Wide range optical studies on single walled carbon nanotubes

Ph.D. Thesis booklet

Áron Pekker

Graduate School of Physics
Budapest University of Technology and Economics

Supervisor: Dr. Katalin Kamarás

Research Institute for Solid State Physics and Optics

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The research topic

Carbon based nanomaterials have been in the center of scientific interest for the last quarter of a century. This interest started with the fullerenes, continued with the nanotubes, and now graphene inspires not only the scientific community (chemists, physicists and even biologists) but industry as well. There is a long way for a new material from the research lab until it is applied in a device as a component. Characterization is a key process in this development: we have to decide whether our material possesses the desired properties. Characterization can be done in many ways and one has to choose the proper method which fits the material. In the Research Institute for Solid State Physics and Optics the laboratory of Katalin Kamarás has a long history in the optical characterization of new materials. I started my work in this lab as a diploma worker on the optical characterization of carbon nanotubes. My PhD thesis is a direct continuation of this previous work.

Carbon nanotubes have fascinating properties due to reduced dimensionality which makes them the perfect playground for physicists and chemists. They exhibit different electronic behavior depending on geometry: they can be narrow- or wide-gap semiconductors, semimetals or metals. This wide range of properties is of huge advantage in applications; however, it can cause substantial difficulties when it comes to working with "real-life" macroscopic samples, which most of the time contain an uncontrollable amount of each type. Moreover, their chemical and physical properties can be altered by chemical modification which opens a new dimension in the possible fields of use.

The thesis was compiled around the nanotube as the material and optical spectroscopy as the characterization method. Their relationship is not without challenges, but if we can overcome the technical difficulties it turns out that the method and the material fit together quite well.

Goals

1. Our first goal was to establish a proper method for the calculation of the optical functions from the measured transmission spectra in the case of carbon nanotube thin films. The conventional methods for sample characterization are based on the optical density (-log(T)). This is reasonable in the near-infrared and visible spectral region, but fails for the infrared and far infrared. The optical density neglects the reflection which can be high in the far infrared and near the transition peaks. For detailed analysis a more rigorous treatment is needed.

2. Macroscopic nanotube samples are usually characterized by optical methods. The most widely used techniques for this purpose are Raman spectroscopy, photoluminescence spectroscopy, and transmission spectroscopy. The first two are particularly suitable to determine the (n,m) indices of the constituting nanotubes. However, they also have limitations. Photoluminescence works only with semiconducting tubes, and for sufficiently high quantum yield the nanotubes have to be individualized. The drawback of Raman spectroscopy comes from its advantage. The resonance condition which always applies for nanotubes enhances the contribution of a few types of tubes. In order to investigate all the nanotube species in the sample, a number of lasers with different wavelength have to be utilized. Transmission spectroscopy lacks the selectivity of the previously introduced techniques and measures all the constituting nanotubes simultaneously. Our aim was to enhance the performance of transmission spectroscopy utilizing the results of the more sensitive methods.

3. One possible way of nanotube modification is covalent sidewall functionalization. Nanotubes are highly insoluble and hence difficult to work with. This can be improved using modified nanotubes, where sidegroups ensure interaction sites for the

solvent molecules. Moreover, simple sidegroups can be replaced by larger moieties which provide new features, or even interconnected networks can be produced linking the tubes together by proper functional groups. Usual nanotube samples contain tubes with different diameters and electronic structure. It is expected that different nanotubes behave differently during functionalization reactions. This variation in the chemical behavior can be the base for nanotube separation. Our aim was to investigate the possible diameter dependence or metallic/semiconducting selectivity of the reaction using transmission spectroscopy.

4. One of the most successful applications of carbon nanotubes is that of transparent conductive coatings. With the development of these products came naturally the demand for unique characterization of film quality. Two parameters have to be balanced in a transparent conductive layer: the transmission in a chosen spectral region (for the most important application, in solar cells, this is preferably the visible region) and the dc conductivity (or sheet resistance). In the literature there is a widely spread procedure for the comparison of transparent conductors. This method is based on assumptions which are not applicable for carbon nanotubes. Our goal was to find a figure of merit for nanotube layers which is easy to calculate and represents the material's performance as a transparent conductor.

Methods

Nanotubes in their most common form are black powders. To perform optical characterization we have to make transparent thin layers from these samples. This was done using nanotube suspensions and vacuum filtration technique. The resulting self supporting samples have thickness around 150nm which ensures considerable transmission in the whole spectral range.

The spectra were measured in a wide frequency range (20-55000 cm^{-1}). The wide spectral range necessitates the use of different instruments. A Bruker IFS 66/v vacuum FTIR spectrometer was used in the far- and mid-infrared region. The near-infrared data were measured by a Bruker Tensor 37 FTIR spectrometer, and the visible and ultraviolet region was covered by a Jasco v550 grating spectrometer.

Besides the optical measurement we extended the investigation to the DC conductivity, as the zero frequency limit of the optical conductivity. The DC sheet conductance was measured using the four point van der Pauw method. In order to obtain the DC conductivity we measured the sample thickness by atomic force microscopy.

The implementation and improvement of these methods was a crucial point of my work. The main issue in nanotube research is often the sample preparation, the most frequently asked question during my work was: How can I prepare measurable samples from the starting materials?

New scientific results

1. Using wide-range transmission data and numerical simulations, I have shown that the optical density approximation holds above 3000 cm^{-1}. In the range of the free-carrier absorption of metallic nanotubes, reflection distorts the linear relationship between optical density and carrier concentration. Therefore, the proper quantity to use for concentration evaluation is wide-range transmission spectroscopy followed by Kramers-Kronig transformation to obtain optical conductivity [1].

2. (a) I performed wide range transmission measurements to determine the diameter distribution of several differently produced single-walled nanotube samples. Utilizing the results of previous Raman and photoluminescence measurements on individualized nanotubes I assigned the different (n,m) species to the optical features [2,3].

   (b) A selectively enriched nanotube sample was measured and compared to its starting material. The enriched sample contains mostly (6,5) type semiconducting nanotubes. I confirmed the enrichment based on the optical spectrum. Using the spectrum of the enriched sample I was able to determine the frequency shift due to bundling.

   (c) The curvature-induced low-frequency gap was analyzed in the case of differently produced nanotubes. The diameter dependence of this peak is in qualitative agreement with theoretical calculations of the curvature gap. These results indicate that the peak reflects the electronic structure of the nanotubes and not their morphology. The values of the modified samples deviate from this behavior. This deviation can be explained with a simple model of p-doping. [3].

   (d) I carried out a detailed analysis on the spectrum of the enriched sample

and showed that the selective enrichment removed almost all metallic species. However, the presence of metallic residue can be demonstrated and I showed that the diameter distribution of the metallic species changed only slightly despite the enrichment process.

3. The effects of covalent functionalization using nucleophilic addition was investigated. With the detailed analysis of the wide range optical conductivity spectra, a diameter dependence was pointed out which can be explained by the curvature induced strain in the electron system. The results were confirmed by Raman spectroscopic measurements [4,5].

4. A new figure of merit was developed for nanotube based transparent conductors. This simple method takes into account the special morphology of the nanotube networks. Moreover, the graphical representation makes it easy to predict the direction of optimization [6].

Publications related to the thesis points

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