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A Figure of Merit for Transparent Conducting Nanotube Films

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ABSTRACT

We propose a wavelength-dependent figure of merit for transparent conducting nanotube networks, composed of the sheet resistance and the optical density. We argue that this would be more useful than previous suggestions, because it relies on more realistic assumptions regarding the optical parameters of real nanotubes.

INTRODUCTION

The use of carbon nanotubes as transparent conductive coatings has been extensively studied in the last years. Several systems were investigated [1] and various manufacturing techniques have been suggested [2-4].

Unique characterization of film quality is imperative if these products are to be manufactured on a large scale. The two parameters to be balanced in a transparent conductive layer are 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). Both quantities depend on the optical and electrical properties and the thickness of the film. Sheet resistance has to be minimized and transmission maximized for an optimal product.

In the literature, the approaches used so far are either completely practical, bearing in mind the feasibility for applications, or more fundamental, starting from the basic physical quantities of the film material and using optical relationships with realistic approximations. The simplest quality indicator would be of course the ratio of transmission at a given wavelength and the sheet resistance. This indicator was introduced by Fraser and Cook for ITO films [5]. Haacke [6] later showed that this figure reaches its optimum value at a thickness where the transmission is 0.37, way too low for the desired applications; he introduced instead the quantity $\Phi_{TC}=T^{10}/R_{sq}$, which shows maximum at $T=0.9$. The exponent can be tuned for more transmitting samples, but in this case the figure of merit loses its uniform character.

Hu, Hecht and Grüner [4] approached the problem from a much more fundamental point of view. They start from a simplified version of the formula introduced by Tinkham [7] for thin metallic films:

$$T(\omega) = \frac{1}{\left(1 + \frac{2\pi}{cR_{sq}} \frac{\sigma_1(\omega)}{\sigma_1(0)}\right)^2}, \quad (1)$$

where T is the transmittance at frequency ω , σ_1 the real part of the optical conductivity ($\sigma_1(0)$ the dc conductivity), c the velocity of light and R_{sq} the dc sheet resistance.

This equation is valid in the microwave and far infrared range, where the real part of the conductivity exceeds the imaginary part, $\sigma_1 \gg \sigma_2$. In this case the ratio $\sigma_1(\omega)/\sigma_1(0)$ is characteristic of the film and independent of frequency. At higher frequencies, however, the above approximation is not necessarily valid and the accuracy of Eqn. 1. has to be examined. Therefore, comparing the visible transmission and the sheet resistance of two different films still gives a good indication of relative film quality, but cannot be used for quantitative estimation of either the dc or the frequency-dependent conductivity.

NEW FIGURE OF MERIT

The metallic model fails for nanotubes in the visible range because a nanotube network cannot be considered metallic at such high frequencies. Assuming a simple Drude model, in metallic nanotubes (which contribute most to the dc conductivity) the plasma frequency is much lower than in ordinary metals and the relaxation rate falls in the infrared. Thus the metallic oscillator strength is already exhausted below the semiconducting interband transitions in the NIR and the $\pi \rightarrow \pi^*$ excitation. (This is precisely the reason why the transparency is high at wavelengths where ordinary metals still absorb very strongly. The case is similar in ITO and other conducting oxides where the free carriers have a low relaxation rate.)

We propose a figure of merit derived from transmittance and sheet resistance which does not suffer from the above limitations, is simple to use and predicts the direction of improvement in a straightforward way. To this end, we take advantage of another approximation connecting transmission to thickness, Beer's law:

$$-\log T(\omega) = \varepsilon n d, \quad (2)$$

where $-\log T$ is called optical density, ε is a constant (the extinction coefficient of the nanotube network), n the density of nanotubes and d the film thickness. The linear dependence holds in the region where the reflectance of the film does not introduce significant corrections; this is true for visible and higher frequencies [8].

Since both the optical density and the inverse of the sheet resistance, $S_{sq}=1/R_{sq}$, depend linearly on d , their ratio is independent of thickness and typical of the given network. The suggested figure of merit will be

$$M = S_{sq}/(-\log T) \quad (3)$$

a number which increases with increasing sheet conductivity and decreases with increasing optical density (decreasing transmittance). If we plot the two quantities against each other for films made of the same material with varying thickness, we will obtain a line with slope M .

EXPERIMENT

To illustrate the suggested figure of merit, we prepared a series of networks from various types of single-walled nanotubes and measured their transmission and sheet conductance. Films were prepared by vacuum filtration [9] and deposited on rectangular quartz substrates. All measurements were taken under ambient conditions. Optical transmittance was measured using an empty quartz plate as reference. Sheet conductivity was determined by the van der Pauw method from four-point measurements with contacts on the corners of the film. The advantage of the van der Pauw method is that the sheet resistance can be determined without measuring the sample geometry (width, length, thickness). Nevertheless, the sheet resistance still remains thickness dependent.

$$R_{sq} = \rho/d,$$

where R_{sq} is the sheet resistance, ρ is the resistivity and d is the thickness. Since R_{sq} is inversely proportional to the thickness, its reciprocal value, S_{sq} , is proportional to the thickness.

We chose four different nanotube types for comparison: arc-discharge produced and purified by oxygen treatment (P2 by Carbon Solutions, Inc.), CoMoCat commercial grade by Southwest Nanotechnologies, HiPco from CNI and laser-deposited nanotubes from Tubes@Rice. The latter were treated by refluxing in nitric acid after production.

RESULTS AND DISCUSSION

Figure 1 shows the properties of the films on a $-\log T$ versus S_{sq} plot. We chose the wavelength of 550 nm, the one widely used for solar cell applications. A higher slope of the fitted line indicates a higher figure of merit, since it means higher sheet conductance at a given transmission value. In this respect, it plays a similar role as the $\sigma_1(\omega)/\sigma_1(0)$ ratio used in Eqn.1 [4], and differs from the Haacke figure of merit [6] in an important aspect. The latter gives a number for a film with given optical functions and *a given thickness*, whereas both our slope M and the $\sigma_1(\omega)/\sigma_1(0)$ ratio are independent of thickness. The points on the individual curves in Figure 1 represent films of increasing thickness as we go farther from the origin. In order to add predictive power to the procedure, we indicate the "optimal" region (above a "threshold" sheet conductance and a "threshold" transmission value) in the upper-left corner of the plot. We used the threshold values $S_{sq} = 0.007 \text{ } \square/\Omega$ and $T = 0.7$ given by Green and Hersam [10], but the region can be easily tailored according to specific applications.

The figure of merit defined this way works well as long as the samples fulfill certain criteria. $-\log T$ is proportional to the thickness provided the reflection of the sample is negligible and $ad \ll 1$ where α is the absorption coefficient. In the visible range the absorption coefficient is small and the reflection is negligible in the case of nanotubes, therefore the linear thickness dependence holds in a wide thickness range. Our samples comprise a variety of nanotube types, like the highly doped, therefore metallic laser tubes, samples enriched in semiconducting tubes (CoMoCat CG) as well as typical samples containing metals and semiconductors in the well-known 1:2 ratio. In every case the points fall on a line indicating that our method is applicable.

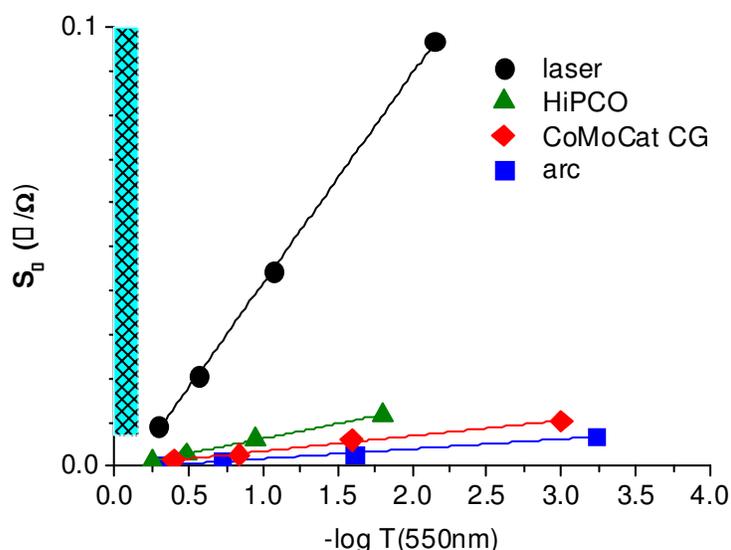


Figure 1. Sheet conductance vs. optical density for four types of nanotubes. The shaded box represents the optimal range for transparent conductive layer applications according to Ref. [10].

The slopes M increase in the order arc \rightarrow CoMoCat CG \rightarrow HiPco \rightarrow laser, with numeric values 0.0022 (arc), 0.0035 (CoMoCat CG), 0.0068 (HiPco) and 0.0477 (laser). The slight difference in the first three types of nanotubes indicates the difference in transmission at the chosen wavelength [11]. This is, in turn, caused by the variety in the mean diameter and diameter distribution of the individual types. An increase by roughly an order of magnitude in sheet conductivity is observed for the laser-deposited sample, and the explanation for this increase is the nitric acid treatment. As shown earlier [12-14], this procedure causes hole doping in the nanotube, and thus increases the dc conductivity.

Comparing the curves with the “optimal” range indicated by the shaded box, it is obvious that neither sample will reach the optimal range by simply thinning the network; instead, fundamental materials properties have to be improved further to increase the slope. Stronger doping, if it can be performed permanently, could be one way of such improvement.

CONCLUSIONS

In conclusion, we propose the ratio of the sheet conductance $S_{\square}=1/R_{\square}$ and the optical density $-\log T$ as a figure of merit for transparent conductive nanotube coatings for the visible frequency range. This figure has the advantage of requiring a very simple arithmetic treatment of the data including a linear fit; the resulting graphical representation is easy to handle and makes it simple to predict the direction of optimizing the sample. We demonstrated by comparing single-walled nanotube networks from different sources that doping can be a successful way of moving toward optimum conditions in solar cell applications.

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