Micromechanical devices with controllable stiffness fabricated from regular 3D porous materials

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Abstract
Hierarchical pore structures can dramatically change the mechanical properties of materials, but current methods for creating porous materials make the mechanical properties difficult to engineer. Here we present template based techniques for making three-dimensional (3D) regular macroporous microcantilevers with Young’s moduli that can vary from 2.0 to 44.3 GPa. The Young’s moduli can be tunable by controlling the porosity and the deformation mode, which is dependent on the pore structure. The template technique allows 3D spatial control of the ordered porous structure and the ability to use a broad set of materials, demonstrated with nickel and alumina microcantilevers.

Keywords: micromechanics, inverse opal, porous, cellular, foam, tunable

1. Introduction
Materials with a hierarchical structure can have dramatically different properties compared to their bulk form [1]. In particular, the hierarchical pore structure of solid foams allows for a large range of densities and material properties [2]. Most solid foams have broad distribution of pore sizes, randomly-located pores, and irregular pore shapes that can be difficult to engineer [3]. However recent advances in self-assembly processes have increasingly offered routes to regular foams with tightly controlled three-dimensional (3D) periodic structures [4, 5]. The regular, ordered nature of these foams allows for new applications including miniature electrical and mechanical devices [6, 7]. Additionally, regular microarchitectures that resemble foams have been used to demonstrate materials with exceptional strength to weight ratios, suggesting that regular macroporous foams could provide similar mechanical properties [8].

Here we demonstrate microcantilevers fabricated from regular 3D macroporous foams having a nickel inverse opal or alumina shell structure. The fabrication, based on an inverse-opal template process, offers 3D spatial control of the ordered foams with unique geometries and composite materials not achievable by subtractive fabrication. The mechanical properties of these devices depend upon the porosity, as expected, however the deformation modes are dramatically different, depending upon the micro-architecture. The Young’s moduli of the microcantilevers ranged from 2.0 to 44.3 GPa, which are comparable to materials ranging in stiffness from Nylon to high strength concrete or magnesium. At a 0.15 solids volume fraction, the Young’s moduli of the inverse opal and shell structures differ by a factor of 10.

2. Methods
Figure 1 shows the fabrication steps for the inverse opal nickel microcantilevers. First, 10nm chromium and 50nm gold layers were sputtered on a double-side polished silicon wafer and patterned to the microcantilever geometry by...
photolithography and gold/chromium etching. The wafers were then soaked in acetone, diced into 1 cm by 3 cm chips, and piranha cleaned. The chips were then immersed in Millipore water with 2.2% by weight 3-mercapto-1-propanesulfonic acid, sodium salt for 3 h. 1.8 ± 0.09 µm in diameter polystyrene opals, measured by transmission electron microscopy, were then self-assembled onto the chips by positioning the chips vertically in a colloidal solution made from 1.2 grams of 8 wt% PS sphere solution and 40 grams of Millipore water. The chips and solution were set on a hot plat at 50 °C, covered, and left for 24–30 h [9, 10]. During evaporation the spheres at the receding water-substrate meniscus are self-assembled onto the substrate into an opal. The substrates were then sintered at 95 °C for 4 h. The resulting polystyrene opal is typically face centered cubic in structure. Nickel was electroplated through the polystyrene opal using a 10 mA cm−2 current density in a commercial electrolyte of Nickel Sulfamate Semi-Bright RTU Mechanical Agitation by Technic. The deposited nickel had a measured Young’s modulus of 174.3 ± 12.3GPa, which is in good agreement with electrodeposited nickel having a <001 > out-of-plane texture [11]. The polystyrene was removed with tetrahydrofuran, resulting in an inverted opal structure. The volume and surface area of a single pore in the inverse opal structure, including half the volume and area of the interconnects between pores, is approximately 4 µm³ and 10 µm².

The microcantilevers were released by first spin coating both sides of the chip with an adhesion layer (AP 8000) at 3000rpm and a thick photoresist layer (AZ 4620) at 1000 rpm for 40 s. The back side of the chip was then exposed under the mask aligner for 25 s and developed for 90 s. Freshly spun photoresist (AZ 4620, 1000 rpm) is used as an adhesive for manually attaching the chip to a carrier wafer, after the wafer was hardbaked at 110 °C on a hotplate for 10 min. The carrier wafer with the chip attached was then hard bake again at 110 °C for 10 min and 130 °C for another 10 min. The silicon substrate was etched through in a PlasmaTherm ICP with the Bosch process. The chip and the carrier wafer were separated by soaking in photoresist stripper (AZ400T) at 70 °C for 4 h. Last, the chip was dipped into 49% HF for 20 s to fully remove the silicon dioxide layer under the microcantilever.

The template shape and additive chemistry can be changed to precisely engineer the hierarchical structure, making the template fabrication advantageous over subtractive techniques. Additionally, the size, shape, and thickness of the nickel inverse opal microcantilever can be readily adjusted by changing the lateral dimensions and geometry of the metal seed layer and the duration of nickel electrodeposition. The solids volume fraction of the nickel inverse opal microcantilevers is initially 0.25. The nickel can be isotropically etched to reduce the solids volume fraction to 0.15 by electropolishing the nickel structure [10]. Electropolishing was performed using the Electro Polish Systems EPS1250 solution under a 4 V pulsed deposition with 1 s on and 10 s rest times. Stainless steel was used as a reference and counter electrodes. The volume of active material removed can be accurately calculated from the current and duration of etching. Figures 2(a),(d) show scanning electron microscopy (SEM) images of released nickel inverse opal microcantilevers. Figures 2(b),(c) show the top surfaces of nickel inverse opal microcantilevers with 0.25 and 0.15 volume fractions. Figures 2(e),(f) show a composite bilayer microcantilever made of gold and nickel. The bimaterial structure was achieved by a second electrodeposition step before the polystyrene was etched. Figures 2(g)–(i) show the complex shapes that can be patterned using the template based fabrication process. The bottom up template fabrication process is advantageous for engineering miniature devices since the material properties can be precisely controlled by independently engineering the size and shape of the polystyrene template materials, the geometry of the patterned seed layer, and the chemical composition of the electrodeposited materials.

Alumina based microcantilevers with a unique regular 3D macroporous structure were formed by conformally coating the nickel inverse opal microcantilever with alumina
followed by etching of the nickel, resulting in a shell structure. Figures 3(a)–(c) show the microfabrication process of a microcantilever with a shell structure. First, the nickel inverse opal microcantilever was coated with 75 nm thick amorphous alumina by atomic layer deposition (ALD). The alumina was deposited by first heating the sample chamber to 80 °C. Trimethyl aluminum was pulsed into the chamber for 0.03 s, followed by vacuum pumping for 65 s. Water was then pulsed into the chamber for 0.03 s, followed by vacuum pumping for 65 s. This cycle was repeated 750 times for an average growth rate of 0.1 nm per cycle. The extreme conformality of the ALD-deposited alumina film allowed for an even coating throughout the 3D structure. Next, the edges of the microcantilever were cut with a focused ion beam (FIB) to expose the nickel. The microcantilever was then soaked in nickel etchant (Transene, type TFB) until only the alumina shell remained. For a 100 µm wide microcantilever, this typically takes 7 h. Figure 4 shows the nickel etching process in the shell microcantilevers. The nickel can be etched in 7 h. Figures 3(d)–(f) shows SEM images of a microcantilever with an alumina shell structure and magnified images of the cross-section. This approach is rather general, and could be applied for any material which can be conformally coated on the nickel structure.

The solids volume fraction of the microcantilevers is calculated using a geometric model of the microstructure unit cell [10]. The solids volume fraction is the cubic unit cell volume, 16.5 µm³, minus the volume occupied by the FCC ordered 1.8 ± 0.09 µm polystyrene spheres, about 12.4 µm³. The electropolishing isotropically increases the void and interconnect volume. The change in the size of the interconnect diameters
between pores was measured in a SEM and used to calculate the increase in pore volume due to etching. The interconnect diameters for un-etched nickel inverse opal microcantilevers were 190 nm with a 6% standard deviation, corresponding to a 0.2% difference in nickel volume calculated. Additionally, the volume of the alumina in the alumina shell structures can be calculated by assuming a uniform thickness deposited on to the nickel inverse opal structure. The thickness of the alumina was measured in a SEM. Cracks and vacancy defects in the opal can contribute to error between the predicted volume fraction and actual volume fraction. Samples with visible defects had 1–5 µm wide cracks in the polystyrene opal, which after nickel electrodeposition increase the nickel volume fraction over the volume predicted from the model by up to 3%. In the presence of defects the model over predicts the volume fraction of the alumina shell structure and under predicts the volume fraction of the nickel inverse opal structure. The model shows that the solids volume fraction can be theoretically as low as 0.05 by using 20 nm coatings of alumina, instead of the 75 nm coating used in this work.

We characterized mechanical properties of the nickel inverse opal and alumina shell microcantilevers. Devices with stiffness greater than 1 Nm⁻¹ were measured in an Agilent Nanoindenter (MT200), while softer microcantilevers were measured in an atomic force microscope (AFM) (Asylum MFP3D) using the Sader method [12]. Figure 5(a) shows the load versus displacement measurements of a nickel inverse opal microcantilever deflected at 30, 80, 130, and 160 µm from the microcantilever end in the nanoindenter. The stiffness of the microcantilever is the slope of the load versus displacement curve at each location. The spring constant was found by fitting the load versus displacement data with a 1/L₃ fit, since stiffness is proportional to 1/L₃. The stiffness at the end of the microcantilever, L/L₀ = 1, is the spring constant of the full microcantilever. The Young’s moduli, E, of the microcantilevers were calculated from the spring constant and geometry using $E = 4kL/Wt^3$, where $k$ is the spring constant, $L$, $W$ and $t$ are the length, width and thickness of the microcantilever [13–15]. The length, width, and thickness were measured in a SEM. Additionally, the Young’s moduli calculations are sensitive to errors in the length and thickness measurements because of the 3rd power dependence. Figure 5(c) shows the thermal spectrum for an inverse opal microcantilever. The thermal spectrum shows the frequency dependent motion of the cantilever due to the Brownian motion of atoms. The cantilever geometry constrains the cantilever to vibrate the most intense at its resonant frequency, which is detected by a large peak in the thermal spectrum. Figure 5(d) shows the resonant frequency versus spring constant for the inverse opal and shell microcantilevers, along with a silicon microcantilever for reference.

3. Results and discussion

The Young’s moduli of the nickel inverse opal and alumina shell microcantilevers can be tuned by controlling the porosity, however, the different micro architecture leads to dramatically
different Young’s moduli. Figures 6(a), (b) show the Young’s moduli of nickel inverse opal and alumina shell microcantilevers with different volume fractions and densities. Table I shows detailed measurements of each cantilever. The Young’s moduli of the nickel inverse opal microcantilevers with 0.15–0.25 solids volume fraction ranged between 19.3 and 44.3 GPa, as compared to the 174 GPa average Young’s modulus measured from fabricated non-porous nickel microcantilevers. The Young’s moduli of the nickel inverse opal microcantilevers can be tuned by controlling the porosity through etching. The alumina shell microcantilevers were fabricated from ALD alumina, which has a 172 GPa average Young’s modulus [16]. The Young’s moduli of the three alumina shell microcantilevers with 0.16 solids volume fractions varied between 2.0 and 3.3 GPa, which is 10× lower than the nickel inverse opal microcantilevers despite having similar volume fractions of 0.16 and 0.15 and similar bulk material Young’s moduli.

The nickel inverse opal devices and the alumina shell devices have different micro architectures that lead to different deformation modes and ultimately different mechanical properties. The nickel inverse opal architecture has solid struts in between large interconnected spherical pores. The alumina shell architecture is based on the same geometry but composed of thin walls surrounding the interconnected spherical pores. The hierarchical structure of the alumina shell microcantilevers changes the deformation mode of the microcantilevers despite having similar pore size and strut width as the inverse opal architecture. Most foam-like and cellular porous materials deform by bending, as opposed to stretching, of the internal nodes or connections between nodes, which causes these materials to be pliant [17].

Here we present a simple analysis of the mechanical properties of the microcantilever structures. The goal of this analysis is to provide further insight into the physics that governs the observed mechanical responses.

The Young’s modulus, $E$, can be related to the solids volume fraction, $\nu$, and non-porous modulus, $E_0$, by $E/E_0 \approx A\nu^n$, where $A$ is a constant that depends on the material pore structure. The
exponent $n$ is dependent on the degree of stretching versus bending deformation, and is near 1 for stretching-dominated deformation and near 2 for bending-dominated deformation [18]. The maximum Young’s modulus a porous material can achieve is given by the rule of mixtures, where $A = 1$ and $n = 1$. Considerable work has gone into designing materials with architectures that maximize the Young’s modulus [19, 20], with the most studied materials having a tetrahedral or octet truss core structure [18, 21–23]. These isotropic micro architectures are limited by the Hashin–Shtrikman (H–S) bounds for isotropic materials, which is lower than the rule of mixtures limit [24]. The upper H–S bounds for the bulk modulus, $K$, and shear modulus, $G$, are the following, where subscripts 1 and 2 denote the bulk property for the first and second phase in the composite:

$$K_{\text{upper}} = K_2 + \frac{v_1}{1 - \frac{K_1}{K_2}} + \frac{v_2}{\frac{K_1}{K_2} + \frac{1}{G_2}}. \quad (1)$$

$$G_{\text{upper}} = G_2 + \frac{v_1}{G_1 - G_2} + \frac{2v_1(K_2 + 2G_2)}{5G_1(K_1 + 2G_2)}. \quad (2)$$

Phase 1 is air for a porous media, so $G_1$ and $K_1$ are assumed to be zero and $v_1$ is the material porosity. The Young’s Modulus can be related by $E = 9K/(3K + G)$ [19]. The relationship between the Young’s modulus and porosity can be dramatically changed by engineering the isotropy and deformation modes of the micro architecture.

From figure 6, the Young’s moduli of the nickel inverse opal microcantilevers lie between the H–S upper bound for isotropic materials and the limit set by the rule of mixtures. (b) The Young’s moduli of the various microcantilevers versus density. The alumina shell structure has a density and Young’s modulus of 0.4 g/cm$^3$ and 2–3.3 GPa.
Table 1. Mechanical properties of microcantilevers with different volume fractions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume fraction</th>
<th>Length (µm)</th>
<th>Width (µm)</th>
<th>Thickness (µm)</th>
<th>Spring constant (N m⁻¹)</th>
<th>Resonant frequency (kHz)</th>
<th>Quality factor</th>
<th>Young’s modulus (GPa)</th>
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<tr>
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4. Conclusion

In conclusion, we have fabricated microcantilevers with an inverse opal and shell micro architecture. These micro architectures are regular, periodic and can be fabricated with a wide variety of materials, demonstrated here with nickel and alumina. The micro architecture and solids volume fraction of the microcantilevers were engineered to allow for broad control of the Young’s modulus between 1.3 and 25% of the material’s bulk Young’s moduli. The different deformation modes in the micro architectures were found to have the largest impact on the mechanical properties.

The ability to control the mechanical properties of a micro-mechanical device could unlock significant new opportunities in a variety of applications. Regular macroporous microcantilevers with inverse opal and shell micro architectures could enable new micromechanical devices with unique and highly controllable mechanical properties, for example micromechanical sensors [27], flexible batteries [6], or chemical sensors [7]. The hierarchical structure of the inverse opal and shell microcantilevers allows for the mechanical properties to be controlled, while the chemical, electrical, and other physical properties remain unchanged. While the present paper considers nearly isotropic materials, an anisotropic opal lattice could be engineered by changing the geometry of the polystyrene opals, from spherical to rods for example [28], or by layering multiple materials within the microarchitecture.

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