Keynote Paper

Optical coatings and metamaterials

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ABSTRACT

An optical surface rarely presents the idea optical behavior desired for the system in which it is employed. Modifying these properties is the task of an optical coating and virtually all optical surfaces in all optical systems carry such treatments. Most often the coating consists of a number of thin layers exhibiting interference effects that yield a suitable performance. Coating performance is constrained by the normal properties of interference. Such behavior could benefit considerably from the use of metamaterials and particularly those exhibiting a negative index of refraction. Unfortunately such true negative index still appears elusive. Negative refraction has been convincingly demonstrated particularly for *p*-polarization and this is certainly useful in a number of applications but metamaterials have not so far yielded the complete set of properties representing the true negative index that could transform the field of optical coating.

Keywords: Optical coatings, optical coating theory, metamaterials, negative refraction, negative index

1. INTRODUCTION

An optical surface rarely presents ideal optical behavior. Modifying the properties is the task of an optical coating and it is usually the specular properties that are of concern. We most often prefer that the surface figure be unaffected, although there is a limited class of coatings deliberately intended to alter the figure in desired ways.

Optical coatings usually consist of a number of thin layers of material applied to the surface under treatment. The coating operates through a combination of interference and the optical properties of the materials. Then, although they cannot strictly be described as an addition to the surface there are some surface treatments involving removal of material that are included within the class of optical coatings.

In the calculation of the optical properties of a coating we take advantage of the linearity of the response and express the properties in terms of a single harmonic wave. Several parameters are then necessary for the design of optical coatings and calculation of their performance. The properties of the materials are usually expressed as the complex refractive index, $(n - ik)$, n being the refractive index and k the extinction coefficient, together with the characteristic admittance, y, the ratio of the magnetic and electric field amplitudes of a propagating harmonic wave. At optical frequencies the absence of direct magnetic interactions implies that y can be expressed as $(n - ik)\mathcal{Y}$ where $\mathcal{Y}$ is the characteristic admittance of free space. Usually we normalize it to $(n - ik)$ with units of the admittance of free space so that numerically it is equal to the refractive index. It is particularly important to note that, although numerically equal, the refractive index and the characteristic admittance are completely different physical parameters with quite different roles. Next, we need also the phase thicknesses of each layer, δ, given by $2\pi(n - ik)d/\lambda$. The most commonly used algorithm for the determination of coating properties expresses each layer as a two by two matrix called the characteristic matrix. These matrices then convert the total tangential electric and magnetic fields at the emergent interface to those at the surface of incidence as:

$$\begin{bmatrix} B \\ C \end{bmatrix} = \prod_{j=1}^{q} \left\{ \begin{bmatrix} \cos\delta & \dfrac{i\sin\delta}{y} \\ iy\sin\delta & \cos\delta \end{bmatrix} \right\} \begin{bmatrix} 1 \\ y_{emergent} \end{bmatrix} \tag{1}$$

where the column matrices are the normalized total tangential electric and magnetic fields. It is convenient to introduce the idea of a surface admittance, expressed as the ratio of the total tangential fields, as Y and given by $\mathcal{H}/\mathcal{E}$ where $\mathcal{H}$ and $\mathcal{E}$ are the fields, usually normalized so that the surface admittance, like the characteristic admittance, is in units of the

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admittance of free space. The fields can readily be converted into reflectance and transmittance and other properties of the coating[1].

Many of our optical coatings consist of quite simple arrangements of dielectric, that is completely transparent films. Such films have zero extinction coefficient rendering the calculation of properties much more straightforward. A quarterwave film exhibits maximum interference effect while a halfwave exhibits no effect and is sometimes termed an absentee layer. Many optical coatings consist of combinations of these two layer types with, of course, different refractive indices.

A stack of quarterwave layers of alternating high and low refractive index gives high reflectance over a limited range outside of which the reflectance falls to a low value. The interference effect repeats itself at one third and one fifth and so on, of the fundamental wavelength. A typical characteristic is shown in Figure 1. Not only is this structure used as our basic high reflectance coating, but it is also the core of notch filters, edge filters, dichroic beamsplitters, and is a component of narrow bandpass filters.

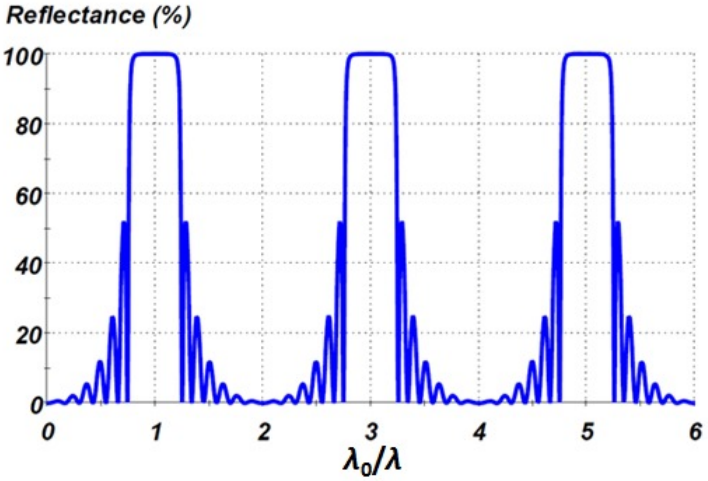


Figure 1. The quarterwave stack, consisting of alternate quarterwaves of high and low index materials, can act as a reflector, a notch filter, an edge filter, or a dichroic beamsplitter. It is also an important component of narrowband filters.

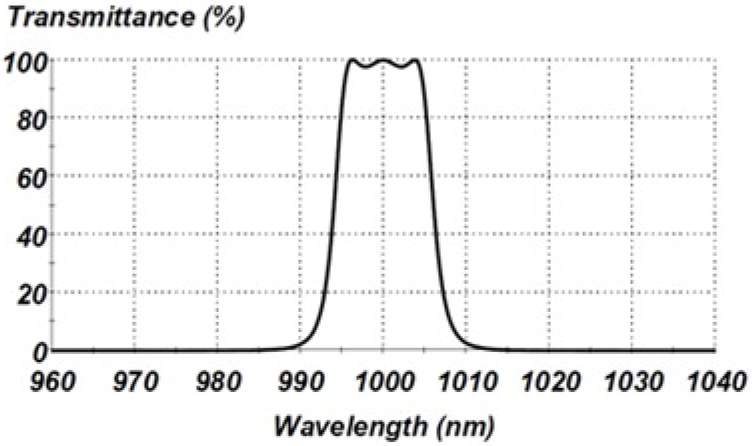


Figure 2. This narrowband filter has structure:

Air | L′H′ HLHLHLH LLLL HLHLHLH L HLHLHLH LLLL HLHLHLH | Glass

where H and L denote quarterwave thicknesses of Ta_2O_5 and SiO_2 respectively at 1000nm. The L′H′ bilayer at the front matches the structure to the Air incident medium. These two layers are not quarterwaves.

Narrowband filters are usually based on repeated cavity structures separated by quarterwave coupling layers. A cavity is a pair of similar quarterwave stack reflectors separated by a layer of halfwave or multiple halfwave thickness. A typical filter made up of three such cavities is shown in Figure 2.

Other applications can involve metal layers. For example there is considerable current interest in the use of surface plasmon resonance as a basis for sensitive detectors[2] and for transport of optical surface waves in devices. Figure 3 shows a basic arrangement for the excitation of a long-range surface plasmon.

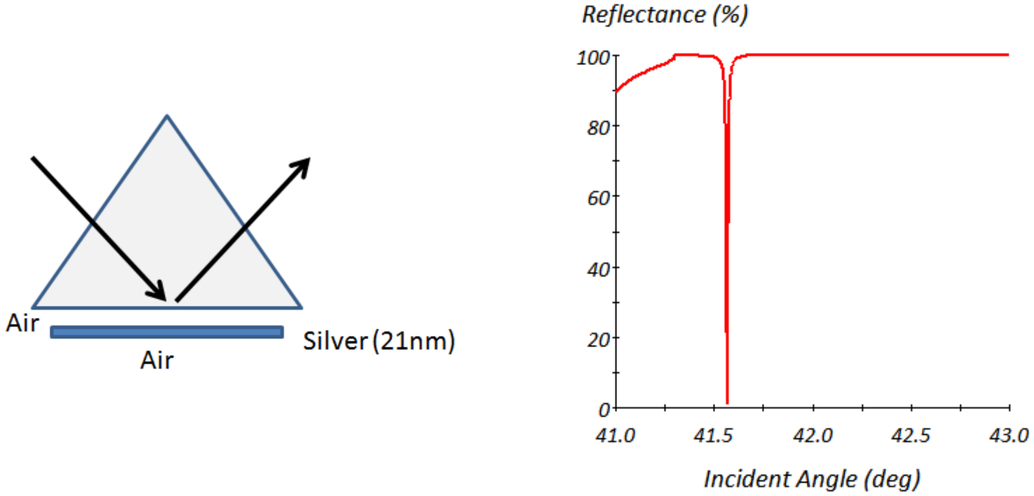


Figure 3. Coupling into the long-range surface plasmon is through the evanescent wave emanating from the input prism on the left. The resulting resonance at 632.8 nm is extremely narrow. Air is shown as the surrounding medium in this simple case.

Nanostructures are already used to some extent in optical coatings and we mention just a few examples. The moth eye coating, so called because its structure mimics the antireflection structure on the eyes of nocturnal moths, consists of a closely packed array of needle-like features over the surface of an optical material[3,4]. Provided these are small enough to minimize scattering, they are essentially equivalent to a material with a gradually reducing index of refraction from that of the underlying substrate to that of the incident medium. Such a graded layer will give excellent antireflection properties at wavelengths for which the total thickness is greater than a halfwave. As long as the variation is monotonic the profile of index versus thickness is relatively unimportant and so tolerances are relaxed. Oblique incidence in deposition accentuates the columnar structure of the deposit and can be used in conjunction with deliberate substrate movement to produce large-scale anisotropy in the films leading to interesting and useful manipulation of polarization[5]. Lithographically produced wire grids are employed as useful polarizers[6]. Their properties are essentially those of birefringent materials exhibiting, in the plane of the film, dielectric behavior in one direction and metallic normal to it.

2. IDEAL METAMATERIALS

The most attractive metamaterials from the point of view of optical coatings would be those exhibiting negative index of refraction. Such materials, predicted by Veselago[7], have negative index but positive characteristic admittance. Since Snell's Law still holds, an isotropic negative index film would exhibit negative refraction. In the characteristic matrix for a thin film the phase thickness, δ, would become negative while the admittance, y, would remain positive. This would be equivalent to a negative thickness and would have profound effects on achievable performance.

We can demonstrate this with two simple examples, a quarterwave stack and a narrowband multiple-cavity filter. Figure 4 shows the astonishing improvement in performance of a regular quarterwave stack reflector when the low-index layers are all replaced with material of equivalent negative index. Now there is an exceptionally broad region of high reflectance. The sharp dips in the lower figure correspond to those wavelengths where the layers are all halfwaves or full waves in optical thickness and, therefore, absentees. The second example, shown in Figure 5, is of a two-cavity narrowband filter. Here the normal performance shows the quite truncated rejection region around the first order peak. It shows also the third order but rather compressed because of the wavelength scale. The enormous improvement when the low index layer acquires an equivalent negative value is shown in the lower figure. These are just two from the enormous range of possible applications of a negative index material.

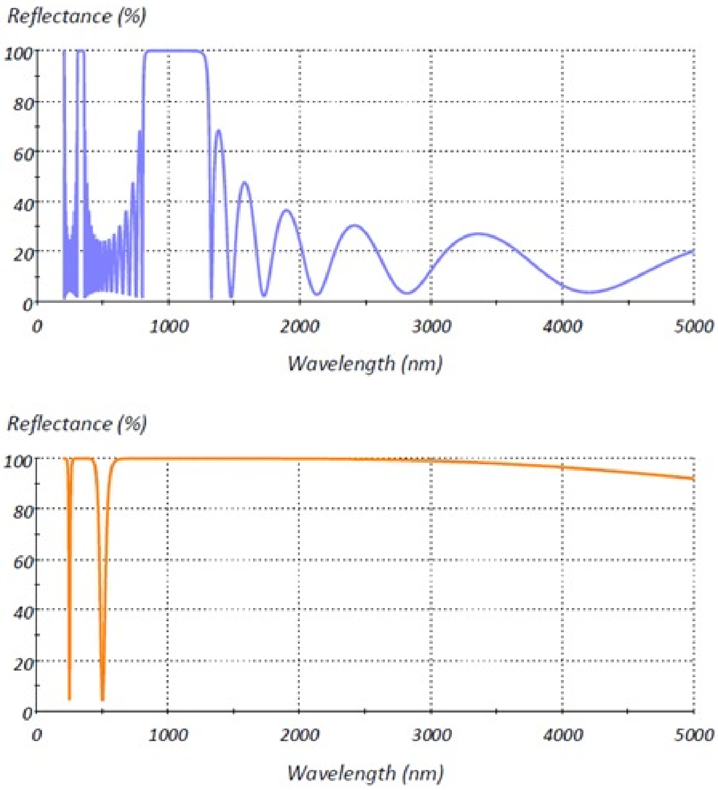


Figure 4. The performance of a regular quarterwave stack is shown in the upper plot. The lower shows the exact same design but with all low index layers of negative rather than positive index. The sharp dips in the lower figure are where the layers are all of halfwave or multiple halfwave thickness.

3. NEGATIVE REFRACTION

Negative index turns out to be elusive at optical frequencies. The problem, of course, is the relative permeability that, stubbornly, remains at unity and is a consequence of the vanishingly small direct magnetic interactions at the very high frequencies of the optical region. This has, so far, prevented the direct application of the techniques that have successfully created negative index materials in the microwave region. Negative index materials like those in the preceding examples may always remain an unrealized dream. However there have been convincing demonstrations of negative refraction[8,9] where a confined beam of light, incident at an angle on the surface, emerges from the system on the same side of the surface normal as the incident beam of light. A typical illuminating arrangement is either a small Gaussian beam, or an essentially two-dimensional arrangement, where a narrow slit on the surface of the coating defines a propagating beam. In any case the emergent position of the beam can be determined, and, together with the physical thickness of the film, can then yield the angle of refraction in the system, from which we can calculate an effective index of refraction. Most, if not all, of the demonstrations have involved *p*-polarized light.

Unfortunately this arrangement of negative refraction does not depend on negative index. The light that propagates through the slit or illuminated spot can be represented as an angular spectrum of plane waves and the illuminated exit spot is then at the point where the phase change on transmission is stationary. Interference effects contribute to the phase change and are primarily responsible for altering the effective index from that expected from the particular material[10].

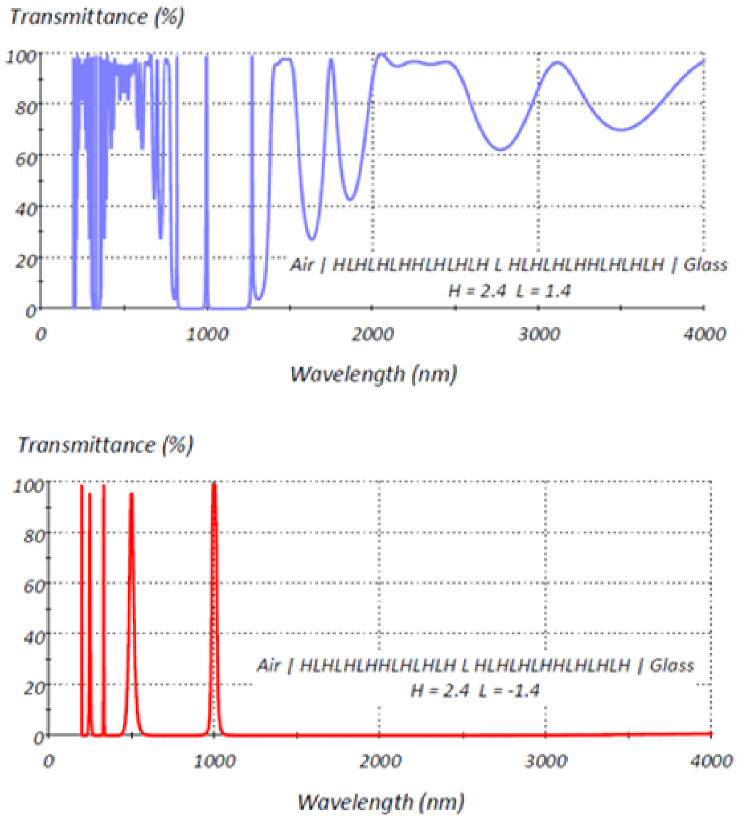
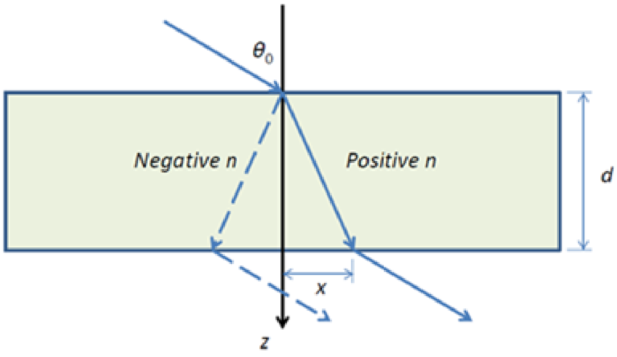


Figure 5. The upper figure shows the performance of a two-cavity narrowband filter. The free spectral range is limited by the performance of the quarterwave stack reflectors. the lower figure shows the same design but with the low index layers of negative value. The extra peaks to shorter wavelengths are alternately halfwave absentees and higher order narrowband peaks.



$$n = \frac{n_0 \sin\vartheta_0 \sqrt{x^2 + d^2}}{x}$$

$$\text{where } \; x = \frac{\lambda}{2\pi n_0 \cos\vartheta_0} \cdot \frac{d\varphi_\vartheta}{d\vartheta_0}$$

Figure 6. The effective index depends on the rate of change of transmission phase change with respect to angle of incidence, which in turn depends partly on interference properties.

A straightforward example is a 5 µm thick film of actual index 1.50 in an air incident medium and at 510nm. Figure 7 shows the effect of interference. Very large displacements of the beam can be found in narrowband filters of telecom quality. However, probably the most interesting results are obtained with metals. Figure 8 shows the effective index of a 50 nm thick film of silver at 510 nm. The effective index is negative for *p*-polarization but positive for *s*. With air as the emergent medium the effective index for *p*-polarization is very close to -1.0. Many demonstrations of negative refraction use silver in some capacity.

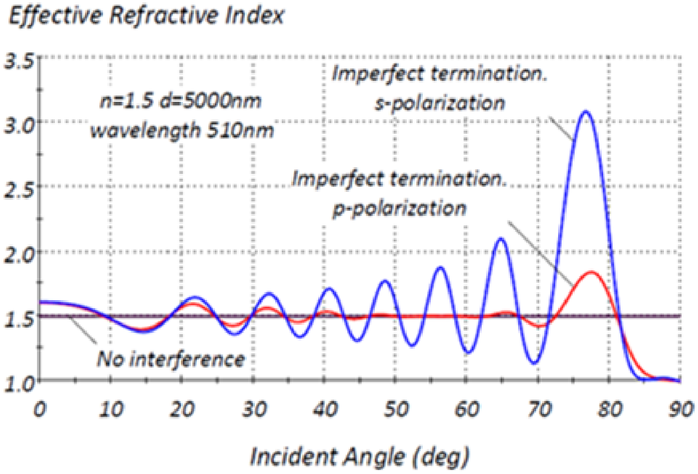


Figure 7. The effective index of a 1.5 index film of physical thickness 5 µm, and with air as incident medium, as a function of incident angle. With perfect termination the effective index is everywhere 1.50. But with air as emergent medium the effective index fluctuates as shown.

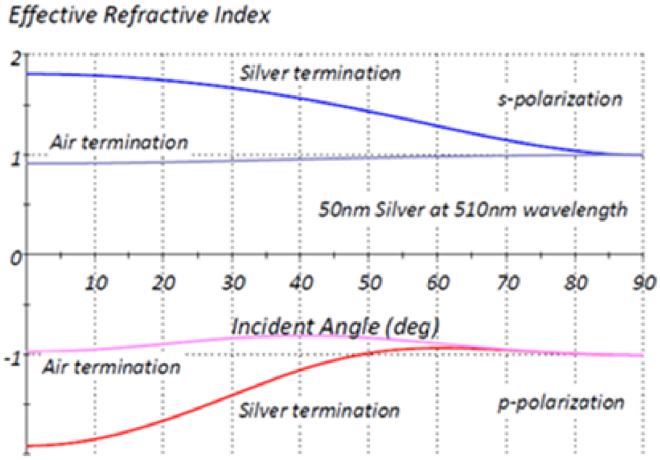


Figure 8. The effective index of silver is affected by the phase shift on passage through the film surfaces and, for p-polarization in a 50nm silver film at 510nm wavelength we obtain an effective index of close to -1.00.

This negative refraction can be used as the basis for lenses similar to those employing true negative index. Unfortunately they are limited to *p*-polarization. This is not too much of a problem when only two dimensions are involved but for three dimensions and illuminating cones the polarization becomes radial.

4. PROSPECTS FOR OPTICAL COATINGS

It is clear that we do already use some metamaterials in optical coatings although we do not always refer to them in such terms The metamaterial we would really like to have for optical coating applications is an isotropic material exhibiting a true negative index over an extended wavelength region. We can hope for this but so far the indications are not promising. What of existing metamaterials?

We have seen that silver is an important ingredient of metamaterials. We make great use already of silver, and indeed other metals, in optical coatings and we understand very well and have many techniques for the optimization of coatings incorporating metal layers. Thus metamaterials consisting of metal dielectric multilayers will likely not bring new useful properties. It is perhaps possible that lithographically structured metal layers could bring some useful properties. We have already used such materials in the far infrared and the successful use of polarizing metal grids at shorter wavelengths is considerably encouraging and such applications are already starting to appear.

Layer thickness is the most important adjustable parameter in the design of optical coatings and so we prefer material properties that are not thickness dependent. One of the more interesting metamaterials that largely meets this requirement consists of a dielectric matrix containing metallic wires or elongated ellipsoids arranged normal to the film surfaces. Its usual embodiment is a set of wires in a matrix of alumina and is commonly produced by anodic oxidation of aluminum and subsequent filling of the pores, a feature of this process, with silver[8]. The resulting material is uniaxially birefringent with the in-plane properties dielectric, but the normal axis metallic. Light that is *s*-polarized simply experiences dielectric behavior and so is rather uninteresting but *p*-polarization properties move from dielectric at normal incidence towards metallic as the angle of incidence increases. We have no natural materials that present us with this behavior.

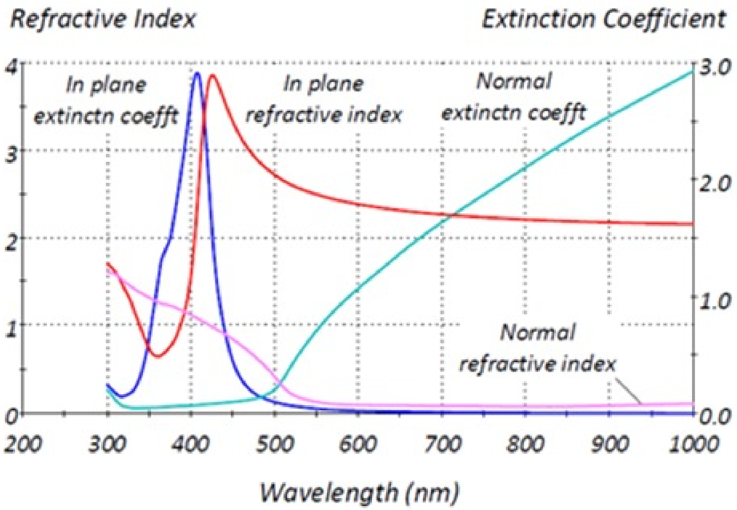


Figure 9. The optical constants of a film of alumina with silver wires and an inclusion factor of 0.234 calculated by the Bragg and Pippard model[11].

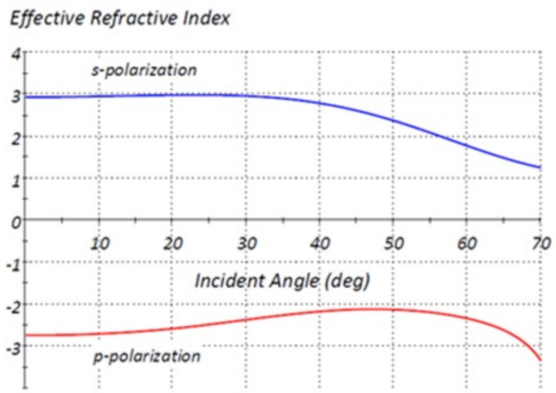


Figure 10. The effective refractive index of 800 nm of the composite material of Figure 9 immersed in air. Again the interesting properties are for *p*-polarization. Wavelength 800 nm.

We can apply effective medium theory to this material[12] and typical results are shown in Figure 9. The behavior is clearly dielectric in plane and metallic normal to the plane from 500 nm to longer wavelengths. This results in an effective index for *p*-polarization that is negative, Figure 10. The variation in the effective index when bounded by air media implies that the performance as a lens would not be as good as silver but the transmittance is much higher and the structure is such that the properties are insensitive to thickness. How might such a material be applied in an optical coating?

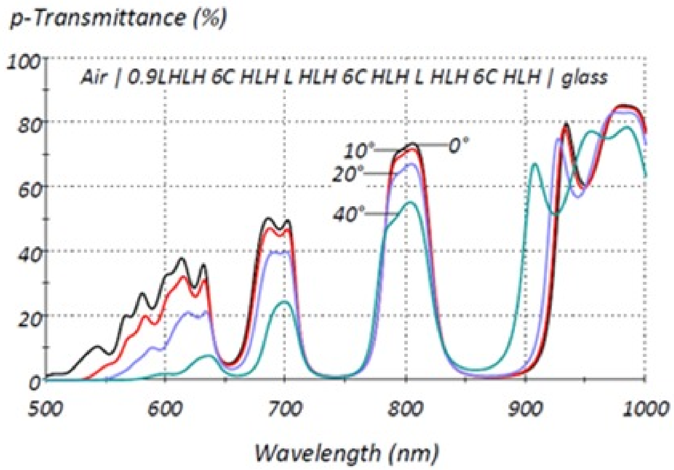


Figure 11. This three-cavity filter consists of SiO2 as L, Ta2O5 as H and the composite material of Figure 9 as C. The design has been adjusted so that the *p*-polarized passband remains fixed in wavelength as the angle of incidence varies.

Our normal sign convention leads to a negative phase thickness. An effective negative refractive index for *p*-polarization implies a negative derivative of phase change with respect to incident angle leading to an increasingly negative phase thickness. Since the absolute magnitude of the phase thickness is increasing, any related characteristic will tend to move to a longer wavelength. Figure 11 shows a three-cavity filter consisting of SiO_2 as L, Ta_2O_5 as H and the composite of Figure 9 as C[12]. The design has been adjusted so that the *p*-polarized passband remains fixed in wavelength as the angle of incidence varies.

Unfortunately this performance is limited to *p*-polarization only. The performance for *s*-polarization shows the usual short-wave shift. In a cone of illumination incident normally, *p*-polarization becomes radial polarization while *s*-polarization becomes azimuthal and so there may be some application connected with that behavior.

5. CONCLUSION

Optical coatings benefit already and could benefit still further from nanostructured materials. There are many more examples than could be included in this contribution. Of some interest are birefringent structures that exhibit dielectric behavior in the film plane and metallic behavior in the normal direction.

REFERENCES

[1] Macleod, H. A., [Thin-Film Optical Filters] CRC Press, Boca Raton, London, New York(2010).

[2] Homola, J., “Surface plasmon resonance sensors for detection of chemical and biological species,” Chemical Reviews, 108(2), 462-493 (2008).

[3] Schulz, U., Munzert, P. and Kaiser, N., “Surface modification of PMMA by DC glow discharge and microwave plasma treatment for the improvement of coating adhesion,” Surface and Coatings Technology, 142-144, 507-511 (2001).

[4] Schulz, U., “Wideband antireflection coatings by combining interference multilayers with structured top layers,” Opt. Express, 17(11), 8704-8708 (2009).

[5] Park, Y. J., Sobahan, K. M. A., Kim, J. J. et al., “Linear polarization-discriminatory state inverter fabricated by oblique angle deposition,” Optics Express, 17(13), 10535-10541 (2009).

[6] Yamada, I., Kintaka, K., Nishii, J. et al., “Mid-infrared wire-grid polarizer with silicides,” Opt. Lett., 33(3), 258-260 (2008).

[7] Veselago, V. G., “The electrodynamics of substances with simultaneously negative values of ε and μ,” Soviet Physics Uspekhi, 10(4), 509-514 (1968).

[8] Yao, J., Liu, Z., Liu, Y. et al., “Optical negative refraction in bulk metamaterials of nanowires,” Science, 321(5891), 930 (2008).

[9] Xu, T., Agrawal, A., Abashin, M. et al., “All-angle negative refraction and active flat lensing of ultraviolet light,” Nature, 497(7450), 470-474 (2013).

[10] Macleod, A., "Optical thin-film metamaterials," Bulletin, 14(Spring), 24-31, Society of Vacuum Coaters (2014).

[11] Bragg, W. L. and Pippard, A. B., “The form birefringence of macromolecules,” Acta Crystallographica, 6, 865-867 (1953).

[12] Macleod, A. and Clark, C., "Some thoughts on optical thin-film metamaterials." 57th Annual Technical Conference, Society of Vacuum Coaters, 195-199, (2014).