₃ and I₂ change the network conductivity in the ways you observed? Does the film thickness have any effect on the response?
4. How could the nanotubes be adapted for use as a sensor?
5. How could the nanotubes be made into a circuit?
6. Are these films good transparent conductors? Why or why not? Of the transparent conductors you made which one is the best candidate to be used practically?

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7. How does the sheet resistance vary with the thickness of the film (i.e., number of layers put down)? Why does it vary in this way? Why are the units of sheet resistance in $\Omega \cdot \text{cm}^{-1}$?

References


