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Precise control of the optical refractive index in nanolattices

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Recent developments in photonic devices, light field display, and wearable electronics have resulted from a competitive development toward new technologies to improve the user experience in the field of optics. These advances can be attributed to the rise of nanophotonics and meta-surfaces, which can be designed to manipulate light more efficiently. In these elements the performance scales are favorable to the index contrast, making the use of low-index material important. In this research, we examine the precise control of refractive indices of a low-index nanolattice material. This approach employs three-dimensional (3D) lithography and atomic layer deposition (ALD), allowing for precise control of the nanolattice geometry and its refractive index. The refractive indices of the fabricated nanolattices are characterized using spectroscopic ellipsometry and agree well with models based on effective medium theory. By controlling the unit-cell geometry by the exposure conditions and the shell thickness by the ALD process, the effective index of the nanolattice film can be precisely controlled to as low as 5×10^{-4} . The proposed index control technique opens a gamut of opportunities and enables better performance in nanophotonic elements used in displays and other integrated devices. © 2023 Optica Publishing Group

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Introduction. The ability to fabricate nanostructures with high precision has resulted in a spectrum of possible developments in the field of integrated devices, materials science, and optics [1]. These include functional materials [2], nanostructured surfaces [3], nanoscale catalysts [4], and optoelectronics [5]. Techniques such as electron-beam, focused ion beam, and two-photon lithography have facilitated the fabrication of intricate nanostructures [6,7]. Alongside these top-down methods, bottom-up self-assembly techniques involving colloidal elements [8], block copolymers [9], and biological molecules [10] have introduced unique nanostructures with functional geometries. These advances enable novel photonic structures and can potentially enhance augmented/virtual reality glasses, 3D displays, and flexible wearable devices [11,12].

In photonics applications, the refractive index contrast of the materials is one of the key factors in determining the device efficiency. Examples include Bragg reflectors and photonic crystals, which are used as wavelength-selective mirrors and can enhance the range of colors in a display. In these structures the control of refractive index contrast is a vital parameter, and previous studies have shown that multilayer reflectors with low index material can increase peak efficiency [13,14]. The use of low-index material in optoelectronics can also result in higher light-extraction efficiency in light-emitting diodes [5]. Therefore, achieving a low-index material with precisely controlled index can improve the performance of photonic structures.

Existing methods to make low-index material include changing the size and concentration of particle inclusions in a silica solute, which changes the porosity of the solgel film. The effective indices are affected by the porosity measured by the volume fraction of solgel mixture, leading to index of 1.29 [15,16]. Twophoton polymerization can also be used to control the effective index within a 3D volume [17–19]. Furthermore, oblique angle deposition methods, or glancing angle deposition (GLAD), have demonstrated porous SiO₂ nanorod layer with an index of 1.08 [20]. Such materials can be implemented in Bragg reflectors as the low-index layer to increase the reflectivity [21]. However, these oblique deposition methods cannot achieve precise control of refractive index, which is limited by the deposition angle. Another potential fabrication technique is to create periodic nanolattices using ALD [22-24]. Recent work has demonstrated that such nanolattices can have a refractive index as low as 1.025 and a low scattering due to periodic ordering [25–27]. While an existing work has demonstrated the fabrication of the material with an index close to 1, it is still challenging to precisely control the index.

This work presents the precise control of refractive index in a low-index nanolattice material by tuning the unit-cell geometry. This approach uses an array of nanospheres as a phase mask to create a 3D polymer nanostructure, which then serves as a template for ALD coating. Upon resist removal, the resulting nanolattice structure is highly porous with a low index. By controlling the unit-cell geometry of the resist template during lithography and the shell thickness during ALD, the nanolattice index can be precisely controlled. The indices of the fabricated samples are measured using spectroscopic ellipsometry to investigate the effect of nanolattice geometry and ALD thickness and agree well with optical models using the Maxwell Garnett (MG) effective medium theory. The results demonstrate that the index control in the order of 5×10^{-4} can be achieved. This result demonstrates the precise control of refractive index of lattices and finds applications in nanophotonics, metasurfaces, and optoelectronic devices.



Fig. 1. (a) Schematic of the nanolattice with period (Λ) and different refractive indices for composing materials. (b) Isotropic thin film with effective index that can be precisely controlled.

Experimental methodology. The proposed nanolattice film with a refractive index that can be precisely controlled is illustrated in Fig. 1. The periodic structure consists of tubular elements with thin shells, the geometry of which controls the porosity and thereby the effective refractive index of the film. This work examines the effects of the lattice unit cell, period, and shell thickness on the measured index. The nanolattices are fabricated using a combination of colloidal phase lithography and ALD, as previously reported [27-29]. The sample silicon wafers are spin coated with an antireflective coating layer (Brewer Science i-con-7) with a 100 nm thickness to reduce backreflection from the silicon substrate, followed by a 300-1000 nm thickness of photoresist (Sumitomo PFI-88). Polystyrene (PS) nanospheres (Polysciences, 2.5% by volume) in aqueous solution are diluted in ethanol and dispersed over the surface of water to form a hexagonal closed packed structure through the Langmuir-Blodgett assembly. The colloidal assembly is transferred on top of the photoresist, which is exposed using a 325 nm HeCd laser at a nominal dose of 90 mJ/cm². This creates a 3D intensity pattern in the photoresist, as governed by the Talbot effect [25–29]. Nanospheres with diameters of 750, 500, and 390 nm are used in our experiments. After development, the samples are coated using Al₂O₃ ALD with a nominal thickness of 21 nm, and the photoresist is removed by post-exposure baking in a furnace at 550°C. Additional information about the fabrication process is described in Supplement 1.

The cross-section SEM images of nanolattice samples fabricated using 390, 500, and 750 nm spheres are shown in Fig. 2. It is noted that nanospheres with different diameters (D) result in different unit-cell geometry, which can be controlled by the normalized parameter $\gamma = \lambda/n\Lambda$, where λ is the exposure wavelength and $\Lambda = D\sqrt{3}/2$ is the nanolattice period [29–32]. A lower γ leads to higher diffraction orders being included in formation of Talbot image, leading to complicated unit-cell geometry. The Talbot distance is then given by $z_t = \gamma \Lambda / (1 - \sqrt{1 - \gamma^2})$. Using the exposure of 325 nm wavelength for nanosphere diameters of 750, 500, and 390 nm, the calculated gamma ratios are 0.31, 0.46, and 0.59, and Talbot distances are 4155, 1784, and 1074 nm, respectively. The heights of nanolattices are controlled by the photoresist thickness, and the samples with 300 and 800 nm photoresist thicknesses are fabricated. Therefore, the samples with higher photoresist thickness can capture more of the intensity pattern and results in formation of taller nanolattice structures.



Fig. 2. SEM images of fabricated nanolattices. (a) Cross-section images of nanolattices with 800 nm height and 24 nm nominal ALD thickness fabricated using 390 nm, (b) 500 nm, and (c) 750 nm diameter spheres. (d) Top view SEM depicting nanolattices fabricated using 500 nm diameter spheres and the resultant structure formed by the hexagonal closed packaging of nanospheres.

Figure 2(a) displays a cross section of samples created with 390 nm diameter spheres and an 800 nm photoresist, revealing the nanolattice's 3D nature due to the thicker resist capturing most of the first Talbot period. Figure 2(b) shows samples made with 500 nm diameter spheres and an 800 nm resist height, highlighting a more cylindrical unit-cell geometry, as the resist thickness is smaller than the Talbot period. Figure 2(c) represents samples fabricated with 750 nm diameter spheres and 800 nm resist thickness. Here, high cylindricity is observed within the unit-cell due to lower γ ratio and lower duty cycle due to larger nanosphere diameter. Figure 2(d) presents a topview SEM of nanolattices, fabricated using a 500 nm diameter and 300 nm resist thickness. These results confirm that nanolattices are highly porous. The samples have Al₂O₃ thicknesses between 215 cycles (approximately 23.6 nm) and 225 cycles, (approximately 24.7 nm).

Theoretical modeling of nanolattice index. We construct a model based on the effective medium theory to predict the refractive index of the fabricated nanolattice films. In this model, the nanolattice is approximated as a periodic array of tubular elements with unit-cell geometry depending on the γ parameter. The work investigates nanolattice samples with different ALD cycles, corresponding to the Al₂O₃ thickness. As the ALD thickness increases, the porosity reduces, and the refractive index is expected to increase. The structure period also plays a role, with a larger period resulting in higher porosity and lower refractive index. For non-magnetic dielectric materials, the MG model [27,31,32] is used to predict the effective refractive index n_{eff} , as given by,

$$\begin{pmatrix} n_{e_{ff}}^2 - 1\\ n_{e_{ff}}^2 + 2 \end{pmatrix} = f\left(\frac{n_m^2 - 1}{n_m^2 + 2}\right),$$
(1)

where $n_{\rm m}$ and f are the index and volume fraction of the Al₂O₃ medium and $n_{\rm eff}$ is the effective refractive index of the nanolattice. To examine the index change versus the number of ALD cycles, the refractive index will be modeled at 632 nm wavelength, where Al₂O₃ has a refractive index of about 1.67 [28,33]. Thereby, depending on number of ALD cycles, the effective refractive index of the lattice varies. The values of f are found to vary between 0.131 and 0.144 for the samples fabricated in our experiments, as described further in Supplement 1. The model



Fig. 3. Measured optical indices versus wavelength for (a) 390, 500, and 750 nm nanolattices with 800 nm height for 213 cycles of ALD, (b) 750 nm nanolattice and 210, 211, 213, and 221 ALD cycles.

enables prediction of theoretical effective refractive index of fabricated nanolattices based on unit-cell geometry, period, and shell thickness.

Results and discussion. The optical indices of the fabricated nanolattices are characterized experimentally using the spectroscopic ellipsometry. The measurements are performed at an incident angle of 70° , and an isotropic Cauchy model is used for the nanolattice film with a thin SiO₂ interlayer on a silicon substrate to emulate the native oxide. The nanolattice uniformity across the sample is quantified by measuring the effective index at 10 different spots on a single sample, which is typically 1 in × 1 in. The standard deviation is found to be 2.3×10^{-4} , which is set as the error bar to consider any non-uniformity and uncertainty in the measurement. More information on the measurement, modeling, and uncertainty calculation is described in Supplement 1.

The broadband refractive indices for 750, 500, and 390 nm nanolattices with 213 ALD cycles are plotted in Fig. 3(a). The measured indices are in the range of 1.0425-1.1323 at 633 nm wavelength and exhibit a typical material dispersion behavior observed for dielectric materials. The samples fabricated with larger sphere diameters lead to a lower refractive index, since for a fixed nanolattice shell thickness a larger period results in higher porosity. The measured indices for 750 nm sphere samples with different ALD cycles are shown in Fig. 3(b). It can be observed that the indices increase across all wavelengths with the number of ALD layers, and very small changes can be measured. This is attributed to the increase in volume fraction of Al₂O₃, leading to increased index at higher number of ALD cycles. It can be noted that measurable index differences for the nanolattices with 210 and 211 cycles can be observed, which is in the range of 6.5×10^{-4} .

To examine the precision of the index control, the index at 632 nm wavelength for the different nanolattice samples with 210 to 225 ALD cycles are compared, as shown in Fig. 4. The experimental data are plotted with and agree well with the MG model. Index values range from 1.0409 for samples fabricated with a 750 nm nanolattice, followed by 1.0661 and 1.1302 for 500 and 390 nm nanolattices, respectively. Refractive indices increase as the nanosphere diameters decrease from 750 nm to 390 nm, which can be attributed to a decrease in the porosity and packing density when equal amounts of aluminum oxide are deposited on smaller period structures. Moreover, the increase



Fig. 4. Measured refractive indices at 633 nm wavelength versus the number of ALD cycles for 750, 500, and 390 nm nanolattices. The solid lines are theoretical prediction using effective medium theory model.

in number of ALD cycles also increases the refractive index due to a decrease in the porosity. For instance, between 215 and 225 cycles of ALD for a 500 nm sphere diameter, the index values increased from 1.0830 to 1.0912. Similar trends can be observed for the 390 and 750 nm samples as well. It can also be noted that the nanolattice height does slightly influence the measured index. This effect can be observed for the 300 and 800 nm height structures for 500 nm spheres, which has a slight index jump between 213 and 215 cycles. The marginal differences are attributed to the difference in the nanolattice geometry since both structures are within one Talbot distance. Other causes include a possible collapse and lattice imperfection in the taller structures. While this work focuses on nanolattices with an 800 nm height, taller structures can be fabricated by using a thicker photoresist. One limitation to scaling up the nanostructure height is the optical absorption of the photoresist, which can lead to an uneven exposure dose along the depth direction for thick films. Prior work has demonstrated that nanolattices with height up to 7 µm are possible [29].

The precision of the index control is examined by calculating the slopes of the index versus the number of ALD layer plots using a linear fit. The calculated slopes are 1×10^{-3} , 7×10^{-4} , and 6×10^{-4} per ALD cycle for the 390, 500, and 750 nm nanolattices with an 800 nm height, respectively. This level of precision is also confirmed by the measured indices for fabricated nanolattice with difference of a single ALD cycle. Specifically, the measured change in indices between 210 and 211 ALD cycles for 390, 500, and 750 nm nanolattices are 3.1×10^{-4} , 5×10^{-4} , and 6.5×10^{-4} , respectively. The index precision agrees well with the MG model, as described further with the raw and tabulated data in Supplement 1. It can be noted that the larger period nanolattice has a finer index precision due to the lower effective index. For the shorter 500 nm nanolattices, the measured slope fit is slightly higher at 8×10^{-4} per ALD cycle, which can be attributed to the height effect on the index.

The results demonstrate that the model accurately predicts the experimentally measured indices and can aid in a precise nanolattice design. However, one challenge is the changes in the nanolattice height, which can influence the measured index. The nanolattice thickness can change during processing and has a maximum deviation of 9.6% from initial photoresist thickness observed in the 750 nm nanolattice. The height reduction can be attributed to a partial structural instability or sag due to the high porosity. This effect can be mitigated by incorporating the height variation in the MG model. In addition, there could also be formation of defects or cracks in the nanolattices, leading to deviations from the model. Future efforts will aim to diminish structural instability in nanolattices by minimizing colloidal assembly defects, fabricating thicker films covering multiple Talbot distances to lower lattice height effect on index, and aims to explore anisotropy as a factor in light propagation. While this work focuses on demonstrating precise index control in nanolattices with index below 1.1, higher index can be achieved using higher ALD thickness or materials with a higher index [28]. The same level of index control is expected for a higherindex nanolattice since the precision is limited by a single ALD cycle.

Conclusions. In this research, we demonstrate precise control of the optical refractive index to as low as 5×10^{-4} in 3D nanolattices. Using 3D lithography and ALD, the nanolattice with periods of 390, 500, and 750 nm and nominal shell thickness of 24.2 nm has been fabricated. It is observed that an increase in number of ALD cycles and decrease in nanolattice period result in an increase in the refractive index, as predicted by models. The fabricated samples are characterized using spectroscopic ellipsometry and demonstrated precise index control as low as 5×10^{-4} per ALD cycle for the 390 nm diameter nanolattice. The experimental data agree well with the constructed MG model, which allows the prediction of the nanolattice index based on unit-cell geometry, period, and ALD thickness. The precise index control opens possibilities for applications in nanophotonics, metasurfaces, and wavelength-selective reflectors.

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Data availability. Data underlying the results presented in this paper are available in Supplement 1.

Supplemental document. See Supplement 1 for supporting content.

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