MATERION

TECHNICAL PAPER

Coating Materials for High Reflectors

Considerations Involved In Design and Production

Author: Samuel Pellicori
Materion Coating Materials News

Introduction

Reflecting coatings that provide near-maximum reflectance are used in all types of optical systems, as well as in solar energy concentrators, general illuminators and instruments using high-energy lasers. Here we discuss applications and coating materials for reflectors used in UV-through IR regions.

High-reflecting mirrors used in the visible range, where the requirements are less demanding, are satisfied by aluminum and silver metals with protective or reflection-enhancing dielectric layers. However, mirrors for long-wave IR wavelengths use coatings of gold. Bare metals provide high reflectance but they are susceptible to chemical attack and abrasive scratching by handling and environmental components. Because of that, they are protected by over-coating with dense (impermeable) hard dielectric layers. Typical protective dielectric materials include aluminum oxide, silicon oxides, and some rare-earth oxides. The choice is dictated by the spectral region of operation. For example, for UV mirrors to ~300 nm wavelength, alumina and silicon dioxide are useful. For LW IR mirrors, the gold coating is protected by hafnia or yttria. Reflectors used in high laser energy applications require special materials and deposition process considerations.

Metal Reflectors

The optical properties of metals are characterized by their refractive index and extinction coefficient (n & k) values dispersed with wavelength. The k values for metal are high and the n values are low, which makes them good reflectors. These properties are in direct opposition to dielectric materials. The large k/n ratio over large wavelength ranges gives these metals high and somewhat neutral reflection. For example, in green light (wavelength 500 nm) n and k for aluminum are 0.65 and 5.5, respectively, resulting in a visible reflectance of ~90% for the bare surface. Aluminum has an absorption band centered at 810 nm that lowers the reflection to ~86%. For silver at 10 µm, $n = 0.06$ and $k = 2.87$, and the reflectance is 98%. When an Al mirror is used at large incidence angles, polarization separation occurs. This results in a lower average reflection in the near-IR.

Metal reflecting layers are typically deposited as a result of thermally evaporating the metal at high deposition rates and high vacuum to prevent oxidation. Substrate temperature needs to be low, ~50° C to maintain high reflection. Protecting oxide layers require E-beam or sputter deposition. E-beam and resistance-heated (RH) deposition heat the substrate, while sputter deposition does not. Most metal mirrors are deposited by a combination of RH and E-beam, or by sputtering from multiple targets.

It would be accurate to conclude that reflectors based on metal layers are an easily implemented solution to the requirement for an efficient reflecting coating for the <400 nm to >1200 nm wavelength region (visible – near-IR). In that example, a metal such as aluminum or silver would be coated with a set of dielectric layers that serve to protect the metal and perhaps to enhance reflection. However, there are issues associated with this solution. A dielectric coating can increase reflection only over a small wavelength span and it will introduce a region of lower reflection than the bare metal outside this enhanced band.

Silver has the highest metallic reflection, >98% avg from ~450 nm to the Far-IR, but is susceptible to corrosion from sulfur-bearing and chlorine atmospheric gasses in the presence of water vapor. Many coaters have derived “solutions” to the long-term stability problem and offer their version of a ‘protected’ silver coating. Typically, it consists of a dielectric layer composed of one or more of the following materials: alumina, silicon monoxide, hafnium dioxide, or tantalum pentoxide. These are used in combinations and thicknesses appropriate for the wavelength coverage. The protection is not a permanent solution for long-term operation in the atmosphere because the permeation of gasses is only retarded by the over-coating layers.

Several contributors to degradation of reflectance and growth of corrosion are: the occurrence of pinholes, or the presence of particulate inclusions of reactive material emanated during deposition. Both defects are known to be initiation sites for corrosive reaction. The successful long-term (years duration) protection of silver mirrors is an ongoing research problem involving deposition process parameter studies as well as improved coating materials.

High Reflectors and Dichroic Beam-dividers

With all-dielectric reflectors, the energy that is not reflected is instead transmitted, since there is no absorption. ***Figure 1*** shows the computed reflectances for Quarter-Wave (QW) designs based on two different high-index materials, tantala and titania, and used at zero incidence angle. Reflectance >99.8% is theoretically possible. All-dielectric mirrors are effective only over band widths restricted by the index ratio.

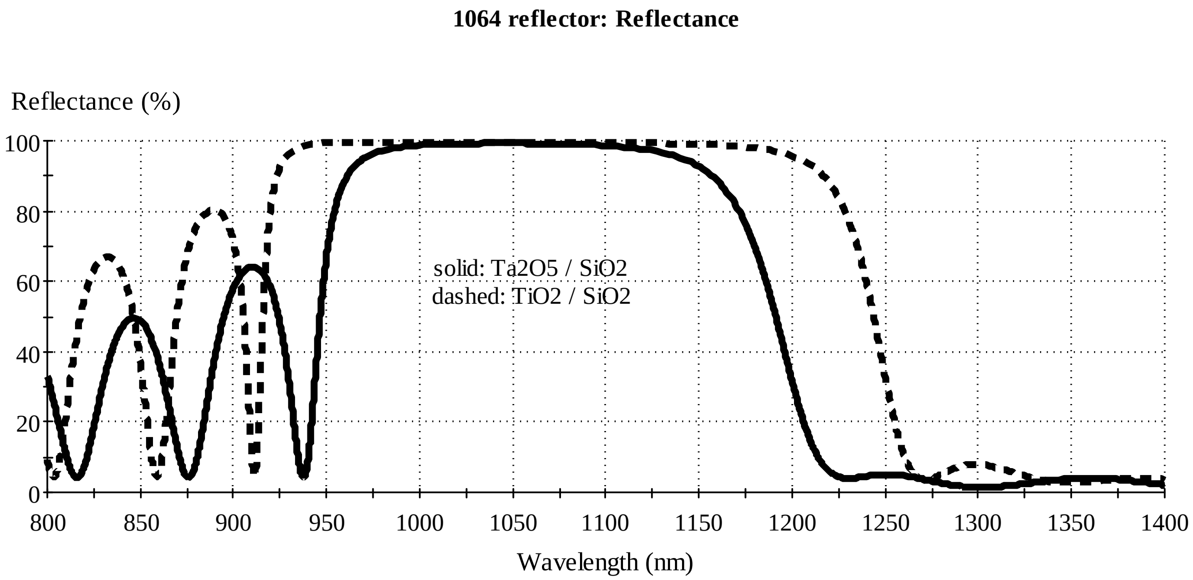

Figure 1. Theoretical reflectance >99% is produced at 1064 nm by an all-dielectric laser mirrors composed of twelve pairs of silicon dioxide with tantala or titania.

For the tantala/silica H/L index ratio ~1.4 used in the design, the high-reflectance (>99.5%) bandwidth is ~150 nm; for titania/silica this width is<200 nm. Wide-band mirrors can be constructed by repeating and shifting the design to wavelengths whose design centers are scaled relative to each other to make a continuous wider high-reflectance region. To cover the visible region, 420 to 680 nm, with R>99.5%, three stacks of 25 layers each are required. Using titania/silica, H/L = 1.54, the reflection band is wider, and fewer layers would be needed to produce this reflector. Further complicating this coating construction is the appearance of ripple from interfering bands, resulting in performance that departs from the flat ~99% reflection goal. A partial solution is to modify the design from all-QW to non-QW layer thicknesses.

Narrow-band High-Reflectors

Wavelengths on either side of the reflection band have low reflection or high transmission. For this example, higher transmission is present at the long-wavelength side. The deep ripples in the short-wavelengths can be smoothed by matching the admittance of the QW stack to the glass substrate and air.

The coating materials used to make high reflectors are chosen based on their absorption edges. ***Table 1*** lists the most commonly used materials and their optimum spectral regions. The high-indices are ~2 (Al2O3 is 1.65) and the low-indices are ~1.45. The oxides (except for $LaTiO_3$) can be sputtered as well as evaporated. Niobia (Nb_2O_5) has become a favored material because it provides higher sputter rates than the other high-index materials. The fluorides used at the shorter UV wavelengths are typically evaporated from resistance-heated containers but can be E-beam evaporated at low power.

Wavelength Region	**400-3000 nm** **Visible to SWIR**	**220-400 nm** **UV- A, B, C**	**<220 nm** **DUV & Excimer**
High-index	Ta_2O5, TiO_2, Nb_2O_5, $LaTiO_3$	HfO_2, ZrO_2, Al_2O_3	LaF_3, GdF_3
Low-index	SiO_2	SiO_2	MgF_2, AlF_3
CMN references	1, 2	3	4

Table 1. Dielectric Materials Recommended for Reflectors in Different Wavelength Regions.

Applications for Beam-Dividers Based on Dichroic Reflectors

In many applications, two wavelength regions are required to be spatially as well as spectrally separated. This is accomplished by tilting the QW reflector. Reflectors built from QW layers that provide this ability are known as a “dichroic mirrors.” Dichroic mirrors are used in many applications to physically separate light sources of different wavelength content or to combine them in a common path. Examples include dental and medical illumination from incandescent lamps, where visible light is directed toward the patient while heat is transmitted away. Also, color video projectors use them to combine R, G, and B signals to compose colored images from individually modulated light channels.

Dichroic coatings can be used for color separation/combination in imaging, scientific and even decorative applications. When tilted to a large incidence angle, complementary spectral components are transmitted and reflected. The photo, ***Figure 2,*** illustrates the separation of the blue and red components of a magenta-reflecting dichroic coating from the transmitted complimentary green component color.

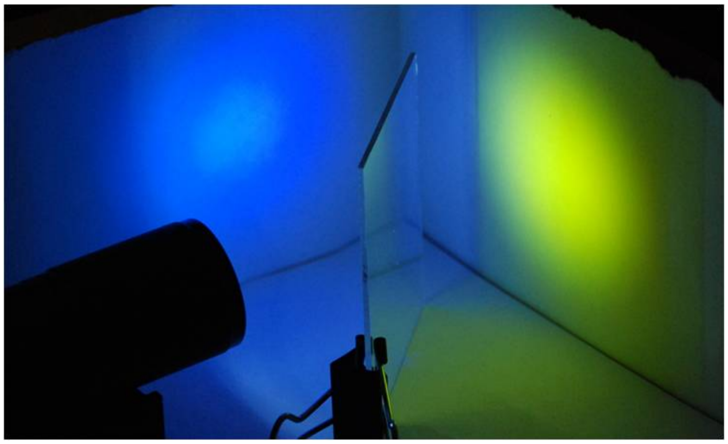

Figure 2. Dichroic coating reflects blue and transmits complimentary color yellow. (Photo by author S. Pellicori).

If the complementary components are absorbed, as in ***Figure 3,*** the dichroic mirrors become colored decorative mirrors.

Figure 3. Colored reflectors are produced by absorbing the transmitted complimentary colors. (Photo by S. Pellicori).

Tilting a QW stack of layers to incidence angles >0° also introduces separation between the perpendicular and parallel polarization planes (S-, and P- respectively). ***Figure 4*** illustrates the creation of a polarizer for 1064 nm laser energy by taking advantage of the separation of both ~99^{+}%. The mean high reflection is essentially unpolarized.

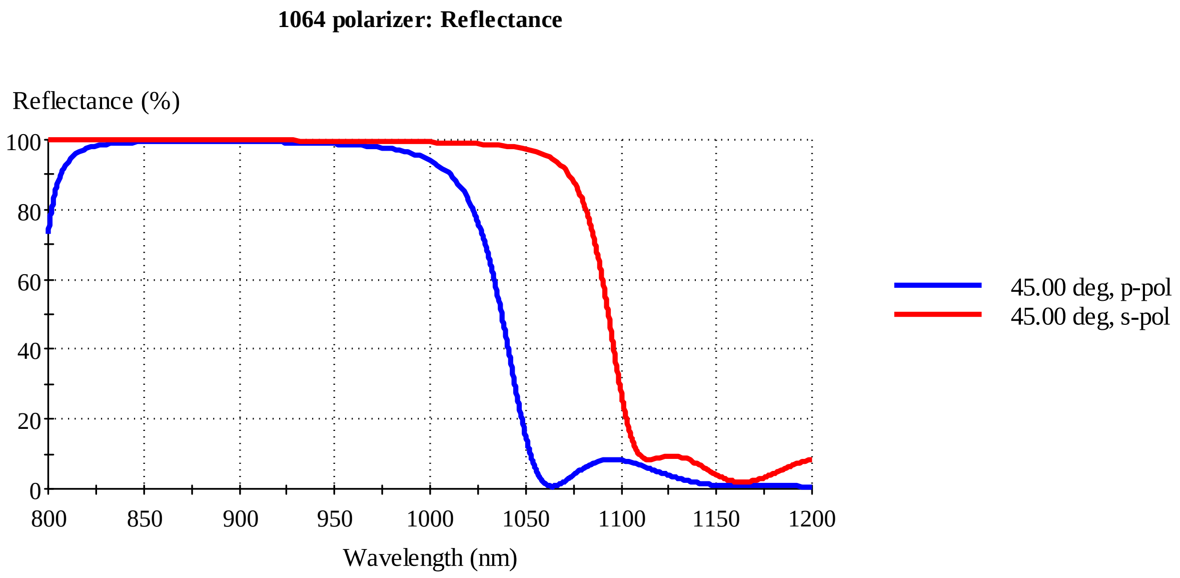

Figure 4. Separation of the polarization components caused by tilting the QW design of Figure 1 produces a polarizer for 1064 nm.

Reflectors for High-energy Laser Applications

Reflectors exposed to high energy laser photons at high fluences are sensitive to coating absorption and nano-structural defects that can initiate damage sites. The inherent presence of absorption in metals negates their use in reflectors that must exhibit high Laser Damage Thresholds (LDT). The absorption in metals is so high that metal mirrors can only be used with low energy lasers.

Laser damage mechanisms also vary depending on the nature of the laser radiation and coating defects. Different damage mechanisms operate with pulsed laser irradiation power, duration and pulse width as compared with continuous irradiation. Laser pulse widths in the pico- and femto-second range require special consideration because peak powers can be at the mega-watt levels. When particulate inclusions or structural defects are present in the coating, the coating is more susceptible to damage by pulsed, high energy lasers. When absorption is present, the coating is more easily damaged by heating from the continuous irradiation. Damage manifests as craters of vaporized and spatter sites with pulsed lasers; and with CW lasers, as melting and buckling.

Design Solution for High LDT Mirrors

The solution for providing high LDT mirrors is to base the design on all-dielectric quarter wave optical thickness (QW) layers. Acceptable dielectrics have *k* <0.001. Pairs of alternating high- and low-index layers compose the reflector. The example of an all-dielectric laser reflector for 1064 nm, shown in ***Figure 1*****,** has a theoretical reflectance maximum reflectance of 99.88%. However, in practice R will be less likely to scatter and achieve non-zero absorption. Laser engineers design these coatings to compromise between lifetime limitations for reflectance value and laser damage. Mirrors for laser systems that convey high energy densities and powers need to be free of absorption and point defects.

Both these imperfections contribute or cause damage to the coating or optic when irradiated by high energy densities present in laser systems. The laser damage threshold (LDT) for coatings that possess absorption is lower for continuous wave (CW) lasers than for pulsed laser irradiation of short pulse length and frequency. In the CW application, localized heating causes the coating to burn or bubble. In the pulsed laser case, defects are the sites for damage initiation because electric field energy is maximized at these points.

LDT is influenced by material composition and layered nano-structure. These properties are determined by the deposition process. For example, E-beam with IAD produces compact layers with high mechanical durability and adhesion. But often, incomplete oxidation can occur and produce absorption and low LDT. Other processes, such as pulsed DC magnetron sputtering (PDCMS), plasma-ion assisted (PIAD) or ion-beam sputtering (IBS), produce coatings with low absorption and complete oxidation (stiochiometry), and consequently high LDTs. IBS produces the lowest coating defect content and absorption among the current deposition processes in use, and therefore high LDTs. For example, mirrors produced by IBS exhibit absorption and scatter values at <20 ppm, and are used in ring laser gyros where millions of bounces are experienced by the mirrors.

Conclusion

This is a short introduction to the complex materials and design considerations that are involved in the production of high reflectors. There are a vast variety of applications, many of which have been cited as examples. While many applications are well established, improvements in the related coating technology continue to evolve.

Materion Coating Materials & High Reflectance

As a global innovator of optical coatings and metals applications, Materion is dedicated to providing sophisticated optical coating materials for the semiconductor, precision optics, high-performance solar and low emissivity industry. In markets where performance dictates success, we employ processes that produce precise optical coatings including high reflectors. For more information on our thin film optical coating materials, please contact Andrew Cohen, Product Marketing Manager at Andrew.Cohen@Materion.com .

References

1. Coating Materials News V16 Issue 1, March 2006
2. Coating Materials News V16 Issue 1, March 2006
3. Coating Materials News V12 Issue 2, June 2002
4. Coating Materials News V17 Issue 2, June 2007
5. Coating Materials News V20 Issue 1, March 2010

Principal Contributor

Samuel Pellicori, Pellicori Optical Consulting, Santa Barbara, CA
Phone: 805.682.1922, Email: pellopt@cox.net

Materion Advanced Materials Group
2978 Main Street
Buffalo, NY 14214
+1 800.327.1355
www.materion.com/advancedmaterials

Materion Advanced Materials Group is a global supplier of premier specialty materials and services. Our offerings include precious and non-precious thin film deposition materials, inorganic chemicals and microelectronic packaging products. In addition, we offer related services to meet our customers' requirements for precision parts cleaning, precious and valuable metal reclamation and R&D. We support diverse industries including LED, semiconductor, data storage, optical coatings, large area glass and aerospace.