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Silica Nanorod-Array Films with Very Low Refractive Indices

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ABSTRACT

The refractive-index contrast is an important figure of merit for dielectric multilayer structures, optical resonators, and photonic crystals. This represents a strong driving force for novel materials that have refractive indices lower than those of conventional optically transparent materials. Silica nanorod-array dielectric films with unprecedented low refractive indices of 1.08 are demonstrated and shown to have viable optical properties including enhanced reflectivity of a single-pair distributed Bragg reflector.

The refractive index of dielectric materials was first introduced by Isaac Newton, who originally called this quantity the *optical density* of a material, motivated by the correlation of this quantity with the mass density of liquids used in his experiments. In the visible spectral range, MgF_2, CaF_2, and SiO_2 with refractive indices of $n = 1.39$, 1.44, and 1.46, respectively, are dense compounds with refractive indices among the lowest available. Although reflector structures with air-gaps have been demonstrated,[1,2] air completely lacks structural stability, thereby making it unsuitable for the majority of applications. This motivates the development of nanoporous materials with a very low refractive index. Such novel optical materials must have very small pore sizes to minimize Mie and Rayleigh scattering, a requirement irrelevant for low-k dielectric materials used in the silicon microchip industry.

In dielectric multilayer structures,[3] optical resonators,[4] and photonic crystals,[5] multiple figures of merit strongly depend on the refractive-index contrast, i.e., the difference in refractive index between the high-index and low-index material. For distributed Bragg reflectors (DBRs), the penetration depth, reflectivity, spectral width of stop band, and angular width of stop band directly depend on the refractive index contrast. In optical microresonators, the effective cavity length, and thus the spontaneous emission enhancement, directly depends on the index contrast. In photonic crystals, the width of the photonic band gap directly depends on the index contrast. Recently, nanoporous SiO_2 with refractive index of 1.23 has been demonstrated for quarter-wave layers.[6] Even lower indices (1.14) were demonstrated for thicker layers.[4] However, spin on sol−gel processes are not suitable for simultaneously both, very thin and very low index layers.

Here, optical films consisting of an array of SiO_2 nanorods with a refractive index as low as $n = 1.08$ are demonstrated and shown to have viable optical properties, thereby making them very desirable for many applications. The optical films are fabricated by electron-beam evaporation of SiO_2 onto a substrate that is tilted with respect to the substrate normal direction by an angle of 80°. Oblique-angle deposition was pioneered in the 1960s.[7] A low-n thin film with very high porosity can be obtained from such deposition method. However, such oblique-angle deposition leaves openings making the films unsuitable for optical multilayer structures. A surface-sealing process can strongly reduce such openings, thereby making the low-n SiO_2 nanorod-array films suitable for advanced multilayers structures.

The optical micrograph of a low-n SiO_2 nanorod-array film deposited on a Si substrate is shown in Figure 1 along with a scanning electron micrograph (SEM) showing the top view and the cross section of the film. The optical micrograph reveals a smooth specular surface with no indication of scattering. The cross-sectional SEM clearly shows the angled array of SiO_2 nanorods. Both the gaps between the SiO_2 nanorods and the nanorod diameters are ≤ 50 nm, i.e., much smaller than the wavelength of visible light, and thus sufficiently small to make scattering small. The SEM top view shows the nanostructure of the film including openings between the nanorods. For a deposition angle of 80° and a deposition rate of 2 Å/s, the growth direction of the nanorods is about 30°, both angles being measured with respect to the surface normal of the sample.

The experimental optical reflectivity of the low-n SiO_2 nanorod-array film is shown as a function of wavelength in

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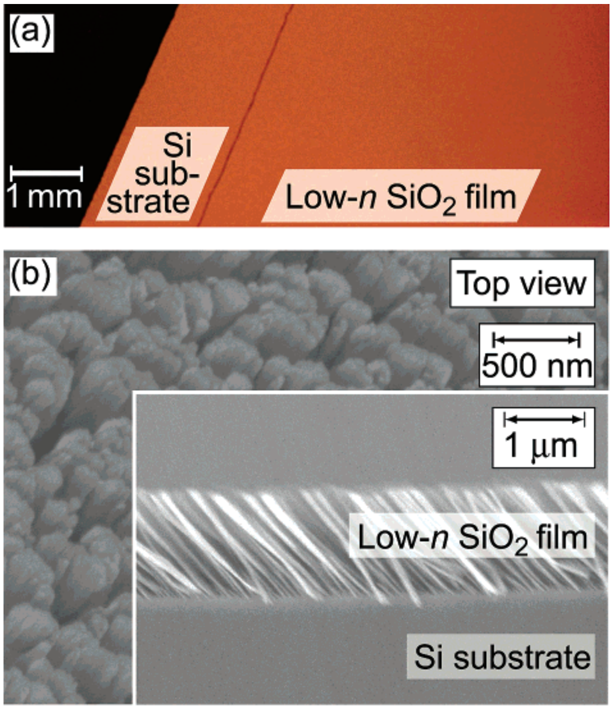

Figure 1. (a) Optical micrograph of low-*n* SiO_2 nanorod-array film deposited on a Si substrate. (b) Scanning electron micrograph showing array of SiO_2 nanorods.

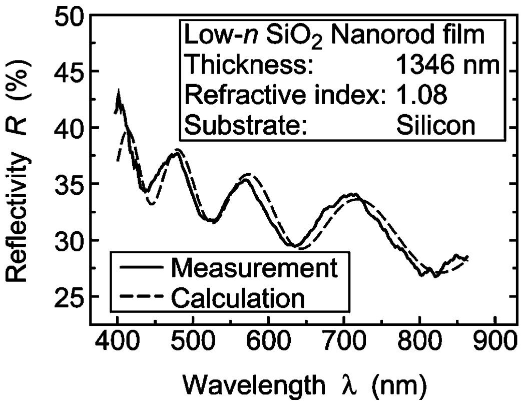

Figure 2. Thin-film reflectivity versus wavelength of SiO_2 nanorod-array film. Theoretical thin-film interference simulations reveal a refractive index of 1.08.

Figure 2. The reflectivity reveals periodic thin-film oscillations. Simulations of the reflectivity reveal that the thin-film interference oscillations are fully consistent with a refractive index of 1.08 and a thin-film thickness of 1.35 μm. These values were confirmed by both ellipsometry measurements and thin-film thickness measurements using SEM. Furthermore, the films were found to be fully transparent with an optical absorption below the detection limit. Because the film is deposited by evaporation (and not spun on), the film thickness can be arbitrarily small.

To demonstrate the viability of the films for use in multilayer structures, we have fabricated a one-pair DBR consisting of a quarter-wave Si layer and a quarter-wave low-*n* SiO_2 layer deposited on a Si substrate. A critical step in the deposition is a surface-sealing step in which a very thin low-porosity SiO_2 nanorod array layer is grown on top of the low-*n* film. In the surface sealing step, the substrate's tilt angle is −45°. Thus the nanorod orientation of the sealing film is nearly perpendicular to the orientation of the main film, thereby reducing the ability of a material deposited on top of the low-*n* film to enter the low-*n* film. This was found to occur in multilayer films without such sealant film. The thickness of the surface sealing layer is <30 nm. Its effect on the optical function of the device can be neglected due to the small thickness.

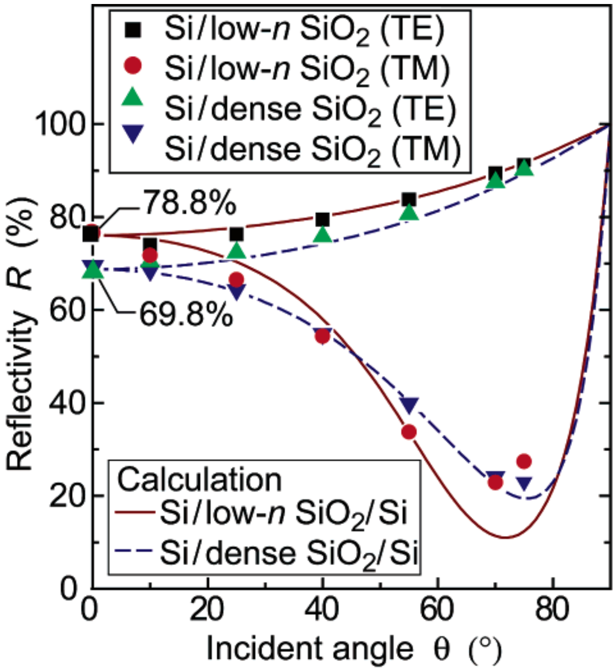

Figure 3. Measured and calculated TE and TM reflectivity at 632.8 nm of one-pair DBR using Si and either a dense SiO_2 or a low-*n* SiO_2 nanorod-array film. At normal incidence, a clear enhancement of the reflectivity is found for the DBR using the low-*n* film.

The angular dependence of the reflectivity of the one-pair DBR structure is shown in Figure 3. Inspection of the figure clearly reveals that the normal-incidence reflectivity is enhanced for the low-*n* DBR compared with the DBR using the dense SiO_2. The experimental normal-incidence reflectivity is 78.8% and 69.8% for the DBR using the low-*n* film and the dense SiO_2 film, respectively. In addition to the normal-incidence results, the experimental and calculated angle-dependent reflectivity is also shown in Figure 3. The experimental results are in excellent agreement with the theoretical results using a refractive-index value of 1.08, 1.46, and $2.94 + 0.143\,i$ for the low-*n* SiO_2, dense SiO_2, and Si, respectively.

In conclusion, dielectric films consisting of an array of SiO_2 nanorods are shown to have extremely low values of the refractive index. Films with a refractive index of 1.08 display excellent optical reflectance and transmittance properties. The refractive index of the low-*n* films is significantly lower that that of conventional thin-film SiO_2. A single-pair Si/low-*n* SiO_2 distributed Bragg reflector is shown to have enhanced reflectivity. Low-*n* films may enable a new generation of dielectric multilayer structures, optical resonators, and photonic crystals with enhanced refractive-index contrast and superior optical properties.

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References

(1) Streubel, K.; Rapp, S.; André, J.; Chitica, N. *Elec. Lett.* **1996**, *32*, 1369.

(2) Marinelli, C.; Bordovsky, M.; Sargent, L. J.; Gioannini, M.; Rorison, J. M.; Penty, R. V.; White, I. H. *Appl. Phys. Lett.* **2001**, *79*, 4076.

(3) Ho, S.-T.; McCall, S. L.; Slusher, R. E.; Pfeiffer, L. N.; West, K. W.; Levi, A. F. J.; Blonder, G. E.; Jewell, J. L. *Appl. Phys. Lett.* **1990**, *57*, 1387.

(4) Schmidt, M.; Boettger, G.; Eich, M.; Morgenroth, W.; Huebner, U.; Boucher, R.; Meyer, H. G.; Konjhodzic, D.; Bretinger, H.; Marlow, F. *Appl. Phys. Lett.* **2004**, *85*, 16.

(5) Temelkuran, B.; Hart, S. D.; Benoit, G.; Joannopoulos, J. D.; Fink, Y. *Nature* **2002**, *420*, 650.

(6) Xi, J.-Q.; Ojha, M.; Cho, W.; Plawsky, J. L.; Gill, W. N.; Gessmann, Th.; Schubert, E. F. *Opt. Lett.*, in press.

(7) van de Waterbeemd, J. G. W.; van Oosterhout, G. W. *Philips Res. Rep.* **1967**, *22*, 375.

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