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Effect of polarization and morphology on the optical properties of absorbing nanoporous thin films

Ashcon Navid, Laurent Pilon *

Mechanical and Aerospace Engineering Department, Henry Samueli School of Engineering and Applied Science, University of California, Los Angeles, Los Angeles, CA 90095, USA

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Abstract

This paper investigates the possibility of tuning the optical properties of thin films by introducing nanopores with different shape, size, and spatial distribution. The complex index of refraction of nanoporous thin films with various morphologies is determined for normally incident transverse magnetic (TM) and transverse electric (TE) absorbing electromagnetic waves by numerically solving the two-dimensional Maxwell's equations. The numerical results are compared with predictions from widely used effective medium approximations. For thin films with isotropic morphology exposed to TM waves, good agreement is found with the parallel model. For thin films with anisotropic morphology, the numerical results for TE waves are independent of the morphology and agree well with the Volume Averaging Theory model. By contrast, for incident TM waves, the retrieved effective optical properties depend on both porosity and film morphology. These results can be used to design nanocomposite materials with tunable optical properties and to determine their porosity and pore's spatial arrangement.

Keywords: Mesoporous; Nanoporous; Optical materials; Nanostructure; Polarization; Optoelectronic devices; Dielectric constant; Waveguides

1. Introduction

Nanoporous thin films have been studied extensively in recent years [1–4]. Potential applications include dye-sensitized solar cells [5–7], low-k dielectric materials [8,9], thermal barrier coatings [10], catalysts [11], biosensors [12–14], and optical devices such as waveguides [15–17], Bragg reflectors, and Fabry–Perot filters [18–24]. In all the above applications, understanding and predicting the effects of porosity as well as pore shape, size, and spatial arrangement on optical properties of nanoporous materials are essential for optimizing device performance. Mesoporous silica thin films with cylindrical nanopores and controlled inter-pore spacing can be synthesized by calcinations of self-assembled surfactant micelles in a silica precursor matrix as reported by Alberius et al. [3] among others. Fig. 1 depicts a transmission electron microscopy (TEM) image of the resulting hexagonal mesoporous silica thin film synthesized in our laboratory with an inset clarifying the geometry and dimensions. The pores are 4.12 nm in diameter, with inter-pore spacing of 4.82 nm, and porosity estimated at 0.68.

Various effective medium approximations (EMA) have been proposed to treat heterogeneous media as homogeneous with some effective properties. The Maxwell–Garnett Theory (MGT) [25] models the effective relative electrical permittivity $\varepsilon_{r,eff}$ of heterogeneous media consisting of monodispersed metallic spheres in glass. The spheres are arranged in a cubic lattice structure within a continuous matrix and their diameter is much smaller than the wavelength of the incident electromagnetic (EM) wave. Then, $\varepsilon_{r,eff}$ is expressed as,

$$\varepsilon_{r,eff} = \varepsilon_{r,c}\left[1 - \frac{3\phi(\varepsilon_{r,c} - \varepsilon_{r,d})}{2\varepsilon_{r,c} + \varepsilon_{r,d} + \phi(\varepsilon_{r,c} - \varepsilon_{r,d})}\right] \quad (1)$$

where $\varepsilon_{r,c}$ and $\varepsilon_{r,d}$ are the dielectric constant of the continuous and dispersed phases, respectively, and ϕ is the volume fraction occupied by the dispersed phase. The MGT is not valid for porosities greater than 52% since spheres begin to overlap. However, it has been extensively used to determine effective properties over the full range of porosities [26–30]. In addition, for non-conducting particles, such as the dielectric spheres or

* Corresponding author. Tel.: +1 310 206 5598; fax: +1 310 206 4830.
E-mail address: pilon@seas.ucla.edu (L. Pilon).

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cylinders, Eq. (1) is not valid. Nonetheless, it has been used for non-conducting dispersed phase materials, non-spherical geometries, and to model properties other than the effective dielectric constant [28,29]. More recently, Grimvall [31] attempted to account for non-spherical geometry through modification of the MGT. Unfortunately, such a model is involved and/or requires specific knowledge of the shape and orientation of the dispersed phase.

The series and parallel models are examples of two other commonly used models for predicting the effective electrical dielectric constant [32,33], index of refraction [28,34], and both thermal [10] and electrical conductivities [35] of two-phase media. The parallel model states that the effective property ψ_{eff} is a linear combination of the continuous and dispersed phases, i.e.,

$$\psi_{\text{eff}} = (1-\phi)\psi_{\text{c}} + \phi\psi_{\text{d}} \tag{2}$$

whereas the series model gives

$$\frac{1}{\psi_{\text{eff}}} = \frac{1-\phi}{\psi_{\text{c}}} + \frac{\phi}{\psi_{\text{d}}} \tag{3}$$

On the other hand, the reciprocity theorem models the effective property as [36],

$$\psi_{\text{eff}} = \psi_{\text{c}}\frac{1+\phi\left(\sqrt{\psi_{\text{c}}/\psi_{\text{d}}}-1\right)}{1+\phi\left(\sqrt{\psi_{\text{d}}/\psi_{\text{c}}}-1\right)} \tag{4}$$

Alternatively, applying the Volume Averaging Theory (VAT) to Maxwell's equations for arbitrarily shaped domains in a continuous matrix predicts the effective dielectric constant and effective electrical conductivity of a two-phase mixture as [37,38],

$$\varepsilon_{\text{r,eff}} = (1-\phi)\varepsilon_{\text{r,c}} + \phi\varepsilon_{\text{r,d}} \tag{5}$$

$$\sigma_{\text{eff}} = (1-\phi)\sigma_{\text{c}} + \phi\sigma_{\text{d}} \tag{6}$$

where σ_{c} and σ_{d} are the electrical conductivity of the continuous and dispersed phases, respectively. The authors discuss the validity of these expressions in depth, and state a set of inequalities to be satisfied [37,38]. Garahan et al. [39] used Eqs. (5) and (6) to derive the effective refraction and absorption indices of a two-phase nanocomposite material as,

$$n_{\text{eff}}^2 = \frac{1}{2}\left[A+\sqrt{A^2+B^2}\right] \quad \text{and} \quad k_{\text{eff}}^2 = \frac{1}{2}\left[-A+\sqrt{A^2+B^2}\right] \tag{7}$$

where

$$A = \varepsilon_{\text{r,eff}} = \phi\left(n_{\text{d}}^2-k_{\text{d}}^2\right) + (1-\phi)\left(n_{\text{c}}^2-k_{\text{c}}^2\right) \tag{8}$$

and

$$B = \frac{\lambda\sigma_{\text{eff}}}{2\pi c_0\varepsilon_0} = 2n_{\text{d}}k_{\text{d}}\phi + 2n_{\text{c}}k_{\text{c}}(1-\phi) \tag{9}$$

Here, n and k respectively refer to the index of refraction and absorption index of the continuous phase (subscript c) and of the dispersed phase (subscript d). Unlike the other models, the VAT model for n_{eff} and k_{eff} depends on the porosity ϕ and on the real and imaginary parts of the complex index of refraction ($m=n-ik$) of both the dispersed and continuous phases, i.e., $n_{\text{eff}}=n(\phi, n_{\text{c}}, k_{\text{c}}, n_{\text{d}}, k_{\text{d}})$ [39]. In the limiting case of non-absorbing composite thin films (i.e., $k_{\text{eff}}=k_{\text{c}}=k_{\text{d}}=0$), the VAT model reduces to the Drude model given by $n_{\text{eff}}^2=\phi n_{\text{d}}^2+(1-\phi)n_{\text{c}}^2$ [40]. Note that the above mentioned EMA do not account for the polarization of the incident EM waves describing the direction of the electric field with respect to the plane of incidence defined by the Poynting vector and the normal vector of the surface on which it is incident. In transverse electric (TE) plane waves, the electric field is perpendicular to the plane of incidence while it is in that plane for transverse magnetic (TM) plane waves. Any arbitrary plane wave can be described as some combination of TE and TM waves. For a dense homogeneous film, the normal vector of the surface and the Poynting vector are collinear such that the plane of incidence and hence polarization cannot be defined. For a heterogeneous film such as that shown in Figs. 1 and 2, the surface is cylindrical such that the normal vector is no longer collinear with the Poynting vector allowing polarization to be defined that causes changes in transmittance and reflectance.

Experimental data for the effective dielectric constant and index of refraction of nanoporous media reported in the literature for various materials, morphologies, porosities, and pore sizes proves inconclusive for determining the best effective medium model. For example, data reported by Loni et al. [15] for the effective index of refraction of porous silicon, agrees with the MGT model while data from Labbe–Lavigne et al. [28] for the same material falls between the VAT and parallel models. Data for the effective dielectric constant of aerogels – an open-cell mesoporous SiO_2 thin film – measured by Hrubesh et al. [33] follows the parallel model while data reported by Si et al. [32] for

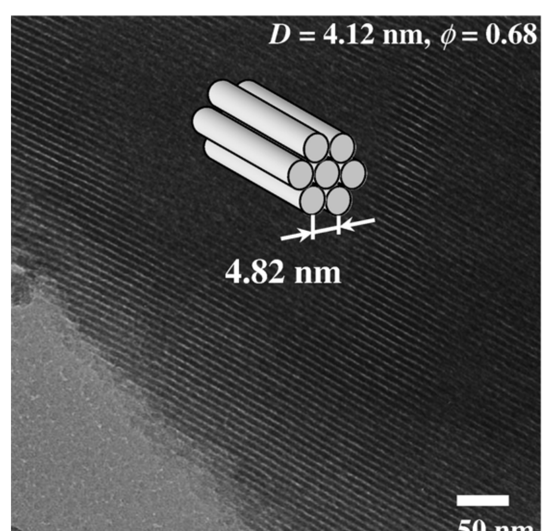

Fig. 1. Transmission electron microscopy (TEM) image of hexagonal mesoporous silica thin films with pore diameter D=4.12 nm and porosity ϕ=0.68.