

Manufacturable extremal low-dielectric, high-stiffness porous materials

S. Torquato^{a)}

Department of Chemistry, Princeton University, Princeton, New Jersey 08544 and Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey 08544 and Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544

A. Donev

Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544 and Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey 08544

A. G. Evans

Materials Department, University of California at Santa Barbara, California 93106-5050

C. J. Brinker

University of New Mexico Center for Micro-Engineered Materials and Department of Chemical and Nuclear Engineering, Albuquerque, New Mexico 87131 and Sandia National Laboratories, Advanced Material Laboratory, Albuquerque, New Mexico 87106

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The drive toward increased semiconductor device densities and improved performance has set in motion the search for low-dielectric-constant materials. While introducing porosity in silica holds promise for reducing the dielectric constant, it remains elusive how to accomplish this without seriously degrading the thermomechanical performance. This article demonstrates a contemporary protocol for materials by design. Applying rigorous cross-property relations, we identify the extremal porous material structure that possesses the desired reduction in the dielectric constant while providing the highest possible stiffness for any given level of porosity. This structural design is crucial to the integration of porous low-dielectric materials into microelectronics and should serve as a guide to future synthetic efforts. Using recently developed self-assembly techniques, we also demonstrate that structures approaching the optimal one can be fabricated. Importantly, our procedure can be applied to general material design problems. © 2005 American Institute of Physics. [DOI: 10.1063/1.1929854]

I. INTRODUCTION

The desire for increased semiconductor device and wiring densities and improved performance is fueling the frantic search for low-dielectric-constant materials.^{1,2} The majority of interconnect structures fabricated to date have been composed of Al conducting lines incorporated within a dense silica dielectric.² This material system has sufficient thermomechanical robustness to assure acceptable durability during processing and as the semiconductor experiences temperature cycles during qualification and in service. In order to lower the device RC time constant, thereby increasing speed, the newest generation of interconnects is designed to embed Cu conducting pathways into a low-dielectric-constant (low- ϵ) host, i.e., a host with a lower dielectric constant than amorphous silica. While it has been possible to identify a wide range of candidate low- ϵ materials,² combining low ϵ with sufficient stiffness, mechanical strength, and thermal stability to resist cracking and ratcheting upon thermal cycling has been elusive.

Reduced dielectric constants can be achieved in amorphous silica, which is preferred due to its compatibility with

current microelectronics processing, by the introduction of porosity, which in order to maintain high breakdown strengths should be of a size much smaller than the line spacing (i.e., nanosize range) and should ideally be closed to avoid metal diffusion. However, most approaches for introducing such fine-scale porosity at volume fractions of interest for low- ϵ dielectrics result in interconnected pores that dramatically reduce the bulk modulus, with serious consequences for thermomechanical robustness. For example, using about 50% porosity distributed randomly, as would occur for sol-gel silica,³ reduces the dielectric constant to about half that for dense silica (the present goal), but diminishes the bulk modulus by almost an order of magnitude.^{4,5} The elastic moduli are also sensitive to the shape, size, and spatial distribution of the pores.

This article discusses the attainment and fabrication of the extremal porous structure that possesses the desired reduction in the dielectric constant while realizing the highest possible stiffness. This is accomplished by applying rigorous cross-property bounds involving the dielectric constant and elastic moduli of composites. It will be demonstrated that the extremal porous material is consistent with the additional requirement that the pores be closed (not interconnected) to assure hermeticity, providing a benchmark structure that sets goals for material design. We will also describe how struc-

^{a)}Author to whom correspondence should be addressed; electronic mail: torquato@princeton.edu

tures that approach the optimal one can be fabricated using recently developed self-assembly techniques.⁶

In Sec. II, we state the relevant cross-property bounds connecting the effective dielectric constant to the effective bulk modulus. The optimal microstructures turn out to be certain multiscale composites. In Sec. III, we show that spherical voids arranged on the sites of Bravais lattices provide excellent approximations to the optimal structures. In Sec. IV, we describe how the nearly optimal single-length-scale structures can be fabricated using recently developed self-assembly techniques. Finally, in Sec. V, we state our conclusions.

II. CROSS-PROPERTY BOUNDS

A fundamental as well as practical question is whether different physical properties can be *rigorously* linked to one another. Such cross-property relations become especially useful if one property is more easily measured than another.⁷ Since the effective properties of heterogeneous materials reflect morphological information about the medium, one might extract useful information about one effective property given an accurate (experimental or theoretical) determination of another, even when their respective governing equations are uncoupled. Cross-property relations are invaluable in determining the possible range of values that different effective properties can possess and thus are of great utility in *multi-functional design of heterogeneous materials*.⁸

Cross-property bounds connecting the elastic moduli of a composite to the effective conductivity or, equivalently, to the effective dielectric constant have been established.^{9–13}

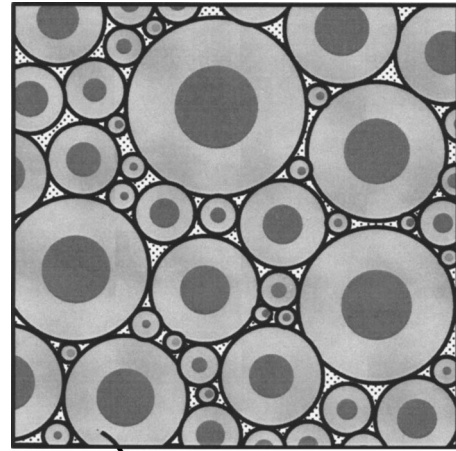
The sharpest bulk moduli/dielectric constant bounds were found by Gibiansky and Torquato^{12,13} for both two- and three-dimensional composites. In this paper, we apply the Gibiansky–Torquato bounds for the special case of voids in a solid three-dimensional matrix of silica.

Let us denote by ε , K , and G the dielectric constant, bulk modulus, and shear modulus of the solid matrix phase, respectively. In the void phase, the phase properties vanish and we denote the porosity by ϕ . In the special case of a porous medium,¹³ the effective bulk modulus K_e is bounded from above by the effective dielectric constant ε according to the following inequality:

$$\frac{K_e}{K} \leq \frac{1}{1 + \left(\frac{K}{2G} + \frac{2}{3}\right)\left(\frac{\varepsilon}{\varepsilon_e} - 1\right)}. \quad (1)$$

This relation is valid for *arbitrary porosities* and is the one we shall apply because we have no constraints on the porosity. An analogous cross-property relation was derived by Gibiansky and Torquato¹³ for a prescribed porosity, but for simplicity we shall not consider that case here. Note that the lower bound corresponding to (1) is trivially zero.

Utilizing the fact that the ratio K/G can be expressed in terms of the Poisson's ratio ν of the solid phase [$K/G = 2(1 + \nu)/(3 - 6\nu)$] enables us to rewrite the upper bound (1) as



K, G

FIG. 1. Optimal coated-sphere model for the effective dielectric constant and bulk modulus. The blue (darker) and red (lighter) regions represent the solid and pore phases, respectively.

$$\frac{K_e}{K} \leq \frac{(1 - 2\nu) \frac{\varepsilon_e}{\varepsilon}}{1 - \nu \left(1 + \frac{\varepsilon_e}{\varepsilon}\right)}. \quad (2)$$

It is important to note that the upper bound (2) was shown by Gibiansky and Torquato to be *optimal*. By this we mean that structures exist that coincide with the upper bound and therefore it is the *best upper bound on the effective bulk modulus (for a given dielectric constant) when the porosity is not prescribed*. The structures that realize the bound are the well-known Hashin–Shtrikman coated-sphere assemblages.^{14,15} The basic building block of this construction consists of a composite sphere consisting of a spherical cavity of radius a , surrounded by a concentric shell of the matrix with outer radius b . The ratio $(a/b)^3$ is fixed and equal to the porosity (cavity volume fraction) ϕ . The composite spheres fill all space, implying that there is a distribution in their sizes ranging to the infinitesimally small (see Fig. 1). Two important features of this construction are (a) that the spherical voids are always “well separated” from one another and (b) that the solid phase is connected. As we will show, porous materials consisting of nonoverlapping equisized spherical voids arranged on the sites of a face-centered-cubic (fcc) lattice ($0 \leq \phi \leq \pi/\sqrt{18} \approx 0.74$) provide excellent approximations to the optimal coated-sphere assemblages.

III. NEARLY OPTIMAL SINGLE-LENGTH-SCALE STRUCTURES

Since the fabrication of the hierarchical multiscale coated-sphere assembly suggested in Fig. 1 is not practical for microelectronic manufacturing, it is desirable to identify single-length-scale structures that can approximate the optimal ones. A simple ordered structure that preserves the topological feature of connectedness of the solid phase, such that the spherical voids are well separated, comprises nonoverlapping spherical voids arranged on the sites of a fcc lattice. The

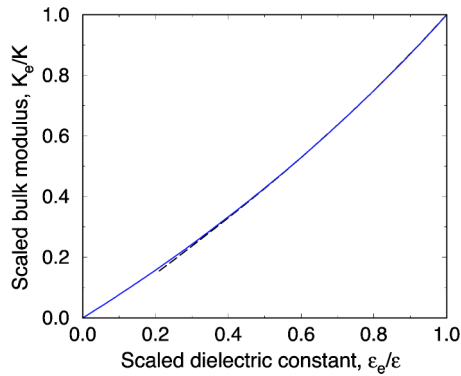


FIG. 2. (Color online) The cross-property upper bound (2) with $\nu=0.2$ (blue solid line) in the ϵ_e-K_e plane. Cross-property relation for identical spherical voids arranged on a fcc lattice (black dashed line) in the ϵ_e-K_e plane.

upper bound (2) is shown in Fig. 2 in the ϵ_e-K_e plane, assuming that the matrix has a Poisson's ratio equal to 0.2, the value for bulk silica. Included in the figure is the cross-property relation for fcc arrays of spherical voids (see Fig. 3) which is obtained from highly accurate structure-dependent relations developed for the effective dielectric constant¹⁶ and elastic moduli¹⁷ of dispersions with particles of arbitrary shape. In the limit where the particles of the dispersion become cavities or voids, these expressions are reduced to

$$\frac{\epsilon_e}{\epsilon_1} = \frac{1 - \phi - (1 - \phi)\zeta}{1 + \phi/2 - (1 - \phi)\zeta}, \quad (3)$$

$$\frac{K_e}{K_1} = \frac{1 - \phi - \frac{5(1 + \nu)}{7 + 5\nu}(1 - \phi)\zeta}{1 + \frac{1 + \nu}{2(1 - 2\nu)}\phi - \frac{5(1 + \nu)}{7 + 5\nu}(1 - \phi)\zeta}, \quad (4)$$

where ζ is a structural parameter that depends upon a three-point correlation function. This parameter has been tabulated for spheres on a fcc lattice (see Table I). We see that the fcc curve in Fig. 2 is remarkably close to the optimal bound. It is noteworthy that the analogous body-centered-cubic (bcc) porous material possesses effective properties that are nearly equal to the fcc material, albeit for a smaller range of porosities [i.e., $0 \leq \phi \leq (3\pi)/(8\sqrt{3}) \approx 0.68$]. Indeed, on the scale of Fig. 2, the results for the bcc porous material are indistinguishable from those for the fcc porous material.

Porous silica consisting of isolated pores must also be able to withstand shear stresses. A porous material, in which the spherical voids are arranged on the sites of the fcc lattice, possesses two independent effective shear moduli. We computed these effective shear moduli using the finite-element technique and found that the two moduli did not significantly differ (i.e., the material properties are nearly isotropic) and were comparable in magnitude to the effective bulk modulus.

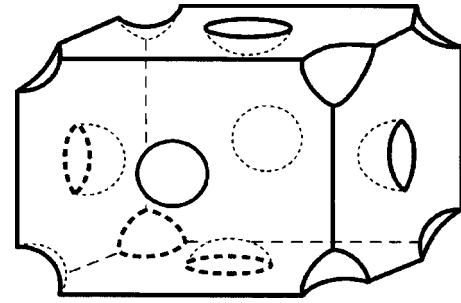


FIG. 3. Nanoporous silica: equisized nonoverlapping spherical voids arranged on the sites of a fcc lattice.

Moreover, a comparison of these moduli to the best available anisotropic upper bounds¹⁹ revealed that the fcc porous material is nearly optimal. Thus, porous silica consisting of isolated spherical pores arranged on a fcc (or bcc) lattice is a single-length-scale composite that is nearly optimal in providing the greatest reduction in the dielectric constant while maintaining the highest possible stiffness to all strain components (i.e., dilatations and volume-preserving deformations).

IV. FABRICATION OF NEARLY OPTIMAL STRUCTURES

Can porous silica with such ordered and isolated arrangements of voids be prepared at the nanoscale? It is now well documented that the phase separation of *AB* block copolymers can result in bcc, hexagonal, bicontinuous, and lamellar morphologies, depending on the volume ratio of the two blocks. Such morphologies can be conferred to silica by co-self-assembly of amphiphilic block copolymers with soluble, hydrophilic forms of silica, as was demonstrated by Templin *et al.*,²⁰ who used poly(isoprene)-block-poly(ethyleneoxide) to form a hexagonal arrangement of poly(isoprene) (PI) rods in a poly(ethyleneoxide) (PEO)/aluminosilicate matrix. *ABA* triblock copolymers have also been used successfully to arrange silica in hexagonal and cubic morphologies,²¹ but for all these synthesis procedures the calcination of the block copolymer templates results in continuous pore networks as determined by nitrogen sorption. Polystyrene₃₅-block-poly(ethyleneoxide)₁₀₉ is known to phase separate into a bcc arrangement of isolated polystyrene (PS) spheres embedded in a PEO matrix [Fig. 4(a)]. Using PS₃₅-*b*-PEO₁₀₉ as an amphiphilic structuring directing agent during evaporation-induced self-assembly²² of hydrophilic silica precursors. Yu *et al.* recently demonstrated that upon solvent evaporation and accompanying siloxane condensation, PEO blocks retract from the silica matrix to form an isolated bcc arrangement of polymer spheres [Figs. 4(b) and 4(c)].⁶ Calcination results in the corresponding bcc ar-

TABLE I. The three-point parameter ζ vs the porosity ϕ for face-centered-cubic (fcc) arrays of equisized spherical voids (Ref. 18).

ϕ	0.10	0.2	0.3	0.4	0.45	0.5	0.6	0.66	0.70	0.71
ζ	0.000	0.0004	0.0021	0.0078	0.0136	0.0232	0.0619	0.1095	0.1596	0.1756

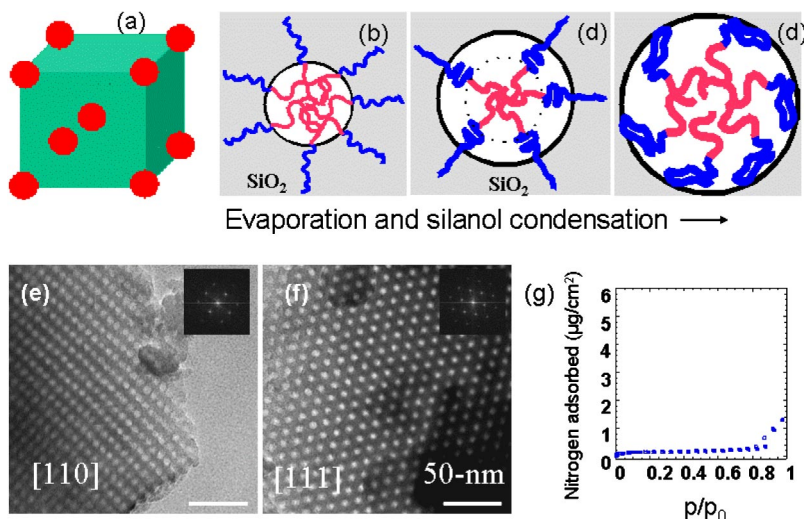


FIG. 4. (Color online) Self-assembly process to create a nanoporous silica film composed of a bcc arrangement of isolated spherical pores. (a) Self-assembly of a PS35-*b*-PEO109 diblock copolymer results in a bcc lattice with isolated PS domains. (b) Using PS35-*b*-PEO109 as an amphiphilic structure directing agent, evaporation-induced self-assembly with an aqueous solution of hydrophilic oligosilicic acid precursors results in an ordered nanocomposite in which the hydrophilic PEO blocks organize the silica and water around the isolated PS blocks. (c) and (d) Evaporation of water combined with silanol condensation to form polysiloxanes reduces the solvent quality for the PEO blocks and they retract from the silica matrix to create an ordered array of monosized, isolated polymer domains. (e) and (f) Calcination of the PS35-*b*-PEO109 templates and continued thermally driven siloxane condensation result in a porous silica film containing a bcc arrangement of isolated spherical pores. (g) N_2 sorption isotherm shows that the film has no porosity accessible to N_2 at 77 K.

range of 4-nm diameter pores as determined by transmission electron microscopy (TEM) images [Figs. 4(e) and 4(f)] and TEM image simulations.²³ Nitrogen sorption measurements indicate no accessible microporosity or mesoporosity, confirming that the pores are isolated [Fig. 4(g)].

While bcc arrangements of isolated spherical pores provide nearly the maximal bulk modulus for porosities ranging from 0 to 0.68, fcc arrangements of isolated spherical pores might enable even higher porosities (lower dielectric constants) to be attained. We anticipate that such fcc arrangements of isolated pores could be synthesized using di- or triblock copolymers in a manner similar to that depicted in Fig. 4,^{24,25} nanocrystal micelles,²⁶ or other spherical monosized nanoobjects as the pore templates.

V. CONCLUSIONS

Billions of years of evolution have provided us many examples of porous and composite materials with desirable properties or combination properties (if not optimal properties). Only recently, however, have advances in theory, modeling, and fabrication enabled the design and synthesis of new materials optimized for use in nonbiological settings. This article has demonstrated a contemporary protocol for materials by design. By combining the most recent computational/modeling tools with novel synthesis and fabrication capabilities, a porous medium has been designed with an unprecedented combination of high stiffness and low dielectric constant. Specifically, the extremal pore topology that possesses the desired dielectric performance while realizing the highest possible stiffness has been identified. The extremal material is well approximated by an oxide with nonoverlapping spherical voids, configured in a face-centered-cubic arrangement. It consists of monosized, nonoverlapping spherical voids arranged on the sites of a fcc lattice. This extremal design is crucial to the development of future generations of low-dielectric films, which require the combination of minimized dielectric constant and maximized stiffness. We showed that films approaching the extremal design can be readily fabricated using a recently developed evaporation-induced silica/block copolymer self-assembly approach. Once such composites are fabricated, it would be

important to measure experimentally the effective dielectric constant and elastic moduli in order to verify our theoretical predictions. It is noteworthy that our procedure can be applied to general material design problems. For example, a recent application of this methodology has been used to design optimal multifunctional composites with interfaces that are minimal surfaces.⁸

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