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Optical properties of thin graphitic nanopetal arrays

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ABSTRACT

Thermal radiative properties of thin graphitic petal arrays are theoretically and experimentally investigated. Finite-difference time-domain (FDTD) simulations are first performed to calculate optical properties of vertical graphitic arrays of different structures, namely, graphitic gratings, periodic graphitic cavities, and random graphitic cavities. For graphitic gratings, the absorptance and reflectance are relatively larger when the incident electric field is parallel to the graphitic plane, while the absorptance and reflectance are both significantly lower when the electric field is polarized perpendicular to the graphitic plane. Ordered graphitic petal cavity arrays show optical properties falling between the above two cases of different polarizations. Random vertical cavity arrays with various angles of orientation show similar properties to ordered petal cavities. For oblique gratings, the reflectance will increase with oblique angle for both polarizations, while the absorptance decreases with oblique angle for the in-plane polarization and increases with oblique angle for the out-of-plane polarization. The oblique effects are explained by the strong anisotropic nature of graphitic petals. The FDTD results are compared to effective medium theory to find that the latter describes the optical properties of the graphitic grating and cavity well, and we propose an approach based on effective medium theory to approximate the dielectric function of graphitic petals with random orientation. The predicted hemispherical total reflectance based on this model gives about 2% reflectance in the visible spectrum and agrees well with experimental data from a fabricated graphitic petals sample.

1. Introduction

Recently optical properties of various nanostructure arrays have received considerable attention for use in a range of potential applications [1–5]. For instance, silicon nanowire arrays demonstrate extremely low reflectance, which is desirable for solar cell applications [3,6]. The low optical reflection in these array structures can be mainly attributed to refractive index matching. Optical resonance in individual nanowires and multiple scattering can also help to trap light very effectively [7–9]. Even with photonic effects in these structures, the absorption in silicon or other semiconductor material is not strong, due to the low intrinsic absorption. In comparison, arrays of aligned multi-walled carbon nanotubes (CNT) exhibit directional emission [10], polarization dependence [11], extremely low reflection [12–14], and relatively high absorption [15,16]. Although it is difficult to build CNT based solar cells, their high intrinsic absorption is important to other engineering applications, such as solar thermal absorbers, radiometric temperature measurements [17], and blackbody sources [18].

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On the other hand, two-dimensional carbon nano-petals can be synthesized under growth conditions similar to those of CNTs [19]. Unlike graphite intercalated compounds such as exfoliated graphene, carbon nano-petals are made without the use of impurity metals, atomically thin, and free-standing. The growth technique and conditions have been discussed in detail elsewhere [20]. The typical thickness of the petals produced using this technique, as estimated from SEM and TEM images, is around 5 nm. Each of these graphite petals grows to a height of order 1 μm. The volume fraction is estimated to be between 8% and 15%, based on the measured mass difference before and after the petal array growth. In more recent experiments it has been observed that selective area growth may be achieved in carbon nano-petal arrays using scratch techniques. Like CNT arrays, these graphitic petals have black color, which implies that they could be an alternative black coating for solar absorption or blackbody source applications. However, the optical properties of such graphitic petal arrays have not been reported yet.

In this study, we perform both theoretical and experimental investigations on optical properties of various vertical graphitic nano-petals. We have calculated the optical properties of graphitic gratings, periodic graphitic cavities, oblique graphitic gratings, and randomly oriented graphitic petals using both FDTD and effective medium theory. Although these structures are idealizations of experimentally synthesized structures, they provide a fundamental understanding of how different collective arrangements can affect the radiative properties of graphitic petals. In addition, we fabricated graphitic petals on highly ordered pyrolytic graphite (HOPG) and have characterized the spectral reflectance. The experimental results are compared with those from theory.

2. Simulation details

Graphitic nano-petals of a few nanometer thickness possess electronic properties similar to that of graphite and thus can be modeled as very thin sheets of graphite. The anisotropic dielectric properties for graphite in the visible regime used in the calculations are taken from Ref. [21]. A few different structures are considered in our simulation, including vertical gratings, periodic cavity, random cavity, and oblique gratings, as shown in Fig. 1. Each graphitic petal has a thickness of 5 nm as typically observed in experiments. The height of graphitic petals in our simulation is 200 nm, which is smaller than the typical height (≈ 1 μm in experiments). It will be shown later that the 200 nm height combined with a perfect-matched layer (PML) can be used to model the top layer of the graphitic structure and obtain the optical absorptance and reflectance spectra of graphitic petals with larger height.

The simulation for each of these cases is set up in a similar manner. The smallest repeating cell is used for gratings, periodic gratings, and oblique gratings. For random cavity, the domain is a square of 200 nm $\times$ 200 nm and the lengths of the petals are randomly chosen a value between 50 and 150 nm. All the simulations have periodic boundary conditions in the *xy* plane and the *z* direction is truncated by PML at the top and bottom. The structure sits on the PML layer to model the very top region of the graphitic arrays except the oblique grating case. For the oblique grating, it is difficult to achieve numerical convergence if the structure touches the PML, so we model a suspended grating by leaving a 1000 nm vacuum gap between the bottom of the grating and PML. The volume fraction of each case is kept to be 10%, except for the oblique grating where the volume fraction f increases with the oblique angle θ ($f = 10\%/\cos\theta$).

A virtual Gaussian source is placed 1000 nm above the upper surface of the graphitic petals. Normal incidence is considered for all our simulations. Two power flux monitors are placed above and below the array to measure the transmitted and reflected flux values, which are then normalized by the source power to obtain the transmittance T and reflectance R. For all cases, the reflectance and transmittance are calculated in the wavelength range of 400–1100 nm. The absorptance A is then calculated using the energy conservation $A = 1 - T - R$. The simulations are automatically shut down when the maximum field in the domain decays to 10^{-6} of the maximum electric field of the source. The spatial resolution is 0.5 nm in the *x* (cross-plane direction), 10 nm in *y* direction, and 10 nm in the *z* direction for the vertical gratings. For cavity and random cavity, 0.5 nm, 0.5 nm, and 10 nm are chosen for *x*, *y*, and *z* directions, respectively. For oblique gratings, 0.5 nm resolution is chosen for *x* and *z* directions and 10 nm is chosen for the *y* direction. The mesh sizes for different structures are chosen after careful convergence tests. The above

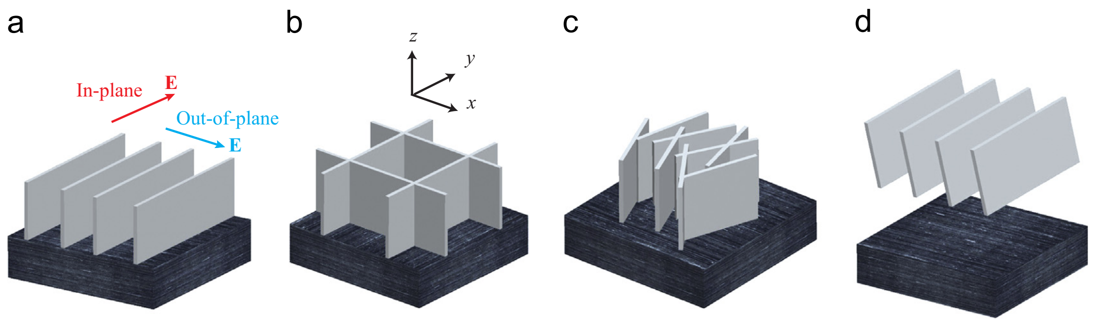

Fig. 1. A sketch of the different graphitic petals we considered: (a) grating, (b) cavity, (c) random cavity, and (d) oblique gratings. For vertical grating and oblique grating, in-plane polarization is defined as the electric field parallel to the graphitic petal and out-of-plane polarization is defined as the electric field perpendicular to the graphitic petal.