Nanotube/Nanodiamond Based Thin Film Coatings

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Abstract—We report on the characterization of thin-film near and short wavelength infrared absorbers comprised of carbon nanotubes dispersed in a polymer. Charged nanodiamond particles are used to effectively and uniformly disperse the carbon nanotubes in the polymer matrix, leading to a very homogeneous film. Using this new technique, we demonstrate an infrared absorption of up to 95% in films with thicknesses <2000 nm. This remarkably high absorption is the result of low reflection off the surface and high absorption across the film thickness. The complex refractive index of the films is extracted using an effective media approximation. Calculations show the film has a wide angle for high absorption and is polarization independent. These films are easy to fabricate, robust and damage resistant, and are compatible with post-processing techniques. These films can be used as the coating layer to boost the efficiency of uncooled infrared sensors and solar-thermal energy harvesters.

Index Terms—Carbon nanotubes, nanodiamonds, infrared sensor, thin films, coating.

I. INTRODUCTION

THIN film coatings and optical metamaterials with engineered absorption, transmission, or reflection properties are critical components of numerous optical devices and systems, including infrared (IR) detectors, filters, modulators, radiation absorbing layers, and energy harvesters [1]–[4]. Specifically for thermal IR detectors, thin film coatings are needed that provide efficient absorption of incident radiation and convert it into thermal energy [5]–[8]. The generated heat is then transduced to other usable forms of energy (e.g. electrical energy) using other materials in contact with the absorber. This principle forms the basis of many thermal detectors, including thermocouples, bolometers, pyroelectric and resonant detectors [5], [6]. Absorber layers for IR detectors require the following attributes [8]: (i) high and polarization independent absorption [2], (ii) low thermal and inertial mass, (iii) good thermal conductivity, (iv) stable and reproducible properties, and (v) manufacturable using a process compatible with detector and electronics fabrication technologies. Similarly, for solar-thermal energy harvesting, a material is required that is an efficient absorber across a broad spectrum ranging from visible to at least near-IR [9].

Popular solutions that meet some of these requirements include thin metal films, resonant cavity structures, plasmonic metamaterials, and porous surfaces. However, ultra-thin metal films are limited in terms of absolute absorbance and are not temperature stable [11]. Porous films and metal-blacks require well controlled etch chemistry and suffer from temperature instability [12]. Surface plasmonic resonances (SPR) and quarter wavelength cavity resonances are good solutions for selective detection with spectral bandwidths on the order of 10% or lower in the visible-IR range, but need precise control of design and fabrication to achieve this goal [2], [8]. Extending these mechanisms to broadband absorption is difficult [13]. Another more recent method utilizes vertically aligned arrays of carbon nanotubes (CNTs) as broadband visible/IR absorbers [1], [4], [14]. The principle of absorption here is based on trapping light in the sparse and tall CNT arrays. The sparsity enables very close matching of the refractive index to that of free space/air. The height of the arrays (tens to hundreds of microns) allows for multiple internal reflections and the eventual absorption of all incident radiation over a large spectral range. While the measured absorption of these arrays is excellent [14], the drawback of this approach is their large mass and thermal loading on the detector. In addition, the high temperatures and catalytic surfaces required for vertical CNT arrays, the precise sub-micron lithography required for SPR absorbers, and the etch chemistry control required for porous metal and metal-black films make these methods prohibitive for economical, large scale fabrication.

In this work, we present a thin film material [15] that has a refractive index \( n \) close to unity and a high extinction coefficient \( k \) at near infrared (NIR) and short wavelength infrared (SWIR) range. The absorber is thin and light so that the transducer is not significantly loaded mechanically or thermally. The film is easy to fabricate on any surface, and at low manufacturing cost. The measured absorption is as high as 95% over a broad spectral range. The absorber material comprises of a mixture of multiwalled CNTs and detonation nanodiamond (DND) particles suspended in a polymer matrix. This material offers markedly high absorption efficiency per unit thickness over a broad range in the NIR/SWIR spectrum, making it an ideal candidate for use in applications requiring low-profile coatings. The low cost, ease of manufacturability,
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Fig. 1. A schematic showing one of the intended applications of the carbon nanotube/nanodiamond/polymer based coating: a focal plane array of resonant IR detectors [10]. Each array comprises of multiple thermal detector “pixels” that are individually addressed, forming an imaging system with high spatial resolution. The detectors are coated with the absorber layer, which efficiently converts the incident radiation into heat.

and ease of integration with electronics and microsystems makes this an attractive material for use in IR detectors and thermal energy harvesters (Fig. 1).

II. EXPERIMENTAL RESULTS

A. Fabrication of CNT/DND/Polymer Nanocomposite

Researchers have previously fabricated horizontally dispersed CNT mats for infrared absorption using vacuum filtration [16]–[19] or airbrushing [20]. Neither method gives the desired combination of very thin films that are mechanically stable and can be further patterned or processed. In the procedure described in detail elsewhere [15] and summarized below, CNT powder is commercially purchased at low cost and mixed with a polymer (i.e., poly-(methylmethacrylate) (PMMA)) [21] in order to provide the eventual film with the required mechanical and thermal stability, and amenability to post-processing. In the spun layers of CNT/PMMA, the orientation of the CNTs is generally horizontal and follows no particular order, other than the strong tendency to agglomerate into bundles due to surface forces [8], [21], [22] (Figs. 2(a) and (b)). The agglomeration of CNTs in the polymer can be prevented by mixing surfactants to separate the CNT bundles. In this work, electrically charged DNDs are used as effective surfactants, counteracting the CNT agglomeration by electrostatic repulsion [22]. Unlike liquid surfactants, the DNDs are not volatile and remain in the film after spinning and baking. The DNDs used in this work have an average diameter of 30 nm and a $\zeta$-potential of +45 mV. Ultrasonication aids with dispersing CNTs in the polymer by shearing the CNTs, but is largely ineffective without the DNDs. The final CNT/PMMA/DND layer is mechanically and thermally stable and can be spin coated on a substrate and patterned using standard photolithography and plasma etching.

Further addition of dimethylsulfoxide (DMSO) as a liquid surfactant helped with achieving lower viscosity and thus thinner films. For films having 0.6 w/v % DND and 0.2 w/v % CNT in DMSO, we were able to achieve excellent dispersion of the CNT films with surface roughness in the range of 50 to 100 nm [15], over a substrate size of 25 mm $\times$ 25 mm (Figs. 2(c) and (d)). This is in stark contrast to the large ($\sim$10 $\mu$m thick) agglomerates encountered prior to the addition of the DNDs (Fig. 2(b)), and thus the addition of DNDs proved crucial to this process. With a low spin speed ($<500$ rpm), we were able to get consistent, visibly black films on a glass substrate, with a thickness on the order of 300 nm per layer. Following the spinning process, the films were baked on a hotplate at 110 °C to evaporate the DMSO solvent and cure the polymer. This bake step represents the maximum temperature used in this entire process. Multiple layers of the film can be sequentially deposited to increase the film thickness if needed (Fig. 3). The films discussed in further sections have multiple layers resulting in measured thicknesses of 1600 nm and 2000 nm (5 and 7 layers, respectively).

B. Infrared Absorption

To characterize the IR absorption properties of the CNT/DND based polymer, normal incidence reflection $R_{\text{exp}}(\lambda)$ and transmission $T_{\text{exp}}(\lambda)$ measurements are acquired on glass slides coated with the thin films using a Perkin
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Fig. 4. A schematic of the normal incidence transmission and reflection test setup. The measurements are normalized using uncoated glass substrates for transmission and a standard gold reference for reflection.

Fig. 5. (a) The reflection, transmission, and the absorption of the 1600 nm and 2000 nm films. (b) Transmission measurement for a 2000 nm thick layer of poly-methylmethacrylate (PMMA) on a glass substrate, indicating that the PMMA itself does not contribute significantly to the IR absorption.

Elmer Spectrum GX in the spectral range of 4000 cm\(^{-1}\) to 14000 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\). Transmission measurements are normalized to an identical uncoated glass substrate, while reflection measurements are normalized to an uncoated glass substrate placed on a gold coated standard (Fig. 4) [23], [24]. Absorption for the film \(A_{\text{exp}}(\lambda)\) is calculated as \(A_{\text{exp}}(\lambda) = 1 - R_{\text{exp}}(\lambda) - T_{\text{exp}}(\lambda)\). Measured results for the two samples demonstrate a high broadband absorption (Fig. 5(a)). The effect of pure PMMA layers is considered (Fig. 5(b)) and measurements prove that it does not contribute significantly to the absorption.

C. Stability and Damage Resistance

With the inclusion of a polymer matrix, the films are fairly resistant to damage. They have endured some standard micromachining processes including evaporation/sputtering, liftoff, and some acid etches. The IR performance of the films does not change significantly after cycling at elevated temperatures (Fig. 6) and the films do not degrade perceptibly.

One of the main requirements of an absorber is to have stability at high irradiation powers. To study the laser damage resistance of the CNT/DND based polymers, preliminary testing has been carried out using a procedure similar to the one reported for gold black [25]. In this experiment, single 6 ns pulses from a 532 nm Nd:YAG laser with a 160 mJ output energy were irradiated onto the sample (Fig. 7). Spot diameter was maintained at 1 mm using a fixed aperture. Various input energy levels were obtained using neutral density filters with known attenuation. Most samples show some slight visible change above energy densities of 13 mJ/cm\(^2\), and are completely ablated above 28 mJ/cm\(^2\). Thus initial results shown in Fig. 8 indicate that these films have similar tolerances to gold black [25] and can be used as detector coatings in high power environments. More rigorous testing is necessary to verify the use of these films in laser radiometry.

III. ANALYSIS

A. Extraction of Optical Parameters

Optical properties of ordered arrays of nanotubes can be analytically modeled [26]. However, because of the random dispersion of CNT/DNDs in the polymer, accurate modeling of the optical properties is challenging for the presented films. Instead, the optical constants are extracted from the
measured results using an effective media approximation. Measured results are compared to Heavens’ model for normal incidence [27], which self-consistently relates $R_{\text{exp}}(\lambda)$ and $T_{\text{exp}}(\lambda)$ with the effective complex refractive index of the material $(n - ik)$. For dominantly absorbing films, Heavens’ relation can be approximated by the following system of equations [28].

$$T_{\text{mod}}(\lambda) = \frac{16n_0n_s(n^2+k^2)}{(n+n_i)^2 + (k+k_s)^2} e^{-\alpha_{\text{ns}}}$$

$$R_{\text{mod}}(\lambda) = \frac{(n_0-n)^2+k^2}{(n_0+n)^2+k^2}$$

$$\alpha(\lambda) = \frac{4\pi kd}{\lambda}$$

where $n$, $k$, $d$, $\lambda$, $\alpha$ describe the refractive index (real part), extinction coefficient, total film thickness, wavelength, and dimensionless attenuation of the thin film, respectively. The subscript $\text{mod}$ refers to modeled values, while the subscripts $s$ and $0$ specify indices for the substrate and free space, respectively. As the measured results are normalized to the substrate, the calculation is effectively for a freely suspended CNT/DND/PMMA film [24]. A bivariate Newton-Rhapson method is used to fit the $(n, k)$ values according to the iterative algorithm given by

$$\left[ \begin{array}{c} T_{\text{mod}} \\ R_{\text{mod}} \end{array} \right]_{p+1} = \left[ \begin{array}{c} T_{\text{mod}} \\ R_{\text{mod}} \end{array} \right]_{p} + J_p^{-1} \left[ \begin{array}{c} T_{\text{exp}} - T_{\text{mod}} \\ R_{\text{exp}} - R_{\text{mod}} \end{array} \right]_p,$$

$$J_p = \left[ \begin{array}{cc} \frac{\partial T_{\text{mod}}}{\partial n} & \frac{\partial T_{\text{mod}}}{\partial k} \\ \frac{\partial R_{\text{mod}}}{\partial n} & \frac{\partial R_{\text{mod}}}{\partial k} \end{array} \right]_p.$$

The error between the modeled and measured results is given by \(\left(\frac{T_{\text{mod}} - T_{\text{exp}}}{T_{\text{exp}}}\right)^2 + \left(\frac{R_{\text{mod}} - R_{\text{exp}}}{R_{\text{exp}}}\right)^2\), and iteration is continued until error is reduced to $10^{-12}$, guaranteeing a very precise fit. Extracted values for $(n, k)$ from the two films are shown in Fig. 9(a) and Fig. 9(b), respectively. Solutions do not converge at the noisy edges of the measurement range close to 700 nm and 2400 nm.

Physically, the absorption in the film has significant contributions from scattering due to the many scattering centers provided by the well-dispersed CNTs with a diameter much smaller than the wavelength, as well as the intrinsic absorption provided by the CNTs. The small DND particles are not expected to contribute significantly to the optical absorption. These well-dispersed and dense films have at least an order of magnitude higher extinction coefficient $k$ than vertically aligned CNT forests of the same thickness [4]. Increasing the density and improving the dispersion homogeneity of the CNTs in the matrix can further increase scattering and improve the effective extinction coefficient of the films. However, this could adversely impact the value of $n$. It can be seen from Fresnel’s equations that $n$ should be as close to unity as possible to provide near-perfect index matching to the free space. The nature of the film surface poses some restrictions on index matching, leading to non-zero reflection. Reflections can be further suppressed by using a very thin anti-reflection coating on the nanocomposite.

A good comparison of the attenuation in the films is achieved by comparing the attenuation per unit thickness $(\alpha/d)$ (Fig. 10(a)). Increasing the number of layers improves the absorption (Fig. 10(b)). When the film thickness reaches a value five times the optical penetration depth, more than 99% absorption is achieved and increasing the film thickness further does not change the $(\alpha/d)$ ratio significantly [24]. This is consistent with the high absorbance in the 1600 nm and the 2000 nm films with penetration depths much less than the film thickness. The penetration depths of the films are simulated using COMSOL [29] and using the measured values for $n$ and $k$ as shown in Fig. 11. The inset of Fig. 11 shows the power absorbed in the suspended 2000 nm film, for normal incidence with two representative wavelengths of 600 nm and 2500 nm. The optical power absorbed in the layer manifests itself as a change in the temperature of the film, which is the desired result. The measured trend is consistent with the reported data, and measurements in the mid ($3 \mu m$–5 $\mu m$) and far IR ($8 \mu m$–$14 \mu m$) range for randomly dispersed CNT mats indicate that the penetration depths are on the order of 300 nm to 500 nm [18]. This makes it possible to realize thin film absorbers with $\geq 99\%$ absorption and still maintain a profile below $\sim 2000$ nm. As mentioned earlier, the film thickness can be further reduced to submicron levels by increasing the CNT density and reducing surface reflections using anti-reflection coatings.
Fig. 10. (a) Measured attenuation per meter $\alpha/d$ of the films. The values are consistent with other published data on dispersed CNTs [18]. (b) Absorption as a function of film thickness at the representative NIR/SWIR wavelength of 1.4 $\mu$m.

Fig. 11. Simulated optical penetration depth as a function of wavelength at normal incidence for the 1600 nm and 2000 nm thick CNT/PMMA/DND films. (Inset) Power absorbed in the suspended 2000 nm film, for normal incidence with two representative wavelengths of 600 nm and 2500 nm, showing the wavelength dependence of penetration depth. Blue arrows indicate time averaged power flow vectors.

B. Angular Dependence

Finite element simulations are used in order to verify the normal incidence measurements and extend the analysis to other angles. The COMSOL simulations agree with the measured data (Fig. 12), confirming that the effective media approximations can accurately describe the optical performance of the fabricated CNT-based nanocomposites.

As shown in Fig. 13, the films remain highly absorbing even at large incidence angles ($\theta_i$), with the absorption efficiency greater than 90% at 45°, and greater than 80% at 60°. Only as $\theta_i$ approaches 85° the reflection overshadows the absorption (Fig. 13). The film is bi-axially symmetric in-plane and therefore, the TE and TM polarization yields similar results. The large range of acceptance angles with a very high absorbance makes this an especially attractive material for thermal detectors and energy harvesters.

IV. CONCLUSION

The results presented in this work demonstrate the potential of CNT/DND based polymer films as efficient absorbers of NIR/SWIR radiation. The measured data indicate IR absorption comparable to thick vertical CNT arrays, but in a considerably thinner film. The addition of the polymer gives the film mechanical stability and makes it possible to pattern the film lithographically. Further work on this material can foreseeably improve attenuation per unit length by increasing the CNT volume fraction and improving the CNT dispersion, allowing submicron films that can absorb as efficiently. Rigorous investigation is also needed to characterize the thermal conductivity, heat capacity, and electrical characteristics of this class of materials as a function of the CNT fraction in the polymer.

The processing used for fabrication of these films is done at low temperatures and is compatible with other upstream and downstream micromachining processes, giving us the possibility to integrate these films into infrared sensors, focal
plane arrays, high optical power detectors, and microscale energy harvesters.

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REFERENCES


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