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Moth-eye effect in hierarchical carbon nanotube anti-reflective coatings

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ABSTRACT

Optical anti-reflection is achieved in natural surfaces by exploiting hierarchical surface morphology. Here, we show that single-walled carbon nanotube (SWCNT) coatings deposited on silicon (Si) realize a broad-band, omnidirectional, and nearly polarization-independent suppression of Si optical reflection, with an increase of film absorption. This is attributed to a biomimetic, hierarchical surface morphology, which introduces a graded refractive index—the so-called moth-eye effect. Moreover, the anti-reflective behavior can be tuned by varying the SWCNT film thickness. The SWCNT random networks are realized by a simple, rapid, reproducible, and inexpensive solution-processing technique and deposited on Si by a dry-transfer printing method, at room temperature. The technology may be used to coat arbitrary substrates such as optical instruments, radiometric applications, light and thermal sensors, solar cells, and light emitting diodes; thus improving the device absorption or emission of light, due to the film optical properties.

1. Introduction

Some insects benefit from anti-reflective surfaces, either on their eyes to see in low-light conditions or on their wings to reduce surface reflections from transparent structures, apparently in order to avoid predators [1,2]. For instance, the moth eye [2] surface consists of hundreds pillars with rounded tips, each approximately 200 nm in diameter and 500 nm in height with a periodicity of around 240 nm. These are arranged in a hexagonal array on micron-scale structures. Therefore, they realize a two-fold surface hierarchical morphology. The smaller surface features, which are sub-wavelength in size, attenuate reflection at short wavelengths [3], while larger features attenuate at longer wavelengths [4]. A great diversity of anti-reflective architectures can be found in nature, which includes microribs with nanoridges, concave multi-layered pits, blazed gratings, and randomly punctuated nanolayers [5].

Effectively, the structure of the moth eye introduces a graded refractive index profile [6,7] at the interface between the protein matrix constituting the insect eye ($n = 1.54$) and air ($n = 1.00$). This structure reduces eye reflectance below 1% over a broad range of the electromagnetic spectrum [4]. A refractive index gradient means that at any depth the effective refractive index is the average of the bulk material and air indices, proportionally weighted to the fraction of material present at that depth, thereby creating an effective medium [4]. Such a particular surface makes moth eyes anti-reflective up to large angles of incidence $\theta > 60^{\circ}$ (omnidirectionality) [8]. Furthermore, as a consequence of the reduction in reflection, an increase in optical transmission occurs, since a continuous matching of the refractive index at the boundary of adjacent dielectric materials is obtained [1]. It is worth noting that the moth-eye effect should not be confused with the reduction of the specular reflectance (zero order) by roughening of a surface. Roughness merely redistributes the reflected light as diffuse scattering (higher orders). Regarding moth eye, there is no increase in diffuse scattering, due to the sub-wavelength characteristic size of the hierarchical morphology [4]. In particular, the incident wavefront is not degraded, as light cannot resolve the surface morphology, and the reduction in reflectance gives rise to a corresponding increase of transmittance in moth eyes [4].

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Recently, the moth-eye effect has been exploited to develop anti-reflective biomimetic surfaces made of semiconductors [8–11], metals [12], glass [4,13], and polymers [1,14]. Depending on their morphology these surfaces may be omnidirectional, broadband, and polarization independent. Different techniques have been reported for producing moth-eye surfaces, including chemical etching [8–11], replication of natural surfaces [5,12], interference-patterning by two coherent light beams [4], solution-processing [14], focused ion beam (FIB) lithography [5], electron beam deposition [13], and by exploiting diatoms and viruses [5]. However, chemical etching produces porous surfaces that can be rather fragile, while lithographic approaches are often either too expensive or unsuitable for making sub-wavelength structures with high aspect ratios over large areas. Indeed, some of the optical nanostructures found in nature have such an elaborate architecture at the nanoscale that they simply cannot be replicated using current engineering techniques or require very expensive efforts [5]. These difficulties have hindered so far the use of biomimetic anti-reflective nanostructures in practical applications.

The optical properties of carbon nanotube films have been recently formulated using an effective medium theory [15,16]. In particular, theoretical calculations predicted an extremely low effective index of refraction ($n_{eff} = 1.01–1.10$) for carbon nanotube random networks, due to their sparseness. The key to this ideal anti-reflective surface is that the average distance between the nanotubes is sub-wavelength. Therefore, in such a nanoporous surface the effective refractive index depends only on the material constituents (*i.e*. carbon nanotube and air), its void fraction, and surface morphology. Furthermore, it has been experimentally reported that carbon nanotube films are ultra-black materials [16–19], which not only reflect light weakly, but also absorb light strongly. Therefore, they may be used for light shielding [20], heat dissipators [21], pyrometers [17,18], light sensors [22], solar cells [23,24], and light emitting diodes [25].

In this work, we report for the first time the anti-reflecting properties of carbon nanotube thin films. In particular, we show that the hierarchical morphology [26] of SWCNT random networks deposited on Si can suppress the Si optical reflection over a broad range of wavelengths, angles of incidence, and for both polarizations of light, by exploiting the moth-eye effect. The peculiar, biomimetical inspired morphology of these SWCNT films is self-assembled [26] following a simple solution-processing technique. It does not require any high-precision, time-consuming, or expensive patterning process. After briefly reviewing conventional anti-reflective coatings, we will analyze the structure and morphology of the SWCNT anti-reflective coatings by microscopy, and characterize their optical properties by ellipsometry and spectrophotometry in transmission and reflection.

1.1. Anti-reflective coatings

Generally, when there is a sharp variation of the refractive index between a material and air, high reflection occurs [27]. A way to solve the problem is to reduce the refractive index variation, finding some material with a refractive index as close as possible to that of air. Conventional artificial anti-reflective coatings typically rely on single-layer, quarter-wave films [27], which are designed to suppress Fresnel's reflection at a specific wavelength $\lambda = 4nd$ and angle of incidence, given their thickness d. However, broadband anti-reflective coatings are needed for many practical applications. Furthermore, the effectiveness of anti-reflective coatings is limited by the availability of materials with RI approaching 1 which would eliminate optical reflection entirely. Generally, dense, single-layer materials with a refractive index 1.00–1.40 do not exist.

In order to address these issues, a multi-layer stack of homogeneous thin films has been investigated extensively [28]. According to Fresnel's law [27], a large refractive index variation will result in higher reflection than many smaller variations. In fact, in graded-index films, each light reflection comes from a different depth from the surface, with a different phase. If the reflection takes place over an optical distance $\lambda/2$, there will be destructive interference among all the phases and the reflectance will fall to zero for most wavelengths.A more effective broadband anti-reflective solution is an inhomogeneous film with a graded index [6]. Compared to multi-layer homogeneous films, gradient-index anti-reflective coatings are less sensitive to the angle of incidence, and can be implemented by surface patterning of fractal textures [29] or sub-wavelength nanostructures, in order to obtain the moth-eye effect.

Applications of graded-index films include broadband antireflection coatings [4,6,8–14], omnidirectional reflectors [30], distributed Bragg reflectors [31], optical micro resonators [32], light-emitting diodes [33], solar cells [10,34], and optical interconnects [12,35].

2. Experimental

2.1. Fabrication of carbon nanotube films

Highly pure SWCNT powder (Sigma-Aldrich, assay >90%, diameter: 0.7–0.9 nm) was dispersed in an aqueous solution (23 μg mL^{-1}) with 2% w/v sodium-dodecyl-sulfate (Sigma-Aldrich, assay >98.5%) anionic surfactant. In addition, to better disperse the suspension, SWCNTs were tip-ultrasonicated (Branson S250A, 200 W, 20% power, 20 kHz) in an ice-bath for an hour and the unbundled supernatant was collected by pipette. The result was a well-dispersed suspension which is stable for several months. Carbon nanotube films were fabricated by vacuum filtration of 1 mL of the dispersion cast on mixed cellulose ester filters (Millipore, 1″ diameter, 0.45 μm pore diameter). Subsequently, films were rinsed in water and in a solution of ethanol, methanol and water (15:15:70) to remove the surfactant was performed. Dry-transfer printing method was used to deposit the SWCNT films on Si (100) wafers.

2.2. Sample characterization

Optical spectroscopy (Agilent Cary 5000 UV/VIS/NIR) in transmission and reflection was performed to characterize the SWCNT films. We estimated the film thickness through the Beer-Lambert law [26,37]. The nanotube film microstructure was imaged by Zeiss Orion Nanofab Plus helium ion microscope (HIM). The surface profiles of the films were measured using a 2 μm radius tip with a Bruker Dektak stylus profilometer. The diffuse reflectance $R_{diff}(\lambda)$ spectra of SWCNT films were obtained by using a combination of the Agilent Cary 5000 UV/VIS/NIR spectrometer and Agilent integrating sphere in double beam mode at a fixed incident angle ($\theta = 0$). The total reflectance $R_{tot}(\lambda)$ spectra of SWCNT films were measured at a fixed incident angle ($\theta = 3^{\circ}20'$) in order to collect also the specular reflectance of the samples. Therefore, the angle-integrated, specular reflectance $R_{spe}(\lambda)$ was obtained by subtracting $R_{diff}(\lambda)$ from Ref. $R_{tot}(\lambda)$.

2.3. Ellipsometry modeling

Ellipsometry (JA Woollam M2000 UI Spectroscopic Ellipsometer) was performed to measure the specular reflectance at different angles of incidence (45–80°) on SWCNT films of different thickness. Data was analyzed, modeled, and fitted by Complete EASE software.