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Feature Article

Low-refractive-index materials: A new class of optical thin-film materials

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The refractive index, a most fundamental quantity in optics and optoelectronics, determines many figures of merit of optical components such as reflectors, filters, and resonators. Here we present a new class of optical thin-film materials that have a very low refractive index. Specular films of high optical quality with refractive indices as low as 1.05 are demonstrated. A single pair DBR incorporating low-*n* material is demonstrated to have enhanced reflectivity, showing the great potential of low-refractive-index films for many photonic device applications.

1 Introduction

In optical sciences, the refractive index of an optical medium is a most fundamental quantity. The refractive index determines the refraction and reflection occurring at the boundary between two media, e.g. a glass and air. The refractive index of a medium also determines the ratio of the speed of light in vacuum and the light's phase velocity in that medium. Not surprisingly, the analysis of light propagation at the boundary between two dielectric media has fascinated many generations of scientists and engineers. Several prominent scientists and engineers, who contributed to the understanding of the refractive index and optical ray propagation in such media, are shown in Fig. 1.

In 1611, Johannes Kepler, a German astronomer, discovered a startling phenomenon, *total internal reflection* that occurs for grazing angles of light incidence in a high-refractive-index optically transparent medium at the boundary between the high-index medium and a lower-index medium. A fascinating characteristic of total internal reflection is that the reflection is *total*, i.e. 100%. Unlike other reflection events which frequently have reflectivities less than 100% (e.g. reflection events involving metals), total internal reflection has a perfect, i.e. 100%, reflectivity. Furthermore, Kepler found that for close-to-normal angles of incidence, the angle of incidence, Θ_{incident}, and the angle of refraction, $\Theta_{\text{refracted}}$, follow the proportionality

$$\Theta_{\text{incident}} \propto \Theta_{\text{refracted}} . \tag{1}$$

In 1621, Willebrord Snell, a Dutch mathematician, discovered the sinusoidal relationship between the angle of incidence and the angle of refraction when a light ray passes from one optically transparent

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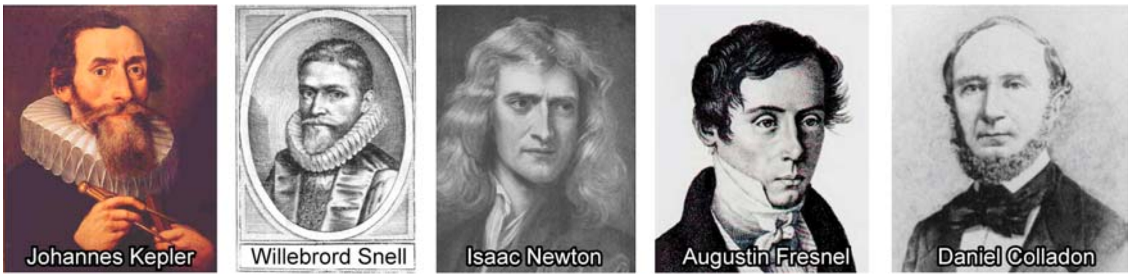

Fig. 1 (online colour at: www.pss-b.com) Johannes Kepler (1571–1630) discovered total internal reflection. Willebrord Snell (1591–1626) discovered sine-law of refraction. Isaac Newton (1642–1727) identified the optical density of a medium (now called refractive index). Augustin Fresnel (1788–1827) quantitatively described reflection at a dielectric boundary. Daniel Colladon (1802–1893) developed the first wave guiding apparatus.

medium to another. The sinusoidal proportionality found by Snell is given by

$$\sin \Theta_{\text{incident}} \propto \sin \Theta_{\text{refracted}} . \tag{2}$$

For small angles, Snell's relationship accurately reproduces Kepler's approximate relationship of Eq. (1).

In the years leading up to 1672, Sir Isaac Newton of the United Kingdom, defined a new optical constant that describes an optically transparent material and its refraction behavior. Using this novel quantity, he was able to convert the proportionality found by Kepler and Snell into the equation

$$n_{\text{incident}} \sin \Theta_{\text{incident}} = n_{\text{refracted}} \sin \Theta_{\text{refracted}} . \tag{3}$$

He was able to attribute an optical constant to an optical medium, including the medium in which the optical ray is incident, n_{incident}, and the medium in which the optical ray is refracted, $n_{\text{refracted}}$. He also found a correlation of this novel quantity with the mass density of the optical medium. For example, the mass density of water and glycerin is 1.00 g/cm^{-3} and 1.26 g/cm^{-3}, respectively; the newly found optical constant of water and glycerin was found to be 1.33 and 1.47, respectively, thereby showing a clear correlation between the mass density and the new optical constant. For this reason, he called this novel optical constant the *optical density*, and we denote it as n. By using the knowledge available today, we can understand this correlation: A high-density medium generally has a higher density of atoms so that the polarizability of the medium is greater. However, additional factors may play a role, including the type of atom, the chemical bonding structure, and so on. For this reason, we call the quantity that Newton introduced as optical density, the *refractive index* of a medium.

However, the newly found optical constant, the refractive index, has significant meaning transcending refraction experiments. It was identified as the quantity that describes the propagation velocity of light in the medium, i.e.

$$n = c/v , \tag{4}$$

where c is the speed of light in vacuum and v is the phase velocity of light in the optical medium with refractive index n. Furthermore, based on Maxwell's equations, the refractive index and the dielectric constant of a medium, ε_r, are, in non-magnetic media ($\mu_r = 1$), related by

$$n = \varepsilon_r^{1/2} . \tag{5}$$

Thus the dielectric constant, which is so important in electrical engineering and microelectronics applications, also can be traced back to Newton.

In 1821, Augustin Jean Fresnel, a French mathematician, presented the laws that allow us to calculate the intensity and polarization of reflected and refracted light at the boundary of two media with a different refractive index. Again, the refractive index plays a key role in the Fresnel equations. Owing to Fresnel reflection, the surface of a computer monitor or of water forming a lake is partially reflective.

In 1842, Daniel Colladon, a Swiss engineer showed the phenomenon of optical waveguiding by using a falling stream of water. Because the refractive index of the water ($n = 1.33$) is higher than that of the surrounding air ($n \approx 1.00$), light rays are guided in the water stream by total internal reflection. Colladon used Kepler's total internal reflection phenomenon for the first time in a way that would, 150 years later, become the basis of the globe's fiber optic communication network.

From ancient stone-aged men looking at their own image in a puddle of water to medieval telescopes, to modern microelectronic and photonic technology, the refractive index is a fundamental, maybe the most fundamental materials constant in optics and photonics.

The available values of the refractive indices are limited, particularly when it comes to optical thin films with very low refractive indices. Silica (SiO_2) and magnesium fluoride (MgF_2), for example, have a refractive index of 1.46 and 1.39, respectively. Dense and viable thin-film materials with a refractive index of, say, 1.10 or 1.20 do not exist. However, such materials would be highly desirable. Let us consider a distributed Bragg reflector (DBR), a periodic structure that consists of an alternating series of a quarter-wavelength thick high-index and low-index material with a refractive index of n_{high} and n_{low}, respectively. Let us look at the following figures of merit of a DBR:

The reflectance of a single interface of a DBR:

$$R = \left(\frac{\Delta n}{n_{\text{high}} + n_{\text{low}}} \right)^2 . \tag{6}$$

The reflectance of a DBR with m quarter-wave pairs:

$$R_{\text{DBR}} = \left[\frac{1 - (n_{\text{low}}/n_{\text{high}})^{2m}}{1 + (n_{\text{low}}/n_{\text{high}})^{2m}} \right]^2 . \tag{7}$$

The spectral width of the DBR stop band:

$$\Delta\lambda_{\text{stop}} = \frac{2\lambda_{\text{Bragg}}\,\Delta n}{n_{\text{eff}}} . \tag{8}$$

The penetration depth of the optical wave into the DBR:

$$L_{\text{pen}} \approx \frac{L_{\text{low}} + L_{\text{high}}}{4r} = \frac{L_{\text{low}} + L_{\text{high}}}{4} \, \frac{n_{\text{low}} + n_{\text{high}}}{\Delta n} . \tag{9}$$

The maximum angle of incidence at which high reflectivity is maintained:

$$\theta_{\text{c}} \approx \frac{n_{\text{low}}}{n_0} \sqrt{\frac{2}{n_0} \, \frac{2\Delta n}{n_{\text{low}} + n_{\text{high}}}} . \tag{10}$$

Inspection of the equations shows that the refractive index contrast, Δn, is a key quantity. Increasing the index contrast would allow one to improve every single figure of merit given above and thus make better DBRs. More importantly, the availability of new low-refractive index materials with a refractive index $1.0 < n < 1.4$ would not only improve DBRs but a wide range of optical components such reflectors, filters, band-passes, photonic crystals, lasers, LEDs [1], and solar cells.

In this publication, we summarize recent results on a new class of optical thin-film materials, low-n materials, which can have refractive indices as low as 1.05 and are very beneficial to a multitude of applications.

2 Low-refractive-index materials

In DBRs [2], the refractive index contrast, which is the difference in refractive index between the two constituting materials, is directly related to the reflectivity, spectral width of stop band, and penetration depth of the optical wave. In optical micro-resonators [3], the effective cavity length and hence the enhancement of spontaneous emission, directly depend on the index contrast. In photonic crystals [4], the photonic bandgap width is directly related to the index contrast. This motivates the development of new highly porous optical materials with a refractive index close to 1.0, which we denote as low-*n* materials.

Additionally, in semiconductor optoelectronics, the optical ambient material is a semiconductor, which has a refractive index of typically 2.5 ~ 3.5. Therefore, the light propagation situation is different from the case with air ($n = 1.0$) as optical ambient. The design of optical reflectors for such semiconductor optoelectronic devices requires materials with very low refractive index. For example, in the omnidirectional reflector designs, the low-*n* material is a key part for the optical performance as demonstrated by Xi et al. in 2005 [5, 6].

Although multilayer structures with air-gaps have been demonstrated [2], the fabrication process requires under-etching and hence is slow and costly. Moreover, air gaps completely lack structural stability, making them unsuitable for the majority of applications. MgF_2, CaF_2, and SiO_2 are materials with refractive indices among the lowest available for conventional, dense optical coatings. However, their refractive indices, $n_{MgF2} = 1.39$, $n_{CaF2} = 1.44$, $n_{SiO2} = 1.46$, are much higher than the air's index, 1.0. Due to the correlation between the refractive index and the dielectric constant of a dielectric material, generally, a low-*k* material can also be used as a low-*n* material. But, as optical materials, low-*n* materials require minimal Mie and Rayleigh scattering, which is irrelevant to low-*k* materials. Therefore, low-*k* and low-*n* materials are distinct classes of materials with unique sets of requirements.

Oblique-angle deposition has been pioneered in the 1950s [7]. It is a technology to grow porous, sculptured thin films [8, 9] enabled by film-thickness fluctuations and self-shadowing effect during the deposition process [10–12]. Since the films resulting from oblique-angle deposition can have very high porosity on the nano-scale, they are very suitable as low-*n* materials. To grow low-*n* materials, dielectric materials are used as the evaporation source. Optical films consisting of an array of SiO_2 nano-rods with a refractive index as low as $n = 1.08$ were demonstrated by Xi et al. in 2005 and 2006 and are shown to have viable optical properties thereby making them very desirable for many applications [13, 14].

Generally, the refractive index of a porous material is related to the degree of porosity and the refractive index of the non-porous, dense material. The porosity and the refractive index are directly related by the Bruggeman effective-media approximation (EMA) [15]. The EMA predicts an approximately linear dependence between the refractive index and the porosity. Here, we report on thin optical films with a refractive index value of only 1.05, the lowest ever reported for a low-n material. The optical films are grown by e-beam evaporation of SiO_2 onto a substrate that is tilted so that vapor flux has a tilt angle of approximately 85° with respect to the substrate normal direction. The evaporation source material is pure SiO_2 granules. During the deposition, the vapor is well controlled to have small and constant vapor flux. The deposition rate is <0.5 nm/s. As a result, such thin films have very low refractive indices and we found no evidence for scattering in the visible spectrum.

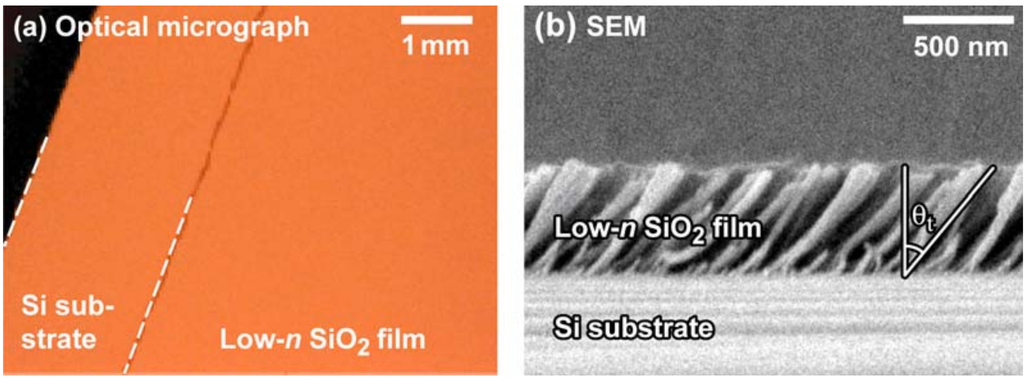

Fig. 2 (online colour at: www.pss-b.com) (a) Optical and (b) scanning-electron micrograph of a low-*n* SiO_2 nano-rod film deposited on a Si substrate.

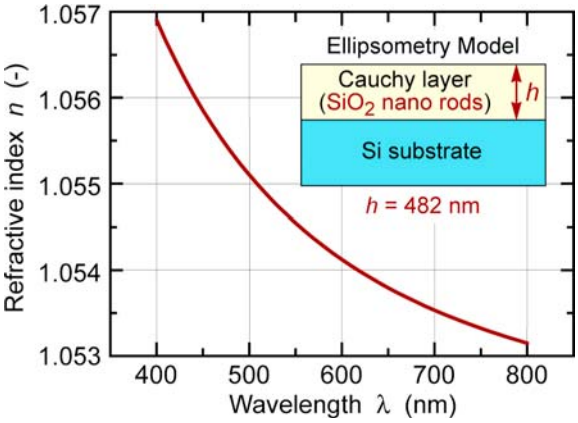

Fig. 3 (online colour at: www.pss-b.com) Refractive index versus wavelength of low-*n* SiO_2 nano-rod film measured by VASE ellipsometry. The measurement indicates that the thickness of the low-*n* film is $h = 482$ nm and the refractive index at 620 nm is $n = 1.054$, the lowest ever reported for a low-*n* film.

The optical micrograph of a low-*n* SiO_2 nano-rod film deposited on a Si substrate is shown in Fig. 2 along with a scanning-electron micrograph showing the cross-section view of the film. The optical micrograph reveals a smooth specular surface with no indication of scattering. The scanning-electron micrograph clearly shows the array of tilted SiO_2 nano-rods. Both the gaps between the nano-rods and the nano-rod diameters are ≤ 100 nm, i.e. much smaller than the wavelength of visible light, and thus sufficiently small to keep optical scattering small. The nano-rods are uniformly distributed with a tilt angle about $\theta_t = 45°$ with respect to the surface normal of the sample. The thickness of the low-*n* SiO_2 nano-rod film is about 500 nm as shown in the scanning-electron micrograph.

The refractive index of this thin film is measured with variable angle spectroscopic ellipsometry (VASE) at beam incident angles of 60°, 65°, and 70°. The ellipsometry model assumes a Cauchy-type layer on a Si substrate. The refractive index versus wavelength is shown in Fig. 3. Within the visible spectrum, the refractive index of the SiO_2 nano-rod layer is extremely low, namely $n = 1.05$. The thickness of the SiO_2 nano-rod layer, determined from the ellipsometry measurement, is $h = 482$ nm, confirming the thickness obtained by scanning-electron microscopy. Oblique-angle deposited films have been reported to be optically anisotropic [16], that is, the refractive index varies as a function of incident angle and polarization. However, no pronounced optical anisotropy is found in our thin SiO_2 nano-rod film, probably due to the high porosity. Assuming a linear dependence between the refractive index and porosity, a refractive index of 1.05 indicates a porosity of 88.9%.

3 Optical multilayer structure with low-refractive-index SiO_2 thin film

To demonstrate the viability of the SiO_2 nano-rod films for use in multilayer optical components, a single-pair DBR with Si/SiO_2 nano-rod layer is fabricated. A low-*n* SiO_2 nano-rod thin film with $n = 1.08$

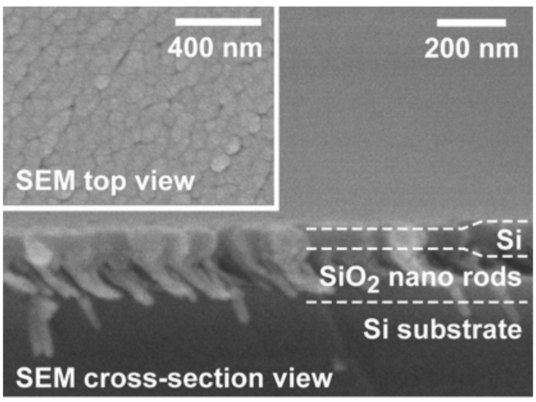

Fig. 4 Scanning-electron micrograph of a single-pair DBR incorporating a SiO_2 nano-rod layer.

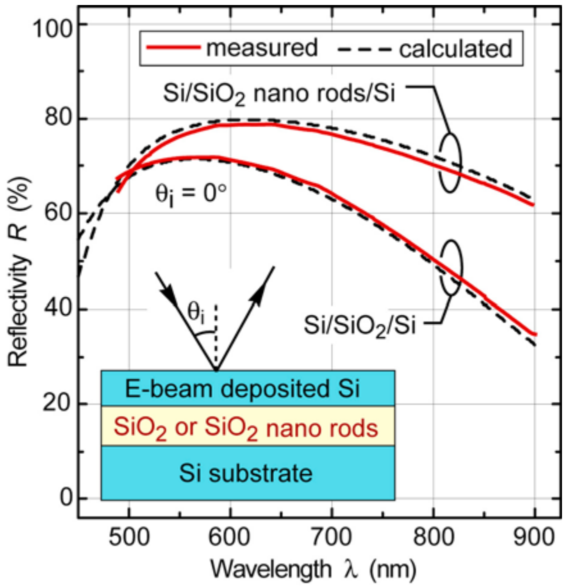

Fig. 5 (online colour at: www.pss-b.com) Reflectivity of a single-pair DBR using Si/SiO_2 nano-rod layer and a single-pair DBR using Si/dense SiO_2. The single-pair DBRs are deposited on a Si substrate. The normal-incidence reflectivity is measured in the wavelength range of 500 nm – 900 nm.

and thickness h = 150 nm is grown on a Si substrate. After a sealant layer, 41 nm thick Si layer is deposited at normal incidence by e-beam evaporation. The scanning-electron micrograph of the Si/SiO_2 nano-rod DBR is shown in Fig. 4. The cross-section view clearly shows that the e-beam-deposited Si is lying on the sealant layer of the SiO_2 nano-rod layer, forming a sharp interface between them.

For comparison, a single-pair DBR with Si/dense SiO_2 is deposited on a Si substrate by normal-incidence e-beam evaporation. The thickness of dense SiO_2 is 107 nm to guarantee that the optical thickness of the dense SiO_2 and the SiO_2 nano-rod layer are equal. The thickness of Si is 41.0 nm.

The reflectivity at normal incidence of the DBRs is measured for visible and near infrared wavelengths. Both the measured and calculated reflection spectra are plotted in Fig. 5. In the calculation, a refractive index of 1.08 and 1.46 is used for the SiO_2 nano-rod layer and the dense SiO_2 layer, respectively. E-beam deposited Si has a refractive index of 2.94 + 0.110i at a wavelength of 632.8 nm. Inspection of Fig. 5 reveals that the normal-incidence reflectivity is clearly enhanced for the DBR with SiO_2 nano-rod layer compared with the DBR using the dense SiO_2. The measured peak reflectivity of the Si/SiO_2 nano-rod DBR and of the Si/dense SiO_2 DBR is R = 78.9% and 72.0%, respectively. Furthermore, the measured reflectivity spectrum agrees very well with the calculated reflectivity spectrum. The difference in experimental peak reflectivity between the two DBRs shows the clear advantage of low-n thin films for optical coatings.

4 Conclusions

In conclusion, a new class of optical thin-film materials with an unprecedented low refractive index is presented. A refractive index value as low as 1.05 is demonstrated for a highly porous specular SiO_2 film with high optical quality. A single pair DBR incorporating low-n material is demonstrated to have enhanced reflectivity, showing the great potential of low-refractive-index films for applications in photonic structures and devices.

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