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ABSTRACT

Single-walled carbon nanotube (SWCNT) films are promising building blocks for diversified applications in electronics, photovoltaics, and photonics. However, their electrical and optical engineering is still a challenging task owing to multiple obstacles, including the absence of fast and easy-to-use methods for the determination of SWCNT film properties. Here, we present a rapid, contactless, and universal technique for accurate estimation of both SWCNT film thicknesses and their dielectric functions. The approach combines broadband optical absorbance and highly sensitive spectroscopic ellipsometry measurements. The observed linear dependence of the film thickness on its absorbance at 550 nm provides a time-effective and contactless method of thickness assignment, which is of significant importance to the practical implementation of SWCNT films in optoelectronic devices. Additionally, our approach revealed that a simple procedure of film densification allows to controllably alter the dielectric response by at least 40% and, thus, to add extra fine-tuning capabilities during material property engineering. Therefore, this express technique as a whole offers an advanced metrological tool for current and next-generation SWCNT-based devices.

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Single-walled carbon nanotube (SWCNT) films have been proven to be prospective candidates for numerous applications in many fields of science and technology. Among the most promising examples of SWCNT implementations are transparent electrodes,^{1,2} smart textiles,^{3,4} ultrasensitive photodetectors,^{5,6} highly-efficient solar cells,^{7,8} light-emitting diodes,^{9,10} and ultrafast lasers for near and mid-infrared wavelength ranges.^{11,12} All these applications, as well as almost any task related to the development of devices based on SWCNT films, strongly require a rapid, versatile, and preferably contactless method to determine the film thicknesses and their optical properties. SWCNT films, in turn, are known to possess a wide variety of structural diversity determined by their chirality, length, orientation, bundling degree, defectiveness, and purity as well as by the presence of surfactants or matrix polymers, providing a wide range of refractive indices (n) and extinction coefficients (k). For example, at 550 nm, the pristine aerosol chemical vapor deposition (CVD) carbon nanotube

films exhibit $n = 1.09$ and $k = 0.31$,¹³ while the CoMoCat CVD-grown¹⁴ manifests $n = 1.54$ and $k = 0.53$, and the arc-discharge method¹⁵ results in $n = 2.21$ and $k = 0.53$.

Nowadays, the optical properties of SWCNT films are characterized by a variety of spectroscopic techniques, including absorption^{16,17} and electron energy-loss spectroscopies.^{18,19} Meanwhile, morphology and geometrical parameters are determined by transmission electron (TEM),^{20,21} scanning electron (SEM),^{22,23} and atomic force (AFM)^{24,25} microscopies. All these methods are time- and resource-consuming and require additional sample preparation steps, which might affect the properties of SWCNT films and, therefore, do not represent the actual properties of films used in applications.

On the other hand, spectroscopic ellipsometry (SE) is free from these disadvantages, allowing to measure the film's thickness and dielectric function at the same time in a non-invasive way.²⁶ This technique is a non-destructive, fast, and very sensitive tool for determining

the optical constants and thicknesses of thin films.²⁶ It measures the changes in light polarization upon reflection at a sample surface. This process can be represented by the complex reflectance ratio $\rho = \tan \Psi \cdot e^{i\Delta} = r_p/r_s$, where Ψ and Δ denote the amplitude ratio and phase difference between p- and s-polarized light waves after reflection, respectively, with $r_p = E_{rp}/E_{ip}$ and $r_s = E_{rs}/E_{is}$ defined by the reflected (E_{rp} and E_{rs}) and incident (E_{ip} and E_{is}) electric fields. SE has already been successfully implemented for investigations of two-dimensional materials, including graphene^{27,28} and transition metal dichalcogenides,^{29,30} as well as films of noble metals^{31,32} and SWCNTs.^{14,33} Battie *et al.*^{14,33} investigated rather thick and, as a result, opaque carbon nanotube films, whereas many applications, especially in transparent electronics, require thin films with low absorption in the visible wavelength range.

Nevertheless, the application of SE for SWCNT thin films is a challenging task since standard ellipsometry analysis demands good initial guess of either the optical constants or the region of full transparency.²⁶ The first requirement is hard to achieve because of the diversity of carbon nanotube synthesis techniques³⁴ and film fabrication methods such as spin coating, electrophoresis, vacuum filtration, gas flow deposition, and others,³⁵ which determine the nanotube length, chirality distribution, packaging density, morphology, and, thus, optical constants. The second requirement cannot be applied to carbon nanotubes since they absorb light in the full spectral range from the ultraviolet (UV) to terahertz spectral region and beyond.¹³ There are several options to tackle these difficulties. One approach is based on a preliminary AFM thickness measurement with a subsequent determination of the dielectric function from SE. However, it does not guarantee good reliable results, as was shown by Barnes *et al.*, where an agreement with an experimental absorption spectrum was demonstrated only within 20%.¹⁵ Besides, the AFM methods are not applicable in the case of freestanding films used in ultrasensitive photodetectors,⁵ efficient ultrasound loudspeakers,³⁶ and extreme UV protective membranes,³⁷ which makes the preliminary thickness assessment a difficult (or even impossible) task. Another approach proposed by Kuwahara *et al.*³⁸ is based on thick film optical constants applied as a reference for thin films. Despite some successful results, the proposed route cannot be generally implemented due to the lack of thick-thin identical counterpart films in many cases. Nonetheless, it has not been widely accepted that all SWCNTs have prominent peculiarities such as π -plasmons in optical spectra, making it possible for unambiguous simultaneous determination of the thickness and dielectric function by spectroscopic techniques alone.

To validate the proposed concept, we investigated high-quality films of randomly oriented SWCNTs produced using the aerosol (floating catalyst) chemical vapor deposition method.³⁹ In this method, carbon nanotubes grow on catalyst nanoparticles suspended in the gas phase in the presence of a carbon source at high temperatures. Carbon nanotubes are collected at the outlet of the reactor on cellulose membrane filters [Fig. 1(a)], allowing the subsequent transfer onto secondary substrates or a frame with an opening by a dry transfer method.^{40,41} These pristine films of SWCNTs demonstrate relatively high absorbance with $k=0.31$ and refractive index close to unity ($n=1.09$) in the visible range,¹³ resulting in reflection suppression down to 1% and making standard ellipsometry measurements challenging for pristine films. In this paper, we examine SWCNT films densified by drop-cast volatile liquid (ethanol) on a spin coater at 2000 rpm to achieve a uniform surface. The film is compressed by

FIG. 1. Synthesis, preparation, and optical characterization of SWCNT films. (a) Schematic representation of the sample preparation steps: aerosol CVD synthesis (1), filtration (2), dry-transfer (3), and densification of SWCNT films (4). (b) Schematics of the SE experimental configuration used to determine the film thickness and optical constants. (c) Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function as well as (d) refractive index (n) and extinction coefficient (k) of the SWCNT film with $T_{550} = 45\%$.

surface tension during the liquid evaporation, resulting in the increase in the density and optical constants and making its properties closer to those of conventional films obtained by vacuum filtration⁴² but without the use of surfactants or hosting polymers as clearly seen from SEM (HR-SEM Merlin, Zeiss) images in Fig. 1(a).

For our experiments, the SWCNT collection time was optimized to obtain films with varying thicknesses and, therefore, transmittance values.⁴³ We prepared macro-scale rectangular freestanding films with a size of $1.5 \times 0.7 \text{ cm}^2$ and with transmittance values T_{550} of 90%, 85%, 75%, 65%, 55%, and 45% at 550 nm and further densified them by an ethanol droplet of 200 μl . Densification slightly affects transparency (the respective spectrum values mainly increase for the thick films and decrease for the thin ones, while remaining almost unchanged for $T_{550} = 75\%$ films), but significantly improves the film conductivity,^{44,45} which is beneficial for optoelectronic applications, including transparent electrodes.^{1,2} A spectrophotometer (Lambda 1050, PerkinElmer, USA) was used for recording transmission spectra in the range of 250 to 3300 nm with a step of 2 nm and the white light spot of $1 \times 4 \text{ mm}^2$. The ellipsometry parameters were measured within a broad wavelength range of 250–3300 nm and at multiple incident angles of 65° – 75° with a step of 1° using an SENresearch 4.0 ellipsometer (SENTECH Instruments GmbH) with the light spot of $1 \times 3 \text{ mm}^2$ at 70° . Several incident angles were chosen to get the values of thickness d and dielectric function $\tilde{\epsilon} = \epsilon_1 + i \cdot \epsilon_2$ (or equivalently complex refractive index $\tilde{n} = n + i \cdot k$) because one angle provides information only about their product $\tilde{n} \cdot d$.²⁶ The experimental setup for SE measurements is schematically displayed in Fig. 1(b).

Since the traditional SE analysis method is not applicable for SWCNT film thickness and dielectric function determination, we applied the following procedure: (i) in the vicinity of π -plasmons (from 250 to 300 nm), SWCNT films are quite opaque, which allows using the analytical formula for estimation of their dielectric function $\tilde{\epsilon}$,²⁶

$$\tilde{\epsilon} = \sin^2(\theta) \cdot \left(1 + \tan^2(\theta) \cdot \left(\frac{1 - \rho}{1 + \rho} \right)^2 \right), \quad (1)$$

where ρ is the complex reflectance ratio and θ is the incident angle as explained in Fig. 1(b). (ii) Then, we used the transfer matrix method (TMM)⁴⁶ for assessing thickness d based on transmission spectra and dielectric function $\tilde{\epsilon}$ obtained in the previous step. (iii) This initial estimation of the thickness and dielectric function allows us to implement the point-by-point inversion⁴⁷ for the 250–3300 nm range to determine $\tilde{\epsilon}$ in the whole spectral range. Then, the dielectric function is fitted by the Lorentz model, which is the most suitable description of the SWCNT properties, since it describes the optical response of bound and conduction electrons alongside their transitions,¹³

$$\tilde{\epsilon} = \epsilon_{1\infty} + \sum_{k=1}^6 \frac{A_k \cdot B_k \cdot E_k}{E_k^2 - E^2 - i \cdot B_k \cdot E}, \quad (2)$$

where $\epsilon_{1\infty}$ is a contribution in the dielectric function of high energy interband transition, E is the photon energy, and A_k , B_k , and E_k are the amplitude, linewidth, and resonance energy of a k -Lorentz oscillator. Afterward, parameters of the Lorentz model and the thickness are varied to fit ellipsometry spectra using the Levenberg–Marquardt algorithm. The resulting exemplified dielectric function is presented in Figs. 1(c) and 1(d) for the SWCNT film of $T_{550} = 45\%$ (optical constants are reproduced for various films with accuracy higher than 90% as shown in Fig. S1 in the supplementary material for all the film thicknesses). It is worth noting that all the features of SWCNTs (Van Hove transitions S_{11} , S_{22} , and M_{11} and a π -plasmon peak) are clearly seen. Moreover, the resulting optical constants are quite high, for example, at 550 nm, the refractive index $n = 1.57$ and extinction coefficient $k = 0.43$ compared to the pristine SWCNT films: $n = 1.09$ and $k = 0.31$.¹³ Of immediate interest is the significant increase in the optical constants by at least 40%. This dielectric response is even higher than that for current record-holder monolayer WS_2 with a 12% modification.⁴⁸ It provides a route for fine-tuning of SWCNT film dielectric response giving rise to carbon-based nanophotonics, for instance, in the production of ultrathin lenses and gratings⁴⁹ based on SWCNTs with controlled film densification.

In order to verify the dielectric function, the absorbance spectra were recorded alongside the SE. Based on the optical constants, we calculated the absorbance predicted by TMM⁴⁶ and then compared it with the experimental one, as demonstrated in Fig. 2(a). The comparison shows a good agreement between calculated and measured spectra with a slight deviation, which we attributed to the uniaxial anisotropy of SWCNT films,^{50,51} which was not included in our isotropic model. Nonetheless, in our case, the resulting spectra are almost insensitive to the out-of-plane dielectric tensor component, which follows from consistent lines of modeled and experimental Ψ and Δ (see the supplementary material, Fig. S2).^{26,52}

Apart from the dielectric function, we also determine the film thicknesses. Since freestanding film thickness measurements by AFM,

FIG. 2. Comparison of ellipsometry results, SWCNT film thicknesses, and dielectric response with traditional techniques: optical absorption and atomic-force microscopy. (a) Experimental absorbance (dashed lines) and calculated absorbance (solid lines) by TMM using SE for several freestanding SWCNT film's thicknesses. (b) AFM topographies and corresponding X-line scans averaged over $2 \mu\text{m}$ along the Y-axis for all six thicknesses. (c) Dependence of the thickness on absorbance at 550 nm. The red and green points are mean values obtained by SE analysis for freestanding and on glass substrate films, while blue points are mean values from AFM measurements of the films on glass, and the filling areas represent corresponding error bars. The straight black line provides the approximation for the SWCNT film on the glass.

SEM, or TEM are quite tricky and challenging, we also prepared SWCNT films on microscopic glass slides (Thermo Scientific). Prior to carbon nanotube film transfer, optical constants of the glass substrate were measured to implement the above-mentioned algorithm for the thickness determination. To prove the method's reliability, we performed the AFM measurements in a mapping mode with the help of a neaSNOM Microscope (Neaspec GmbH, Munich, Germany). The resulting topography maps and their corresponding X-line scans averaged over $2 \mu\text{m}$ along the Y-axis are shown in Fig. 2(b). As expected, the resulting scans reveal a small roughness of only about 5 nm with almost equal values for all films, even for the thinnest one in which absolute roughness is as small as 3 nm. The acquired thickness dependences (for the freestanding films as well as on the glass substrate) on the film absorbance at 550 nm (A_{550}) are gathered in Table I and plotted in Fig. 2(c). From the figure, one can conclude that ellipsometry gives the same thickness as the AFM measurements. In accordance with the Beer–Lambert–Bouguer law, the points can be approximated by a linear function, depicted by a straight black line in Fig. 2(c) and given by the formula $\text{Thickness (nm)} = 239 \times A_{550}$ with confidence intervals in Table I, demonstrating how well the particular thickness is described by this relation. It enables a momentary and contactless approach for thickness determination from the

TABLE I. SWCNT film's thicknesses obtained by different methods.

SWCNT film		Measured thickness			Calculated thickness Thickness = $239 \times A_{550}$ (nm)
		Spectroscopic ellipsometry		AFM	
		Freestanding (nm)	On the glass substrate (nm)	On the glass substrate (nm)	
T_{550} (%)	A_{550}				
45	0.347	66 ± 8	76 ± 9	89 ± 7	83 ± 8
55	0.260	53 ± 5	60 ± 6	63 ± 5	62 ± 6
65	0.187	36 ± 6	48 ± 5	44 ± 5	45 ± 5
75	0.125	22 ± 5	19 ± 6	33 ± 4	30 ± 7
85	0.071	14 ± 4	16 ± 3	18 ± 2	17 ± 3
90	0.046	8 ± 4	7 ± 4	8 ± 3	11 ± 5

transmission spectra at 550 nm only. Surprisingly, the freestanding films show a small deviation toward the smaller thickness [Fig. 1(c)] attributed to efficient densification, which occurred due to the evaporation of the solvent from two sides of the film in contrast to the film on the glass. It is worth pointing out that for differently synthesized SWCNTs, the purity, packing density, chiral distribution, and tube diameters could be different. For this reason, the relation between the thickness and absorbance can vary among various carbon nanotube samples; for instance, Mikheev *et al.*⁴³ obtained the correlation coefficient of 417. Nevertheless, the linear dependence is conserved, which implies that the density of carbon nanotubes is the same for different thicknesses. Besides, we leveraged only the fundamental properties of the carbon nanotubes, and therefore, the procedure can be potentially applied to any SWCNT films and beyond the realm of carbon nanotubes, including recently introduced transition metal dichalcogenide nanotubes.⁵³

In conclusion, we have demonstrated the contactless method to measure simultaneously the optical constants and thickness of SWCNT thin films, both in the freestanding configuration and on a substrate. We systematically studied the SWCNT films with varying absorption between 90% and 45% at 550 nm and determined the broadband (250–3300 nm) refractive index and corresponding thickness of the films. We also found that the thickness is linearly correlated with absorbance at 550 nm with a 239 correlation coefficient and, thus, provides a rapid technique for thickness estimation. Furthermore, we have demonstrated a noticeable change in SWCNT film optical constants, by at least 40%, after the densification procedure, hence, enabling an efficient mechanism for light manipulation using carbon nanotube networks. To sum up, we anticipate our assay to be a starting point for more sophisticated carbon nanotube optical characterization and applications in science and technology.

See the [supplementary material](#) for optical constants of all SWCNT films used in this study.

AUTHORS' CONTRIBUTIONS

G.A.E. and A.P.Ts. contributed equally to this work.

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The authors declare no competing interest.

DATA AVAILABILITY

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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