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Optical Properties of Single-Wall Carbon Nanotube Films Deposited on Si/SiO₂ Wafers

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Abstract

The paper describes a set of simple experiments performed to develop an optical model to describe Si/SiO₂ substrates coated with two transparent films of carbon nanotubes. The final goal is to use such optical model to investigate the interaction of proteins with carbon nanotubes. Experiments were performed to assess light reflection as a function of the wavelength or angle of incidence using two substrates (same material, different amounts) composed of oxidized carbon nanotubes. The experimental results indicate that the selected carbon nanotubes layers are anisotropic and significantly different from each other. Experiments performed by spectroscopic ellipsometry (as a function of the wavelength and incident angle) enabled the development of an Effective Medium Approximation model consisting in a two-fraction phase (arc-evaporated carbon and void space). Furthermore, the model enabled calculating the amount of protein adsorbed on the surface of the carbon nanotubes film.

1. INTRODUCTION

Carbon nanotubes (CNT) are conductive, well-ordered, all-carbon hollow nanomaterials with a high aspect ratio [1]. Just like other nanostructured materials [2–5], CNT have shown unique properties (thermal, mechanical, electrical, biological, etc.) not found in other allotropic forms of carbon, such as graphite or diamond. Most of these extraordinary properties are linked to higher surface area, surface roughness, surface defects, and altered electron distributions [6]. For these reasons, CNT have contributed to the development of basic and applied studies in the fields of physics, chemistry, and material sciences. In particular, single-wall carbon nanotubes offer a well-defined atomic structure, high length to diameter ratio, and chemical stability. Depending on the atomic structure, single-wall CNT exhibit specific electronic, chemical, and physical properties [7]. Among biomedical applications [8–11], single-wall CNT are particularly useful as substrates for the preparation of biosensors because they are biocompatible [12,13] and stable over a large range of conditions, demonstrate catalytic activities towards many reactions [14–16], and provide significant increases in surface area [14]. Due to their small size and conductivity they can also be regarded as the smallest possible electrodes, with diameters as small as one nanometer [17]. When using CNT as substrates for biosensors it is crucial to understand the interaction between the recognition element (typically a protein) and the CNT because they can affect the protein conformation [18–22], cellular adhesion [23], and biocompatibility

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[18,24,25]. To understand the roots of these interactions, a detailed characterization of the CNT substrates must be performed.

Several techniques have been used to perform a morphological and structural characterization of CNT. Among others, scanning tunneling microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, neutron diffraction, X-ray diffraction, infrared spectroscopy, and Raman spectroscopy are the most commonly reported characterization techniques [26]. The main problem associated with these techniques is their limitation to perform *in-situ* measurements of adsorption of biological molecules under physiological conditions. An alternative technique to perform *in-situ* measurements is ellipsometry. [21]

Ellipsometry is an optical technique that measures changes in the reflectance and phase difference between the parallel (R_p) and perpendicular (R_s) components of a polarized light beam upon reflection from a surface. Using Equation 1,

$$\tan(\Psi)e^{i\Delta} = \frac{R_p}{R_s} \quad \text{Equation 1}$$

the intensity ratio of R_p and R_s can be related to the amplitude ratio ($\tan \Psi$) and the phase difference (Δ) between the two components [27]. Because ellipsometry measures the ratio of two values (R_p and R_s) originated from the same signal, the data collected are highly accurate and reproducible. The changes in polarization measured by ellipsometry are extremely sensitive to film thickness (down to the monolayer level), optical constants, and film microstructure (such as surface roughness, index grading, and intermixing). Most importantly, ellipsometry (and specifically the set-up described in this manuscript) enables investigating the adsorption of proteins in real-time, on a variety of substrates, and using aqueous environments. However, because the measurement is affected by the optical constants, thickness, and film microstructure, the interpretation of ellipsometric data requires an optical model. This is probably the biggest limitation of the technique, which will enable formulating conclusions that are only as good as the selected optical model.

Considering of the potential advantages of using ellipsometry to study the interaction of biomolecules with single-wall CNT, the objective of this paper was to develop a model able to describe the optical properties of transparent layers of single-wall CNT. To develop the model, the optical properties of two different substrates were investigated as a function of the wavelength and incidence angle using reflection and ellipsometric experiments. Finally, the model was used to gain insight into the interaction kinetics between a selected protein and carbon nanotubes [21].

2. MATERIALS AND MEASUREMENTS

2.1. Substrates

Single-wall CNT-coated silica (Si/SiO₂/CNT) surfaces were used for the present studies. As described in earlier studies [20,21,28], Si/SiO₂/CNT surfaces were prepared by Eikos Inc. (Franklin, MA), using <100> silicon wafers (Sumco, Phoenix, AZ) as substrates. According to the provider, a layer of CNT was deposited on the wafers using arc-produced single wall CNT having about a 1.3 nm diameter. The raw material formed in the arc reactor was purified, to remove metal catalyst and non-tubular forms of carbon, by a process of acid reflux, followed by washing and centrifugation. This process is known to introduce carboxylic acid groups on the surface of the CNT, and therefore the results discussed in this paper should not be broadly applied to CNT films prepared by other methods. Once purified, the nanotubes were dispersed in water and alcohol to form an ink. This dispersion was then

spray-coated onto the Si/SiO₂ wafer heated to 65 °C while monitoring deposition rate. The coating formed is essentially a layer of pure single-wall CNT and contains no residual organic additives or polymeric constituents. For the experiments described in this paper, two types of CNT films were prepared in the same way, but containing different amounts of single-wall CNT. These two films will be denoted as Si/SiO₂/CNT_{LOW} (for the film containing the lowest amount of CNT) and Si/SiO₂/CNT_{HIGH} (for the film containing the highest amount of CNT). Control experiments were also performed using the same Si/SiO₂ wafers without the CNT layer.

2.2. Spectroscopic ellipsometry

As described elsewhere [21], the substrate characterization as well as the dynamic adsorption experiments were performed at room temperature using a variable angle spectroscopic ellipsometer (VASE, J.A. Woollam Co; Lincoln, NE). Initially, different substrates were analyzed using light reflection for p-polarization and s-polarization by varying the angle of incidence from 60° to 85°, in 0.5° increments. Ellipsometry data (amplitude ratio (Ψ) and phase difference (Δ) as a function of wavelength (λ) or time) were obtained and modeled using the WVASE[®] software package (J.A. Woollam Co; Lincoln, NE). The difference between the experimental and model generated data was assessed by the mean square error (MSE) defined by Equation 2,

$$MSE = \frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\Psi_i^{\text{mod}} - \Psi_i^{\text{exp}}}{\sigma_{\Psi,i}^{\text{exp}}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^2 \right] = \frac{1}{2N - M} X^2 \quad \text{Equation 2}$$

where N is the number of Ψ and Δ pairs used, M is the number of parameters varied in the regression analysis, and σ is the standard deviation of the experimental data points. Although smaller MSE values indicate better fittings, MSE < 15 are typically considered acceptable [28,29].

In all cases, the sample under investigation was mounted on a micrometer-position-controlled translation stage with the gradient direction perpendicular to the plane of incidence. Substrates were initially characterized in air, varying the incident angle between 60° and 70° (with respect to the substrate), and the wavelength between 250 nm and 900 nm. The structure of the adsorbed films of protein was evaluated in aqueous media using a commercial cell (J.A. Woollam Co; Lincoln, NE). More details of the cell can be found elsewhere [21].

2.3. Reagents and solutions

All aqueous solutions were prepared using 18 M Ω -cm water (NANOpure Diamond, Barnstead; Dubuque, Iowa) and analytical reagent grade chemicals. Sodium pyrophosphate (Na₄P₂O₇), sodium chloride, and sodium hydroxide were purchased from Fisher Scientific (Fair Lawn, NJ). The pH of the solutions was adjusted using either 1 M NaOH or 1 M HCl (Fisher Scientific; Fair Lawn, NJ) and measured using a glass electrode and a digital pH meter (Orion 420A+, Thermo; Waltham, MA). D-amino acid oxidase (Sigma; Saint Louis, MO) from porcine kidney was purchased as a lyophilized powder (1.5 U·mg⁻¹) and kept at -4 °C until used. Stock solutions of protein (0.1 mg·mL⁻¹) were prepared by dissolving a known amount of protein in pyrophosphate buffer. Other solutions of proteins were prepared by diluting the corresponding amount of stock in pyrophosphate buffer. In all cases, the concentration of the stock solution was confirmed by spectrophotometry (Genesys 10uv, Thermo Elec. Corp.).

3. RESULTS AND DISCUSSION

3.1. Optical Characterization

Despite the enormous technological relevance, there are only a few reports describing the optical properties of thin CNT films [7,30]. The most relevant problems associated with these measurements stem from the fact that CNT films are typically composed of a mixture of metallic and semiconducting scrambled carbon nanotubes. As a consequence, CNT films are neither flat nor smooth. Recently, Wu et al. described the optical properties of self-standing CNT films (240 nm thick) in the IR region of the spectrum [31]. Barnes *et al.* reported optical and electrical properties of single-wall CNT films deposited on glass and quartz substrates [28] and noted a large absorption peak at around 4.4 eV (~282 nm). This peak was attributed to the π -plasmon resonance of the metallic single-wall CNT. However, they pointed out that although absorption spectra can be determined simply by subtracting the transmission and reflection spectra from unity, it is not known if neglecting the reflection data is an acceptable approximation for CNT films. In order to explain the optical reflectance of thick films of single-wall CNT and taking advantage of the reflective nature of the Si/SiO₂ substrates, reflection measurements were performed at p-polarization (parallel to the plane of incidence) using 70° and 80° as the angles of incidence (in air). The first angle (70°, Figure 1) was selected because it is the incident angle in the liquid cell used for the protein adsorption experiments and it is close to the Brewster angle of most substrates. Based on preliminary experiments, the second angle (80°, Figure 2) was selected to highlight the differences between the two CNT films under investigation. In both cases, the spectra corresponding to the three selected substrates showed two reflection peaks at approximately 265 nm and 365 nm, corresponding to energy values of 4.69 and 3.41 eV, respectively. However, when 80° was used, a third reflection peak was obtained at 334 nm in the Si/SiO₂/CNT_{HIGH} substrate. These electronic transitions have been associated with π -electrons present in the CNT network that (in the case of nanoscale objects) could be collectively excited originating a surface plasmon [32]. To identify the magnitude and position of these transitions is relevant because they can be related to specific properties of single-wall CNT such as anisotropy [28,33], structure [26,34], size distribution [35], chirality [36], or method of synthesis. Specifically, it has been reported that a dominant feature is present at approximately 4.5 eV when the CNT are randomly oriented, but shifts to approximately 5.25 eV if the film is vertically aligned on the substrate [37]. Although the results shown in Figure 1 and Figure 2 indicate that both peaks could be attributed not only to the CNT layer but also to the SiO₂ substrate, the position of these features are in agreement with the presence of a film of randomly distributed CNT with the expected anisotropic behavior [28]. A comparison of R_s (as a function of the wavelength, data not shown) with respect to R_p (Figure 1 and Figure 2), along with the relatively sharp reflection peaks observed at both angles, suggested that the propagation of the electric field (normal to the substrate plane) couples more strongly than the electric field in the substrate plane, again supporting the anisotropic behavior.

The two single-wall CNT films (Si/SiO₂/CNT_{LOW} and Si/SiO₂/CNT_{HIGH}) and the Si/SiO₂ substrate were also investigated as a function of the angle of incidence (in the 60° to 85° range) at a wavelength of 365 nm. This wavelength was selected based on the absorption peak observed in Figure 1 and Figure 2. As shown in Figure 3, the reflectivity curves generally possess a parabolic dependence with respect to the incident angle. It is also evident that although the two studied CNT films exhibit different optical properties, the film Si/SiO₂/CNT_{HIGH} showed the most significant difference with respect to the Si/SiO₂ substrate. According to these results, pseudo-Brewster angles of 81°, 80°, and 71° were observed for the Si/SiO₂, Si/SiO₂/CNT_{LOW}, and Si/SiO₂/CNT_{HIGH} substrates, respectively. The relevance of these results is threefold. First, considering that shifts in pseudo-Brewster angles as small as 1° indicate the presence of a layer with significantly different properties,

the shifts observed in Figure 3 (up to 10°) confirmed the need to characterize these films individually. Second, the results demonstrate that even simple experiments performed with the ellipsometer could provide complementary information regarding the substrates that other techniques (such as atomic force microscopy or scanning electron microscopy) can not provide. Third, because the ellipsometric parameters are most sensitive to changes in the vicinity of the Brewster angle, experiments performed in commercial liquid cells may require additional considerations to overcome the limitations imposed by the fixed angle of incidence. Although shifts in the pseudo-Brewster angle have been linked to different phenomena,[38–40] our results are in agreement with previous reports stating that angular shifts can be correlated to increased layer phase thickness.[41]

The two single-wall CNT films ($\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$ and $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$) and the Si/SiO_2 substrate were also investigated using spectroscopic ellipsometry (SE). Figure 4 and Figure 5 show the dependence of ψ ($^\circ$) and Δ ($^\circ$) as a function of the wavelength (λ) of the incident light beam using air as the ambient for $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$ and $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$, respectively. Although both substrates were investigated using 65° , 70° , and 75° as incidence angles, only the results obtained at 70° are shown in the figures. In agreement with the data previously discussed, both CNT-coated samples and the Si/SiO_2 substrate showed two distinctive features at 265 nm and 362 nm. By comparing Figure 4 and Figure 5, it is also evident that both samples (although made with the same starting material) displayed significantly different optical properties. The most challenging aspect of these results was to develop an optical model that could describe both substrates.

3.2. Optical Model

Carbon films have been represented by a wide variety of optical models including Tauc-Laurencz [42–44], effective medium approximation (EMA) [45], and general oscillators [28]. However, the validity of these models is heavily influenced by the particular composition and microstructure of the substrate. Consequently, several different models were evaluated in order to describe the selected substrates in terms of the refractive index (n), extinction coefficient (k), and thickness (d). Based on the difference between the experimental and model-generated data, the mean square error (MSE) was used to select the most appropriate optical model. According to our results, the best fit was obtained when the substrates were modeled by three uniform uniaxial layers, with optical axes parallel to the substrate surface. The dielectric functions of the substrates were described using a layer of Si (bulk; $d = 1$ mm), a layer of SiO_2 ($d = 3$ nm), and a two-media Bruggeman EMA model consisting of a fraction (f) of arc-evaporated carbon [46,47] and a fraction of void space ($1-f$). The thickness of the EMA layer ranged between 15 to 40 nm depending on the substrate used. As shown in Figure 4 and Figure 5, the same optical model could be used to accurately describe the properties of both CNT films ($\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$ and $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$) with MSE values of 5.03 and 7.54, respectively. The main difference is that the fraction of void space in $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$ was found to be 98%, while the fraction of void space in the $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$ film was found to be 30%. This optical model is in good agreement with previous reports [20] but differs slightly from other models used to describe CNT films prepared under different conditions [28,31,33,48]. This singularity was expected, as nanotubes prepared (or purified) by different methods may have different electrical and optical properties due to different excitonic transitions between the van Hove singularities [49–53].

It is worth noting that the model was also able to describe substrates with the same fraction of void space but ranging in thicknesses from 15 nm up to 40 nm (data not shown). The calculated thickness values as well as the structure of the film used in the optical model were verified by performing atomic force microscopy and scanning electron microscopy on the selected substrates (data not shown). SEM pictures of the substrates have been previously

reported in literature [21]. Although it is not possible to precisely quantify the empty space from the SEM and AFM pictures, it is clear that the proposed model is consistent with the physical characteristics of the films. It is worth mentioning that ellipsometry (light spot $\sim 1\text{mm}^2$) was not sensitive to slight variations (spot-to-spot and sample-to-sample) observed by microscopy.

As previously stated, the dielectric functions of the substrates were described using a layer of Si, a layer of SiO_2 , and a two-media Bruggeman effective medium approximation (EMA) model consisting of arc-evaporated carbon and void space. The corresponding values of n and k values for the three materials used in the manuscript (arc-evaporated carbon, the CNT layer of $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$, and the CNT layer of $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$) are provided in Figures 6A, 6B, and 6C, respectively. As it can be observed, the dependence of n and k in the three substrates is very similar, but decreasing in magnitude as the amount of CNT in the films decreases.

3.4 Adsorption of Proteins to CNT

As previously stated, the goal of this paper was to develop an optical model that enables studying both the formation kinetics as well as the structure of proteins adsorbed to the single-wall CNT layers by spectroscopic ellipsometry [21]. Spectroscopic ellipsometry experiments were performed by placing the substrates in the liquid cell, covering them with buffer, and measuring the ellipsometric angles (as a function of wavelength) using water as the ambient medium.

Although the proposed optical model was able to describe the optical properties of the $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$ (98% void) substrate ($\text{MSE} = 5.0$) when immersed in aqueous solutions (and using water as ambient), a significant disagreement was obtained between the experimental and the model-generated data for the $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$ (30% void) substrate ($\text{MSE} > 20$). Preliminary results (to be reported) suggest that the substrates containing a higher load of singlewall CNT ($\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$, 30% void) may significantly swell (up to 3 times) when submerged in buffer ($\text{pH}=5.6$) for ~ 10 hours. For this reason, further experiments related to the interaction of proteins to carbon nanotubes were performed using the $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$ (98% void) substrates.

For the adsorption experiments, the adsorbed proteins were modeled with an additional non-absorbing layer (denoted as “protein” in Figure 7), whose optical constants were described using a Cauchy parameterization model, according to Equation 3,

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad \text{Equation 3}$$

where A , B , and C are computer-calculated fitting parameters and λ is the wavelength of the incident beam. Figure 8 shows the dependence of the ellipsometric angles (Ψ and Δ) as a function of the wavelength (in the 250 to 850 nm range) for a layer of protein (D-amino acid oxidase, DAAO) adsorbed to a $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$ (98% void) substrate. The thickness of the protein layer was calculated to be 5.2 ± 0.1 nm. As can be observed, a very good agreement ($\text{MSE} = 3.49$) was obtained between the experimental data and the data generated by the proposed optical model. As reported elsewhere [21], these results suggest the formation of a monolayer of DAAO on the CNT surface. Considering that DAAO exhibits an elongated ellipsoidal framework with approximate dimensions of 11 nm (length) $\times$ 4 nm (width) [54], the thickness values obtained under the selected experimental conditions indicate that DAAO adopted a tip-to-surface alignment (slightly tilted) with respect to the CNT surface. The amount of adsorbed protein (Γ , expressed in $\text{mg}\cdot\text{m}^{-2}$) can be determined using Equation 4,

$$\Gamma = \frac{d(n - n_0)}{(dn/dc)} \quad \text{Equation 4}$$

where d is the thickness value of the adsorbed layer, n is the refractive index of the protein, and n_0 is the refractive index of the ambient (H_2O) [55]. In accordance with previous reports [56–59], the refractive index increment for the molecules in the layer (dn/dc) was assumed to be $0.187 \text{ mL}\cdot\text{g}^{-1}$. Under these conditions, the amount of adsorbed DAAO, calculated from Figure 7 was $3.8 \pm 0.2 \text{ mg}\cdot\text{m}^{-2}$.

Table 1 summarizes the most important results related to the thickness of each layer in the studied films. Two other aspects are also worth noting. First, the reflection peak observed at $\sim 275 \text{ nm}$ (at Ψ axis in Figure 8) was attributed to an absorption band of the adsorbed DAAO molecules. This absorption peak was verified by measuring a spectral curve of DAAO in solution under the same experimental conditions (data not shown). Second, the use of alternative optical models, such as those considering the possibility of DAAO penetrating in the CNT layer, or those including surface roughness did not yield any significant improvement in the MSE value.

4. CONCLUSIONS

The paper describes a set of simple experiments performed to develop an optical model to describe Si/SiO₂ substrates coated with two different transparent films of single-wall CNT. Although a considerable contribution from the Si/SiO₂ substrate overlapped with the expected π -plasmon resonance of the CNT, the obtained results (p-reflection as a function of the incident wavelength or incidence angle) suggest that the single-wall CNT layers are anisotropic and significantly different. Experiments performed by spectroscopic ellipsometry (as a function of the wavelength and incident angle) enabled the development of an EMA model consisting of a combination of arc-evaporated carbon and void space. Although one of the films (Si/SiO₂/CNT_{HIGH}, 30% void) significantly changed when introduced in water (possibly swelling), the other film (Si/SiO₂/CNT_{LOW}, 98% void) enabled studying the interaction of a protein (DAAO) with single-wall CNT. It is expected that further developments in the area of ellipsometry will enable the systematic investigation of the interactions of proteins with nanophased materials.

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Figure 1. Reflection at p-polarization for substrates of Si/SiO_2 , $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$, and $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$ as a function of the wavelength at an angle of incidence of 70° .

Figure 2. Reflection at p-polarization for substrates of Si/SiO_2 , $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$, and $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$ as a function of the wavelength at an angle of incidence of 80° .

Figure 3. Reflection at p-polarization for substrates of Si/SiO_2 , $\text{Si/SiO}_2/\text{CNT}_{\text{LOW}}$, and $\text{Si/SiO}_2/\text{CNT}_{\text{HIGH}}$ as a function of the angle of incidence, collected using 365 nm as the incident wavelength.

Figure 4.

Ψ - Δ curves for substrates of Si/SiO₂/CNT_{LOW} as a function of the wavelength collected at an angle of incidence of 70° and using air as the ambient (MSE= 5.51).

Figure 5.

Ψ - Δ curves for substrates of Si/SiO₂/CNT_{HIGH} as a function of the wavelength collected at an angle of incidence of 70° and using air as the ambient (MSE= 6.97).

Figure 06A

Figure 06B

Figure 06C

Figure 6. Optical constants (n and k) for the materials used in the manuscript. A) arc-evaporated carbon, B) the CNT layer of Si/SiO₂/CNT_{HIGH}, and C) the CNT layer of Si/SiO₂/CNT_{LOW}.

Figure 7.

Optical model proposed to describe the formation of a layer of DAAO on the Si/SiO₂/CNT_{LOW} substrate. Adsorption conditions: 5 mM pyrophosphate buffer pH = 5.75 and [DAAO] = 0.01 mg/mL; flow rate: 1.8 mL/min.

Figure 8. Ψ - Δ relationship obtained from the spectroscopic ellipsometer for DAAO layer (5.2 ± 0.1 nm) adsorbed on the Si/SiO₂/CNT_{LOW} (98% void) substrate (MSE= 3.49).

Table 1**Soetedjo, Mora, and Garcia**

Summary of the composition, thickness of each layer (Si, SiO₂, CNT, and DAAO), ambient, and mean square error (MSE) calculated for the selected substrates described in the corresponding figures.

Substrate	Void	Si	SiO ₂ (nm)	CNT (nm)	DAAO (nm)	MSE	Ambient	Fig.
Si/SiO ₂ /CNT _{LOW}	98%	Bulk	3.0 ± 0.1	22 ± 2	-	5.51	Air	4
Si/SiO ₂ /CNT _{HIGH}	30%	Bulk	3.0 ± 0.1	21.5 ± 0.1	-	6.97	Air	5
Si/SiO ₂ /CNT _{LOW}	98%	Bulk	3.0 ± 0.1	24 ± 2	-	2.77	Buffer	7
Si/SiO ₂ /CNT _{LOW}	98%	Bulk	3.0 ± 0.1	24 ± 2	5.2 ± 0.1	3.49	Buffer	7