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Y. Battie*, D. Jamon, A. En Naciri, J.-S. Lauret, and A. Loiseau

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Y. Battie,1,a) D. Jamon,2 A. En Naciri,1 J.-S. Lauret,3 and A. Loiseau4
1LCP-A2MC, Institut Jean Barriot, Université de Lorraine, 1 Bd Arago, 57070 Metz, France
2Université de Lyon, Université Jean Monnet, EA 3523, Laboratoire Télécom Claude Chappe, 25 rue du Dr Rémy Annino, 42000 Saint Etienne, France
3Laboratoire de Photonique quantique et moléculaire (LPQM), CNRS UMR 8537, ENS Cachan, 94245 Cachan, France
4Laboratoire d’étude des microstructures (LEM), ONERA-CNRS UMR 104, 29 Av. de la Division Leclerc, 92322 Chatillon, France

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We report an experimental technique that determines the chirality distribution in single wall carbon nanotube (SWCNT) films. Films of CoMoCat SWCNTs and SWCNTs enriched in (6,5) chirality are considered. Classical methods like photoluminescence spectroscopy frequently give incomplete distribution. In this way, spectroscopic ellipsometry is used to determine the dielectric function of SWCNT film. The chirality abundance obtained by analysing the ellipsometric data with a tight binding model is compared with that deduced from photoluminescence excitation spectroscopy. We demonstrate that ellipsometry is an efficient tool for a complete and quantitative determination of the chirality distribution and the metallic/semiconducting ratio. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4795154]

Single-walled carbon nanotube (SWCNT) is a one dimensional hollow cylindrical nanostructure, which can be viewed as a rolled graphene sheet. A SWCNT is entirely defined by its chiral index (n,m). Depending on their chirality, SWCNTs exhibit various electrical and optical properties and can have a metallic or a semiconducting behaviour. SWCNTs are considered as promising candidates for future electronic and optical devices such as field effect transistor,1 gas sensors,2,3 optical bolometer,4 laser source,5 and saturable absorber.6 However, as shown previously,7 the performance of these devices can be drastically affected by the chirality distribution.

Despite progress towards monocurvature samples,7 the chirality distribution of the fabrication of SWCNTs always produce a mixture of different chiralities. Several post-synthesis separation methods,8–13 such as density gradient ultracentrifugation (DGU),12,13 have been developed to sort SWCNTs by their electronic properties. The emergence of sorted SWCNTs requires the development of new investigation tools to estimate their chirality distribution. Although the structure of individual SWCNTs can be determined by electronic diffraction14 or tunnelling electron microscopy,15 both methods are too time consuming to be routinely used to obtain a statistical analysis in a large SWCNT collection.

Due to their one dimensionality, the electronic density of state of SWCNT consists in a series of Van Hove singularity (VHS). The optical properties of semiconducting SWCNT are closely related to the transitions between the first or the second pair of VHS, denoted S11 and S22, respectively. The optical properties of metallic SWCNTs mainly provide from the transitions between their first VHS pairs, labelled M11. As the transition energies M11, S11, and S22 depend on the nanotube structure, optical spectroscopy, such as absorption spectroscopy,16 Raman scattering,17 or photoluminescence excitation (PLE) spectroscopy,18 is a prime tool for the SWCNT characterization. In the case of absorption spectroscopy, overlapping of absorption bands prevents a precise chirality identification. Moreover, the π plasmon band in UV region generates an undesirable absorption tail in the visible/near infrared spectral range, which is frequently unphysically subtracted before the data analysis.16 Raman scattering is based on the relationship between the diameter and the frequency of radial breathing modes (RBMs). The signal intensity of the RBM mode strongly depends on the laser excitation wavelength. Indeed, the laser excitation wavelength must be in resonance with the optical transition of SWCNT. Although Raman spectroscopy is highly selective, several laser lines are required to estimate the chirality distribution of a bulk SWCNT sample. Finally, PLE is a powerful characterization technique based on the electronic transitions of SWCNTs. Maximum in the emitted intensity occurred when the excitation and the emission energies are in resonance with optical transitions of SWCNT.18 Both energies are specific to SWCNT chirality. However, since metallic carbon nanotubes are not fluorescent, only semiconducting SWCNTs can be detected. The formation of SWCNT bundles also quenches dramatically the fluorescence and prevents the use of PLE for dense film analysis.19,20

Spectroscopic ellipsometry21 is a non-destructive optical characterisation technique which is highly sensitive to the optical properties of materials. Ellipsometry was recently exploited to characterise thin films with different SWCNT densities.22 Using an effective medium approximation, the authors claimed that the interactions between SWCNTs reduce the electronic confinement. Moreover, for high SWCNT density, the film exhibits a metallic behaviour suggesting that the percolation threshold can be estimated by ellipsometry. The optical anisotropy of orientated SWCNTs...
films has been also investigated by ellipsometry\textsuperscript{23,24} without taking into account the chirality distribution. This anisotropy was attributed to the dependence between the selection rules and the polarisation.\textsuperscript{23} In the present paper, spectroscopic ellipsometry was used to evaluate both the optical properties and the chirality distribution of raw and DGU enhanced (6,5) chirality SWCNT films. Contrary to previous works,\textsuperscript{22–24} only thick films of randomly oriented SWCNTs are considered. The measured dielectric function of both films was directly correlated to the SWCNT chiralities. By analysing ellipsometric data with a tight binding model, we demonstrate that ellipsometry gives quantitative information on the SWCNT chirality distribution.

Purified CVD growth CoMoCat SWCNTs purchased from SouthWest Nanotechnologies, Inc., are used as raw SWCNTs. Their average diameter, obtained from TEM measurements (inset of Fig. 1), is 0.85 nm. SWCNTs are sorted using non-linear DGU process as described by Gosh et al.\textsuperscript{13} Sorted SWCNT and raw SWCNTs are spread on cleaned glass substrates by filtration process.\textsuperscript{2,3} Both films are composed of randomly oriented SWCNTs network and have a good optical quality. Their thickness, estimated from mechanical profilometry, is around 300 nm. In accordance with transmission spectroscopy measurements (not shown), these films are completely opaque in the considered spectral range (0.8–5 eV).

Figure 1 shows contour maps of the photoluminescence intensity of raw and sorted SWCNT suspensions as a function of excitation and emission wavelengths. The PLE map was obtained on SWCNT suspensions with a home build set up. The excitation wavelength varied from 1.77 eV to 2.75 eV. The photoluminescence signal, recorded in the 0.95 eV–1.37 eV spectral range, was corrected by the number of incident photons. In accordance with transmission measurements (not shown), these films are completely opaque in the considered spectral range (0.8–5 eV).

The dispersion curves extracted from ellipsometric data are shown in Fig. 2. The roots means square error between the complex dielectric functions estimated at 60° and 70° angles of incidence (not shown) is around 0.007 for both films confirming their isotropic behaviour. Electronic transitions in perpendicularly polarised SWCNTs have low oscillator strength.\textsuperscript{24,25} In other words, the optical properties of these films are mainly related to SWCNTs polarised along their axis.\textsuperscript{24,25} The imaginary part of the dielectric function of raw SWCNT film is different to the dielectric function of sorted SWCNT film. Considering that both films are sufficiently thick and opaque to neglect the back reflection from the film substrate interface, the films composed of randomly oriented SWCNTs can be modelled as semi-infinite medium. Assuming an isotropic behaviour, the complex effective dielectric function $\varepsilon$ was determined energy by energy from the following equation:\textsuperscript{21}

$$
\varepsilon = \sin^2 \theta_0 \left( 1 + \frac{1 - \tan(\Psi e^{i\Delta})}{1 + \tan(\Psi e^{i\Delta})^2} \tan^2 \theta_0 \right),
$$

where $\theta_0$ is the angle of incidence.

The effective dielectric function of SWCNT films can be described by a sum of Lorentzian oscillators,\textsuperscript{24}

$$
\varepsilon(\omega) = \varepsilon_0 + \sum \frac{f_{(n,m)Xjj} \omega^2}{\omega^2 + \omega^2 + i \gamma_{(n,m)Xjj} \omega},
$$

where $\varepsilon_0$ is the static dielectric constant and $\omega$ is the photon energy. The parameters $f_{(n,m)Xjj}$, $\omega_{(n,m)Xjj}$ and $\gamma_{(n,m)Xjj}$ are,
respectively, the strength, the resonance energy, and the line-
width of the transition Xjj of a (n,m) SWCNT. Two oscilla-
tors per semiconducting SWCNT chirality are used to
describe both the S11 and S22 transitions, while one oscillator
per metallic SWCNT chirality is used to model the M11 tran-
sition. An other oscillator is added for the π plasmon band.

This phenomenological model insures the Kramers-Kronig
consistency and does not required unphysical background
subtraction as absorption spectroscopic measurements. The
Levenberg Marquardt algorithm is used to minimize the
mean square error (MSE) between the measured and calcu-
lated dielectric function. To reduce the number of parameters
involved in the ellipsometric model, different numbers of
oscillators are tested. The choice of the initial guess model is
guided by PLE (Fig. 1) and the previously reported chiral-
ities in CoMoCat sample.7,29 Moreover, since ellipsometry
estimates both the real part and the imaginary parts of the
dielectric function, it gives more information than a simple
absorption measurement. Due to the high complexity of the
dielectric function, we converge quickly toward a model
which consists in 9 semiconducting chirality and 2 metallic
chirality.

Fit results are reported in Fig. 2. We found a good agree-
ment between the measured and the calculated dielectric
function. The MSE is estimated to 0.02 for both films. All
elements of the correlation matrix between each parameter
(not shown) are smaller than 0.532, confirming the independ-
ence between the model parameters. The average linewidth
of oscillators is 0.16 eV ± 0.04 eV. This value is larger than
the linewidth of isolated SWCNTs.30 This suggests that
SWCNTs are aggregated into bundles.30 As reported by
Lolli et al.,7 the M11 transitions comes from the (6,6) and
(7,7) metallic SWCNTs. By comparing the S11 and S22 tran-
sition energy to the tabulated one (Fig. 3),18 semiconducting
SWCNTs are assigned to (6,5), (7,5), (7,6), (8,3), (8,4),
(8,6), (8,7), (9,7), and (9,8) SWCNTs. These films contain
nearly armchair SWCNTs.7 Small variations between
the tabulated and the measured transitions energy can be
attributed to environmental effects.31 Indeed, the dielectric
environments are expected to screen the Coulomb interac-
tions and shift the transition energies.

By neglecting the interaction between SWCNTs and the
optical response of tubes polarised along their diameter, the
oscillator strengths $f_{(n,m),Xjj}$ of the transition $X_{ij}$ and the PLE
intensity $a_{(n,m)}$ are assumed to be proportional to the concen-
tration $N_{(n,m)}$ in (n,m) species

$$f_{(n,m),Xjj} = N_{(n,m)} F_{(n,m),Xjj},$$

$$a_{(n,m)} = N_{(n,m)} A_{(n,m)},$$

where $F_{(n,m),Xjj}$ and $A_{(n,m)}$ are the intrinsic oscillator strength
and PLE intensity of an individual (n,m) SWCNT, respectively.
$F_{(n,m),Xjj}$ and $A_{(n,m)}$ must be evaluated to perform a quantitative
estimation of the chirality distribution. The $A_{(n,m)}$ values are
extracted from the tabulated ones.32 $F_{(n,m),Xjj}$ can be expressed
as a function of the dipole vectors $\langle \Psi_{\epsilon} | \nabla | \Psi_{\epsilon} \rangle_{(n,m),Xjj}$ of
involved transitions $X_{ij}$.32

FIG. 2. (a),(c) Real part and (b),(d) imaginary part
of dielectric functions of (a),(b) a raw SWCNT film
and (c),(d) a sorted SWCNT film, obtained by a
direct inversion (dotted curve). The fit results are
also reported (solid lines).

FIG. 3. Comparison between the tabulated and measured S11 (blue dots) and
S22 (red dots) transition energies.
where $\Psi_c$ and $\Psi_v$ are the wave functions of the conduction and valence bands, respectively. The dipole vector of a SWCNT polarized along its axis can be expressed by using tight binding theory. The model is based on the relationship

$$\langle \Psi_c | \nabla | \Psi_v \rangle_{(n,m),X_{ij}} \propto \frac{\mu_1 \sin\left(\frac{\pi}{6} - \theta\right) + \mu_2 \cos\left(\frac{\pi}{6} - \theta\right)}{\omega X_{ij}},$$ (5)

$$\mu_1 = \cos(k_x a) - \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{\sqrt{3} k_x a}{2}\right),$$ (6)

$$\mu_2 = \sqrt{3} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{\sqrt{3} k_x a}{2}\right),$$ (7)

where $\theta$ is the chiral angle, $a = 0.246$ nm is the atomic lattice constant, and $(k_x,k_y)$ are the coordinates of the wave vector $k$. More complex model, beyond the aims of this paper, can be used to take into account excitonic effect or trigonal wrapping.

Zone folding approximation allows explaining the wave vector as a function of the reciprocal lattice vectors $\mathbf{K}_1$ and $\mathbf{K}_2$ of the 2D Brillouin zone33

$$\mathbf{k} = \mu \mathbf{K}_1 + \frac{k}{|\mathbf{K}_2|} \mathbf{K}_2 \left(1 \leq \mu \leq N_h, -\frac{\pi}{|\mathbf{T}|} < k < \frac{\pi}{|\mathbf{T}|}\right),$$ (9)

where $\mathbf{T}$ is the translational vector along the tube axis and $N_h$ is the number of hexagons in the SWCNT unit cell.

Fig. 4 summarizes the diameter dependence of the intrinsic oscillator strength of a $(n,m)$ tubes normalised to the oscillator strength of the $S_{11}$ transition of $(6,5)$ SWCNT. Consistent with recent theoretical works,32,33 the oscillator strength increases linearly with the tube diameter. This justifies the necessity to include the intrinsic oscillator strength in the data analysis. Moreover, the intrinsic oscillator strength of the $S_{11}$ transition band is higher than the $S_{22}$ one. As a consequence, the $S_{11}$ bands found by ellipsometry are more pronounced than the $S_{22}$ bands. Thus, the fitted parameters of $S_{11}$ oscillators are determined with a better accuracy than the $S_{22}$ ones (not shown). In the following, only the oscillator strengths of the $S_{11}$ transitions of semiconducting SWCNTs are considered to predict the semiconducting SWCNT distribution. Note that the oscillator strengths of the $M_{11}$ transitions are also used to determine the amount of metallic SWCNT.

Fig. 5 compares the abundance of each SWCNT species in both films deduced from ellipsometry and PLE. This was calculated by dividing the oscillator strengths found by ellipsometry and the PLE intensities by their intrinsic values. Both methods give similar chirality distributions. Since quantification of semiconducting tubes from PLE is a well established technique,29 this demonstrates the feasibility of ellipsometry for the estimation of the chirality distribution. Metallic and large diameter semiconducting SWCNTs such as $(6,6)$, $(7,7)$, $(9,8)$, $(9,7)$, $(8,7)$, and $(8,6)$ SWCNTs are not detected by PLE. Indeed metallic SWCNTs are not fluorescent. The $S_{11}$ and $S_{22}$ transition energies of larger semiconducting SWCNTs are too low to coincide with the accessible experimental spectral range of PLE measurements. On the contrary, ellipsometry gives insights on the whole population of SWCNTs. Raw SWCNTs contains 16% ± 2% of $(6,5)$ SWCNT and 70% ± 2.4% of semiconducting carbon nanotubes. The $(6,5)$ concentration is 3 times higher in the sorted film revealing efficiency of the sorting process. In accordance to the blue shift of the $\pi$ plasmon band, the concentration of semiconducting SWCNT in the sorted film has increased to 82% ± 2.5%. However, a large number of metallic SWCNTs still remained. Iterative orthogonal sorting technique, as suggested by Green et al.34 can be used to improve the chirality enrichment by removing metallic SWCNTs in a second DGU step. This argues in favour of ellipsometry to get a complete and quantitative chirality distribution.

In summary, we have highlighted the complex dielectric function of CoMoCat and $(6,5)$ enriched SWCNTs films. We have demonstrated that ellipsometry provides a robust and straightforward tool for tailoring the $(n,m)$ species in macroscopic SWCNT ensembles. Coupled with tight binding model, ellipsometry measurement gives a complete and quantitative chirality distribution. It was particularly useful to control the overall success of a chirality or semiconducting SWCNT enrichment.


