MATERION ADVANCED CHEMICALS
COATING MATERIALS NEWS
December 2011 Volume 21 Issue 3

OPTICAL COATING BASICS: THEORY AND MATERIALS

Visit Materion online at www.materion.com/AdvancedChemicals.

View our online catalog for a complete listing of Advanced Chemical Products.
It is found in the Resource Center under Tools.

Previous issues summarized the many applications for optical coatings and the use of materials appropriate for the specific application. In this issue we review some of the basic theory behind optical coatings. Methods for determining the optical properties of thin films are also discussed. The third topic is a short discussion of the use of rare earth materials in color display, LED lighting, and X-ray imaging applications.

OPTICAL THICKNESS, THE OPERATING PARAMETER IN COATINGS

Coatings employ thin film layers of materials that provide low-, medium-, and high-refractive indices to control transmission or reflection of light of different wavelengths. To accomplish these functions, coatings are constructed of multiple layers of alternating index value arranged according to specific design rules. The behaviors of single layers of materials with medium-index and low-index (relative to the glass substrate index) are shown in Figure 1. The layer physical thicknesses are chosen to produce quarter wave (QW) and half wave (HW) optical thicknesses at desired wavelengths. In the figure, the layers are 5 QW optical thickness at 550 nm. Optical thickness is the path that light travels and is equal to *index x thickness*, OT = nt. Illustrated in Figure 1 curves is behavior as a function of varying wavelength; we see that OT will change from being QW to HW in a repeating cycle. When OT equals the HW, the reflectance returns to that of the substrate, i.e. it is as though the substrate is uncoated at the even-number of QW points. At the QW positions, an index lower than that of the substrate will lower reflectance; and an index higher than the index of the substrate will increase reflectance.

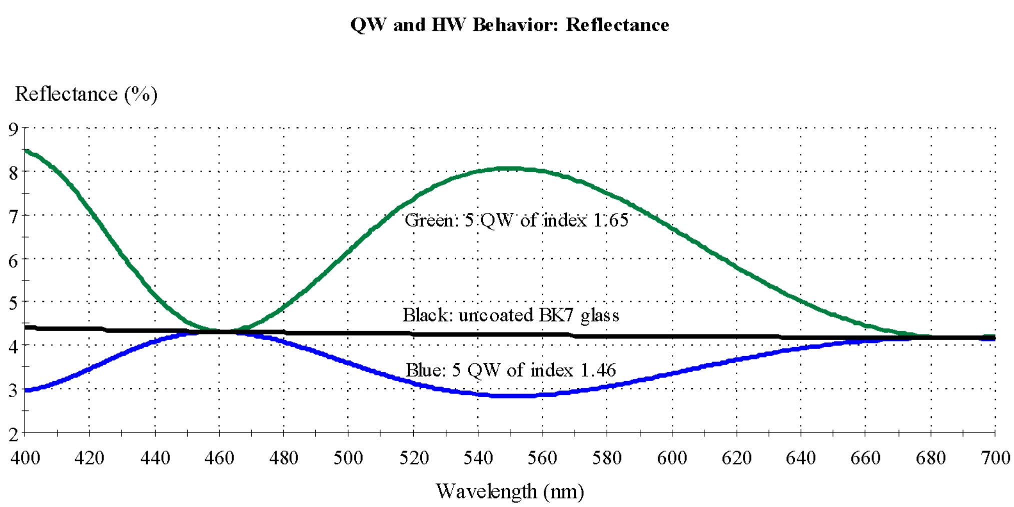


Figure 1. Reflectance for single layers of SiO_2 and Al_2O_3 each 5 QW OT at 550 nm. The departures from the reflectance of uncoated glass are shown..

Custom-designed infrared filters are used in a wide variety of photonic-related applications including:

- Optical detection of fire
- Motion and body heat detection
- Remote sensing
- Thermal imaging

MATERION ADVANCED CHEMICALS
407 N. 13th Street Milwaukee, WI 53233
5520 Midway Park Place NE
Albuquerque, NM 87109

North America: 414.289.9800
Europe: +44 1 488.686056
Asia: +65.6559.4450

Materion Corporation
www.materion.com

MATERION

In our continuing efforts to be a conscientious global neighbor, our newsletter is going digital!

We are committed to bringing you the latest innovative information on thin film coating materials and applications.

To continue to receive Coating Materials News, please send us an email at ACNewsletter@materion.com stating you wish to continue to receive the Coating Materials Newsletter through email. Please include your name and company as well as comments and suggestions for future articles.

www.materion.com

To produce practical AR coatings with broader wavelength coverage, combinations of high-, low-, and medium- index materials are used to design a multi-layer coating. We have previously shown examples of visible broadband AR coatings used for ophthalmic and general glass coating that consist of four layers using titania (n = 2.25) and silica (n = 1.46).

Alternating high- and low-index materials are used in designs to make all-dielectric reflectors also. Typical applications are heat-reflecting and cold-reflecting filters for applications that need to exclude IR energy or short-wave energy, respectively. An example common to everyday experience is the filter assembled into digital cameras that prevents near IR light from being sensed by the silicon detector array, while transmitting the visible RGB light spectrum. Figure 2 shows the performance of a design that has a total of 28 layers consisting of silicon dioxide and titanium dioxide. It is desirable to use materials that provide as large an index contrast as possible between the High and Low indices, because the greater the index ratio, the larger is the reflection bandwidth. In the IR reflector example, a single QW stack does not reflect IR wavelengths to the sensor sensitivity limit, therefore a second reflecting stack centered at a longer wavelength was needed.

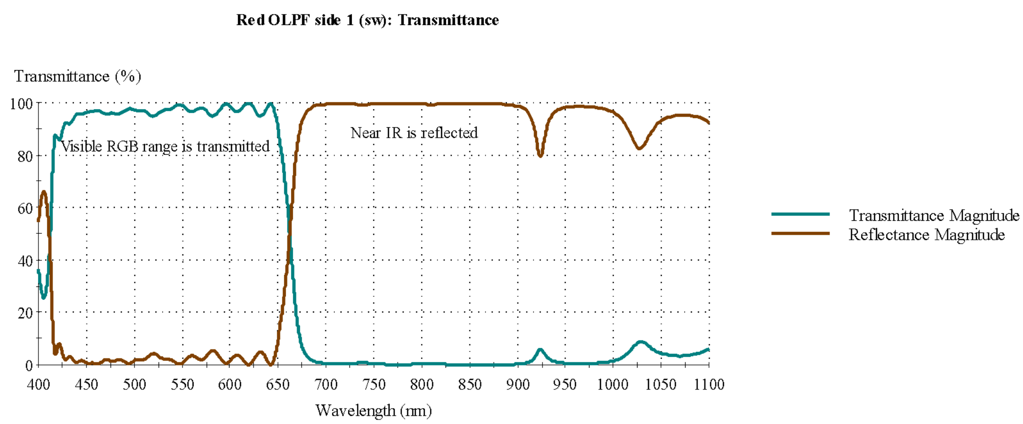


Figure 2. The IR filter used in digital cameras removes near IR light to prevent its being sensed by the sensor array.

REFRACTIVE INDEX DETERMINATION

Optical properties of thin films are characterized by their refractive index, *r.i.* = *n-ik*, where *n* is the component responsible for refraction; and *k*, the extinction coefficient, is the component that designates the absorption of the film. All materials absorb energy at some wavelengths. Generally, absorbance increases toward higher photon energies or shorter wavelengths. Specific absorption bands might also exist that are intrinsic to the material composition. In addition, extrinsic influences such as bound water will impose absorption bands as specific wavelengths. Finally, atom deficiencies in a compound can introduce absorption; an example is incomplete oxidation of an oxide compound, often due to improper evaporation / deposition conditions.

The spectral behavior of single layers illustrated in Figure 1 is also used to determine the refractive indices of thin film layers of coating materials. Transmittance and reflectance measurements using spectrophotometers are made of samples of thick films on substrates of known optical characteristics. The layers are deposited to be many QWs in optical thickness so many QW and HW positions can be used to compute r. i. over a large wavelength range. Both *n* and *k* are wavelength-dependent quantities, and therefore dispersive data is needed for the design of coatings that must operate over a wide spectral region. Mathematical algorithms have been developed that permit the determination of *n*, *k* at the extrema positions, and physical thickness *t* from data such as that in Figure 1. More accurate and higher spectral resolution of continuous wavelength increments are made using spectroscopic ellipsometry (SE). In that technique, polarized light incident at a high angle (>60°) is analyzed to measure the ratio of the reflected polarized components and their phase difference. Using complicated math models, *n*, *k*, and *t* can be extracted from films whose thickness can be sub-QW to many QW's.

An example of the optical properties of $LaTiO_3$ determined from SE is given in Figures 3 and 4. The dispersion with wavelength in both values is evident.

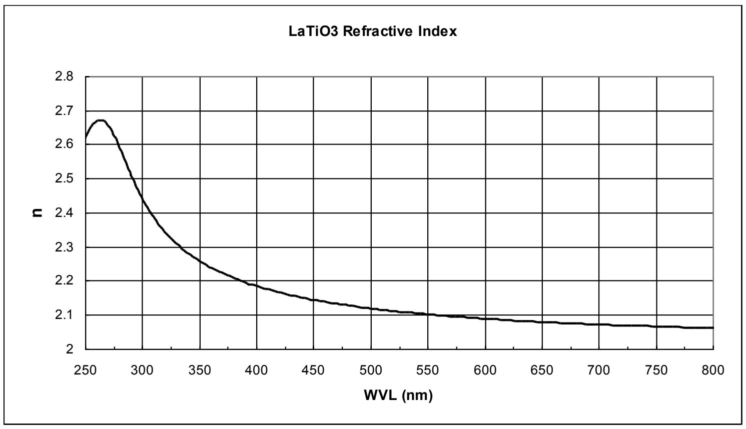


Figure 3. Refractive index of a $LaTiO_3$ layer as determined by spectroscopic ellipsometry.

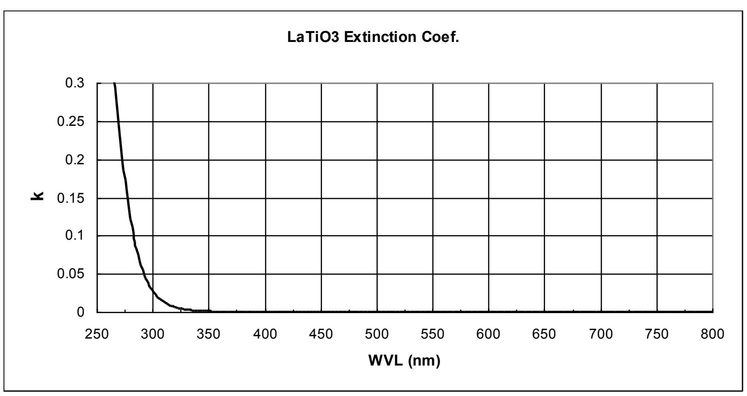


Figure 4 . Extinction coefficient of a $LaTiO_3$ layer as determined by spectroscopic ellipsometry. k falls to 0.001 at 400 nm.

RARE EARTH MATERIALS

With the exception of Scandium and Yttrium, the other 12 rare earth elements (REE) are those elements having atomic numbers from 57 (La) to 71 (Lu). RE oxides and fluoride compounds are used in optical thin films and provide properties that are absent in the more common refractory oxides. Table 1 lists some of the characteristics of thin films of commonly used rare earth compounds. RE fluorides transmit to shorter wavelengths than oxide compounds. For applications shorter than ~250 nm; some of the RE fluoride compounds are the only alternatives to silica, which has a transmission limit of ~200 nm. Laser systems for lithography and other applications that operate in the Deep UV (to 200 nm) or Vacuum UV (to ~140 nm) require high-low index combinations of fluoride compounds selected from Table 1.

Rare Earth Materials

Fluorides
For a variety of IR and low index thin film optical applications.

Metallics
Found in reflecting, adhesion and reacted thin films.

Oxides
Applications include AR, UV and high index optical thin films.

Sulfides
Used in a number of precision IR devices.

Selenides
High index components in IR thin films.

Table 1. Properties of Common Rare Earth Film Layers.

Compound	Trans. (nm)	Index (vis)	Application
YF_3	<200 – 13000	1.5	IR repl. for ThF_4
YbF_3	<200 – 13000	1.55	“ “ “
LaF_3	~200 – 13000	1.6	DUV to IR
NdF_3*	~200 – 12000	1.6	DUV to IR
CeF_3	<300 – 12000	1.65	IR repl. for ThF_4
Y_2O_3	300 – 11000	1.8	Medium n, hard
Sc_2O_3	250 - 11000	1.9	Near UV, hard
La_2O_3	300 - >10000	1.9	Near UV
Pr_2O_3	350 - >10000	1.95	Medium n
CeO_2	350 - 16000	2.2	High n, IR

* GdF_3 and DyF_3 have similar properties.

Fluorescence of La_2O_2S:Tb Layer using Deep UV Excitation

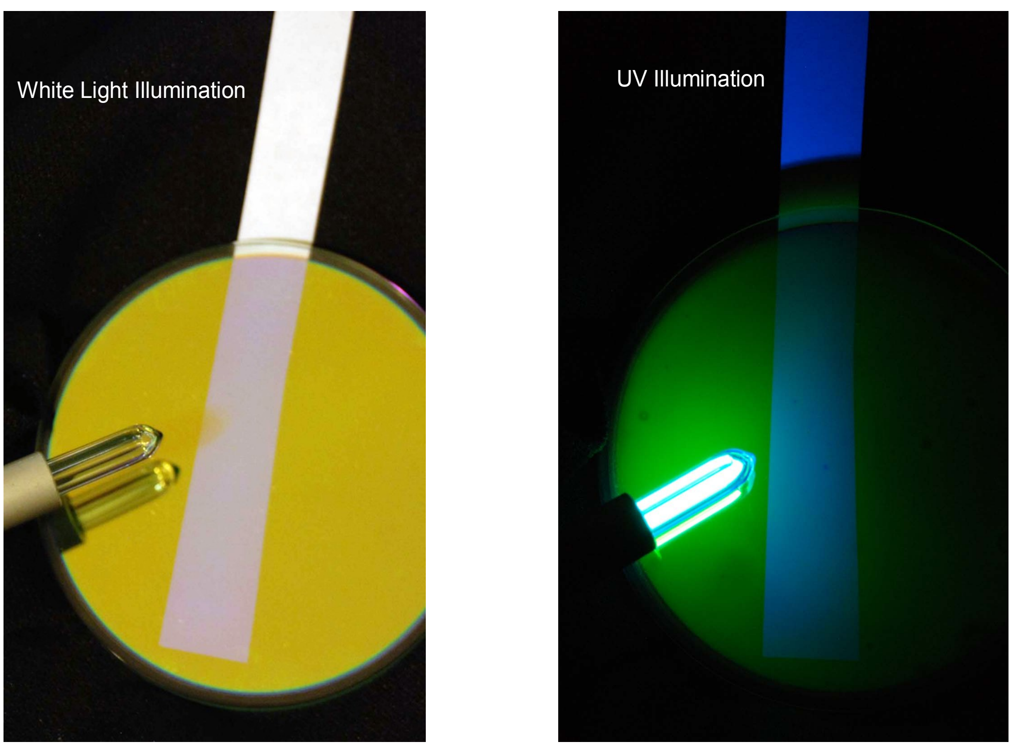


Figure 5. White light reflection (left) and UV–excited green emission of a RE compound deposited in thin-film form (right).

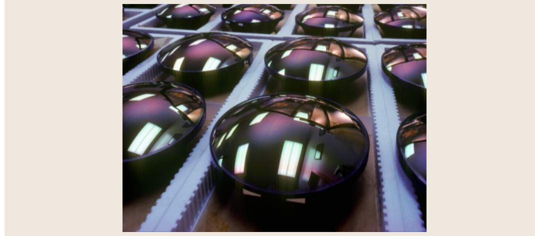
RARE EARTH PHOSPHORS

REEs possess a unique property of fluorescing in the visible wavelengths when excited by higher energy photons. Oxide compounds prepared using certain RE elements provide a variety of spectral line emissions that form the basis of color displays based on phosphor pixels [1, 2, 3]. CRT TV screens, electroluminescent panels and lamp phosphors are constructed of RGB pixels whose colors are produced by RE ions, specifically: R at 625 nm from Eu^{3+}, G at 550 nm from Tb^{3+}, and B at 450 nm from Tm^{3+}.

Emitted colors are produced by Gd^{3+} for blue and Nd^{3+} for blue-violet. These phosphor layers are deposited as a host oxide such as La_2O_3 or Y_2O_3 that is doped with a few % of the RE ion to emit the desired wavelength (color). Color emission can be excited by high-energy stimulation by UV below ~400 nm, by electrons, or by x-rays.

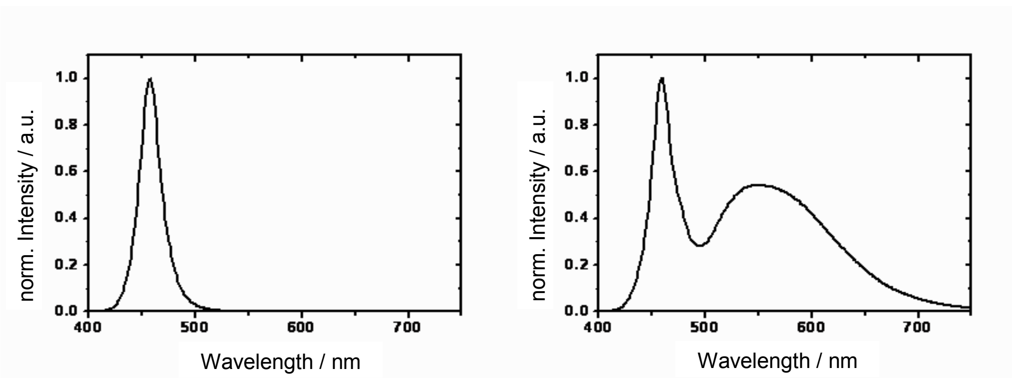
Recently, digital x-ray conversion plates made from RE phosphors have replaced silver-based film, and benefit the patient by requiring lower X-ray exposure. For these plates, the doped emitter layers need to be hundreds of micrometers thick to provide a great enough cross section to the x-rays for high emission efficiency. Figure 5 shows an example of phosphor emission excited by UV.

Demands for increased commercial and domestic lighting efficiency have led to the development of solid state white LEDs. White LEDs offer efficiencies that exceed by 1.5x fluorescent light efficiency, and are currently approaching 120 Lm/W. This value is 10x the luminous efficiency of traditional tungsten bulbs. White light emission is accomplished by either of two methods. In the more efficient method, the emitted output of a blue LED is combined with the yellow fluorescent emission created in the RE phosphor [4, 5].



The yellow emitter is, for example $Y_3Al_5O_{12}$ doped with Ce(III), known as (YAG:Ce). The emission spectra are shown in Figure 6 [4]. RE additives mentioned above are used to adjust the color rendition and apparent white balance (chromaticity) by shifting the combined emission spectrum toward the red or green regions. In the second, less efficient method, white light output is obtained by mixing R, G, B phosphors and exciting the mixture with a UV LED. A higher color rendering index (CRI) is obtained, but the efficiency is lower.

Figure 6. Left - Emission spectrum of a blue LED. Right - Combined emissions of the blue LED and the yellow phosphor to give a rendition of white light (from [4]).



In this issue, we have introduced some fundamentals of optical film technology and briefly reviewed material-related applications.

REFERENCES

1. Robert A. Buchanan, Melvin Tecotzky and Kenneth A. Wickershein, US Patent 3,725,740 (1973).

2. Robert A. Buchanan, Ronald V. Alves, T. Grant Maple, and Leon E. Sohan, US Patent 3,825,436.

3. Stuart M. Jacobson, Steven M. Jaffe, Hergen Eilers, Michael L. Jones, US Patent 5,496,018.

4. HolgerWinkler, Holger Enderle, Clemens Kuehn, Ralf Petry, and Tim Vosroene, "Advanced Phosphors for LED Applications," Proc SPIE Vol 6797, 67970A-3.
Carl M. Lampert, "Booming Market of Solid State Lighting," Soc. Vacuum Coaters. Spring Bulletin, 10 (2011).

Markets and Applications for Phosphor Formulations utilized in high brightness LEDs:

Backlighting
- Flat Screen TVs
- Smart Phones
- Computer Monitors

Automotive
- Turn Signals
- Interior Lighting
- Exterior Lighting

Signage
- Safety
- Traffic
- Displays

General Illumination
- Soft White Light

MATERION

MATERION ADVANCED CHEMICALS
407 N. 13th Street, Milwaukee, WI 53233

COATING MATERIALS NEWS is a quarterly publication published by Materion Advanced Chemicals.

MATERION ADVANCED CHEMICALS
407 N. 13th Street
Milwaukee, WI 53233
Phone: 414.289.9800
Fax: 414.289.9805

Web: www.materion.com/AdvancedChemicals
Email: AdvancedChemicals-Info@materion.com

EDITOR:
David Sanchez
Sr. Materials & Application Scientist
Materion Advanced Chemicals

PRINCIPAL CONTRIBUTOR:
Samuel Pellicori
Pellicori Optical Consulting
P.O. Box 60723
Santa Barbara, CA 93160
Phone/Fax: 805.682.1922
Email: pellopt@cox.net

For a free subscription to CMN, please email your name and address to: ACNewsletter@materion.com.

Guest articles or topic suggestions are welcome.

An electronic version of this publication can be accessed from the Resource Center/Literature page of the Materion Advanced Chemicals web site at: www.materion.com/AdvancedChemicals.