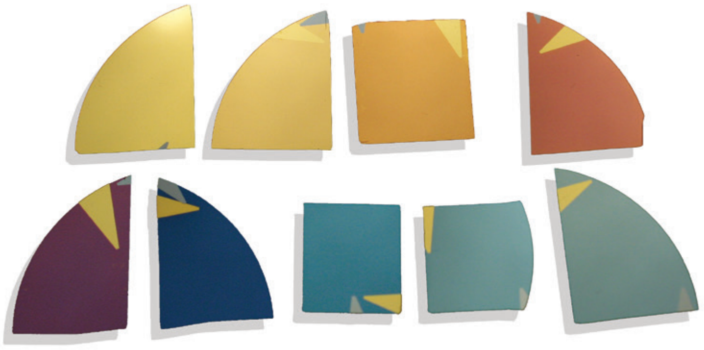

Thin-Film Interference

in Lossy, Ultra-Thin Layers

**Mikhail A. Kats, Romain Blanchard,
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Although much thinner than conventional optical interference coatings, nanometer-thick films made of optically absorbing materials can display strong interference effects. This new class of coatings shows promise for coloring and labeling, optical filters, tunable absorbers and emitters, and energy harvesting.

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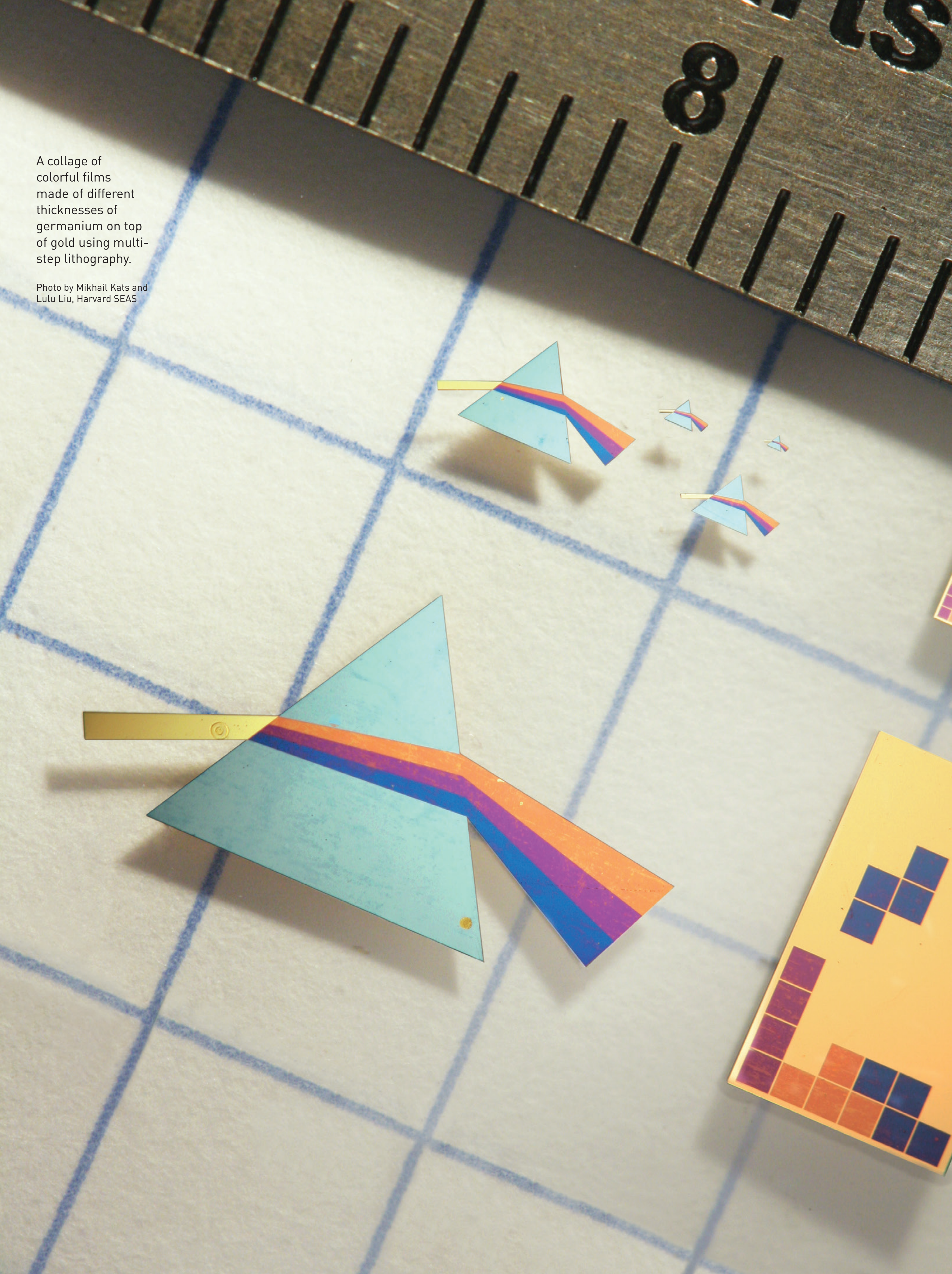


A collage of colorful films made of different thicknesses of germanium on top of gold using multi-step lithography.

Photo by Mikhail Kats and Lulu Liu, Harvard SEAS

Thin-film interference is the ubiquitous optical phenomenon responsible for the colorful, iridescent reflections that we see in oil films on water, soap bubbles and peacock feathers. It occurs in structures composed of one or more transparent thin films, whose typical thickness is similar to the wavelength of light.

Light incident on a single transparent thin film will both reflect and refract at the top interface. Light transmitted into the film propagates until it reaches the bottom interface, where a portion is reflected and a portion is transmitted. This process repeats multiple times—light bounces back and forth between the two interfaces, with some light leaking out at every bounce.

Because of the wave nature of light, each portion of it can be imagined as a partial wave with its own wavelength, amplitude and phase. The way these partial waves interfere—constructively, destructively or neither—ultimately determines which wavelengths are transmitted and which are reflected. The amount of optical phase that a partial wave accumulates as it makes a trip through the film depends on the so-called "optical thickness," which is a function of the layer thickness, the incidence angle and the refractive index. As a result, the destructive and constructive interference conditions—and hence the emergent colors—depend on the refractive indices of the film and surrounding regions, the film thickness, and the viewing angle.

Thin-film interference is prominently featured in all areas of optical science and engineering. For example, in the July/August issue of *Optics & Photonics News*, Greg Gbur described how Jean-Baptiste Perrin, a 20th century French physicist, carefully observed interference fringes from soap films and deduced the thickness of the films, which varied by increments of 4.5 nm. Thus, Perrin calculated the length of the soap molecules along their longest axis and directly demonstrated the discontinuous (molecular) structure of matter.

> **In our research, we considered the counter-intuitive situation in which films were not only highly absorbing, but also very thin.**

In optical technology, thin-film interference forms the basis of thin-film optical coatings, which can be found in almost every optical system—from eyeglasses to microscopes. The functionalities of optical coatings include anti-reflectivity, high-reflectivity, spectral filtering and beam-splitting.

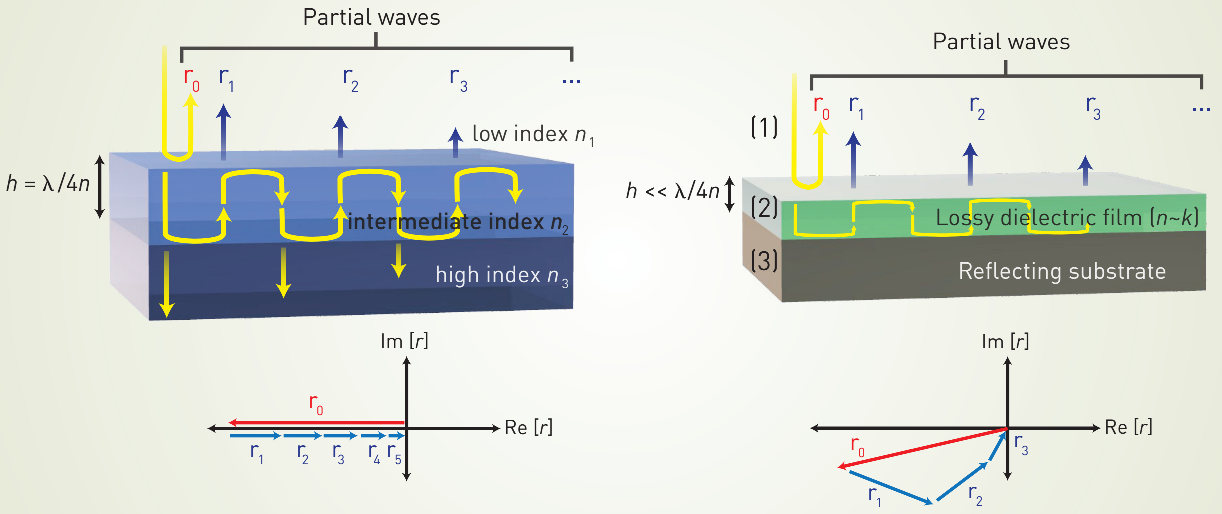
Phasor diagrams as a way to visualize interference

The partial wave description of reflection from a thin film can be expressed graphically by using plots called phasor diagrams (illustration, p. 43). Since each reflected partial wave is described by its own complex number r_0, r_1, … r_m, these can be plotted as vectors in the complex plane and then graphically added. The amplitude and phase of the overall reflected light can then be immediately read from such a diagram.

For the single-layer AR coating, the first phasor r_0 represents the first partial wave; it points directly to the left because it has a phase of π due to reflection from a lower-index material to a higher-index material. The next phasor corresponds to light that enters the film, propagates a distance h corresponding to a quarter wavelength, reflects from the film/glass interface, and then propagates another distance h before exiting back into the air. As a result of the round trip through the film, r_1 has a phase of 2π, which is equivalent to 0, and so the corresponding phasor points to the right along the real axis. Performing this type of analysis for all of the other phasors shows that each has a phase of 0 as well, and as such points to the right.

From the phasor diagram of the single-layer AR coating, one can see that the partial waves r_1, r_2, … r_m all destructively interfere with the first partial wave r_0. If the amplitude of r_0 balances the combined amplitudes of r_1, … r_m exactly, which occurs when $n_2 = \sqrt{n_1 n_3}$, this destructive interference leads to a complete

Partial wave description of reflection from a thin film



(Left) Conventional quarter-wave anti-reflection coating. (Right) Reflection suppression using an ultra-thin, lossy layer on a reflecting substrate.

Phil Saunders/Adapted and modified from Kats et al., Appl. Phys. Let. **101**, 221101 (2012).

suppression of reflectivity. Since there are no losses in this structure, all of the light is transmitted.

Interference coatings with lossy materials

Most optical coatings in use today have two defining features: They use low-loss dielectric films, and their film thicknesses are on the order of the wavelength of light, with the quarter-wave AR coating often considered to be the thinnest useful interference coating. Optical losses due to absorption are frequently a detriment; when they are necessary to absorb or filter out some fraction of light, they can be considered a perturbation in the optical design in the sense that the interference conditions do not change significantly.

Highly absorbing dielectrics are typically not considered for optical coatings. This is because, by the time that light propagates through a wavelength-scale film of such absorbing material, it is almost completely attenuated and can no longer interfere with itself.

In our research, we considered the counterintuitive situation in which films were not only highly absorbing, but also very thin—significantly thinner than even a quarter wavelength of light—such that not all light is attenuated in a single pass.

Although at first the reasoning appears circuitous, the use of materials with large optical losses actually opens the door for using ultra-thin films as interference coatings. In lossless dielectric coatings, optical phase is accumulated upon propagation through the film. The interfaces can contribute either a phase change of 0 or π upon reflection—but no other value. However, when one or both of the materials has large enough losses that the imaginary part of the complex refractive index is significant, the situation is very different: The reflection coefficients take on complex values, corresponding to a phase that is neither 0 nor π, and this phase change can take the place of phase accumulated via propagation through a thicker film.

We discovered that an ultra-thin lossy dielectric film deposited on an opaque, lossy metallic substrate is a particularly good example of thin-film interference with highly absorbing materials. This structure allows for suppression of reflectivity ("enhanced absorption") through destructive interference between all of the reflected partial waves, as shown in the phasor diagram above. Unlike in a conventional AR coating, where the reflected phasors all lie on the real axis, here the phasors trace out a loop in the complex plane yet still return to the origin, indicating complete destructive interference of the reflection. Even if the phasor path does not exactly return to the origin but terminates somewhere in its vicinity, substantial destructive interference is achieved.

Thin-film coatings on lossy metals are known in the context of metal anodization, an electrolytic technique that forms a layer of oxide with controllable thickness on a metal substrate. One example is anodized titanium: At visible wavelengths, titanium is a lossy metal, whereas titanium oxide is a transparent dielectric. By controlling the thickness of the oxide layer, different colors emerge. However, using highly-absorbing dielectrics (e.g., germanium) instead of lossless ones (e.g., titanium oxide) allows us to observe these interference effects for even thinner films.

Oil films on water can appear as any color of the rainbow, even though small quantities of oil and water are mostly transparent.

Refractive indices of dielectrics and metals

The optical properties of metals can be fully described by a complex refractive index. Purely real refractive indices describe lossless dielectrics and, as a rule, materials with a complex refractive index n such that real(n) > imag(n) typically describes an absorbing dielectric, while a material with real(n) < imag(n) describes a metal.

A metal with infinite electrical conductivity for all frequencies is sometimes called a “perfect electric conductor,” and has imag(n) → infinity. This idealization often approximates the behavior of metals at terahertz frequencies and below.

Color differences from handfuls of atoms

In our initial demonstration of ultra-thin-film interference at visible wavelengths, we used gold as the lossy metallic substrate, and amorphous germanium as the lossy thin film.

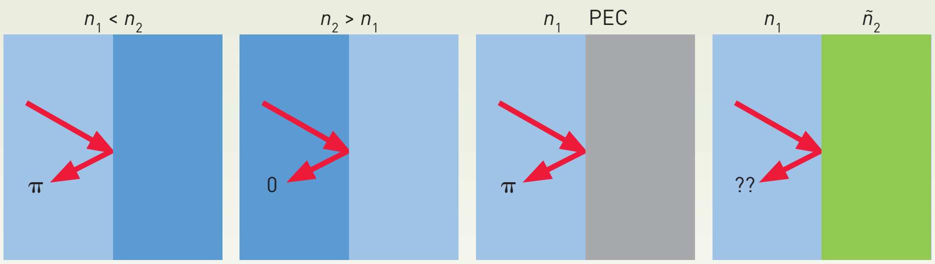
Calculations and experiments showed that germanium films between 5- and 25-nm-thick deposited on gold substrates yielded an array of colors from pink to blue, even though bulk germanium is gray. The appearance of the colors resulted from a dip in reflectivity, which corresponded to a peak in absorptivity, the wavelength of which red-shifted as a function of film thickness. This shift—approximately 20 nm in wavelength for every 1 nm change in film thickness—is a result of the thin-film interference condition changing with wavelength. The degree of absorption in the film is surprisingly large: At the absorptivity peak, about 70-80 percent of the incident light is absorbed within the 10- to 15-nm-thick film.

As a colorful demonstration, we used multiple steps of photolithography and electron-beam evaporation to create five-color images on a glass slide, featuring a mock-up of light refracting through a prism, a Tetris game in progress, and the logo of the Harvard School of Engineering and Applied Sciences. The five colors—gold, pink, violet, dark blue and light blue, correspond to bare gold and gold coated with 7, 11, 15 and 25 nm of germanium. Patterned in this way, one can appreciate the huge effect of thin-film interference with ultra-thin, highly absorbing films: the difference in color between the pink and violet regions, for example, is the result of an extra 4 nm of germanium, which corresponds to just eight germanium atoms in thickness.

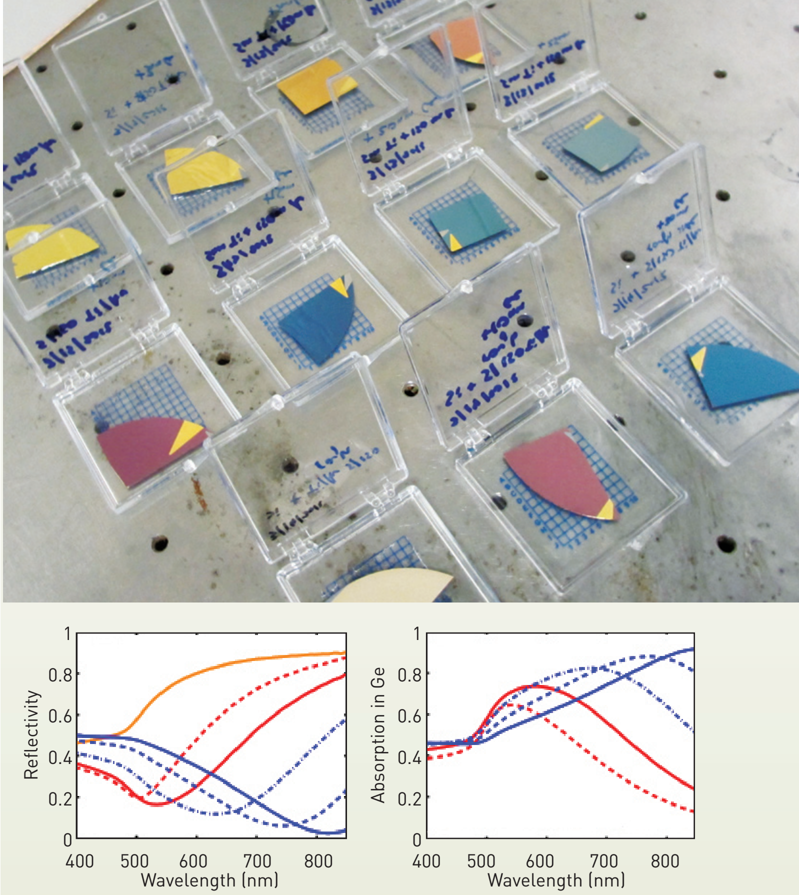
Distinguishing between pigments and interference colors

Suppose one desired to color an object such as a flat piece of metal. Two common processes come to mind: painting

The phase of REFLECTED LIGHT



Light reflected at an interface between two lossless materials can acquire either a phase of π (when incident from a lower-index material) or 0 (when incident from a higher-index material). Light incident on a perfect electric conductor (PEC) always acquires a phase of π. When one or both materials has a significant degree of loss, the phase of the reflected light can be anything; it depends on the precise complex refractive indices of the two materials.



(Top) Samples of gold coated with germanium films between 0 and 25 nanometers in thickness. (Bottom) Reflectivity and absorbancy of these films for different thicknesses of germanium.

Kats et al., Nature Mat. **12**, 20 (2013).

and thin-film interference (or other types of "structural coloration"). With the application of paint, the metal acquires the color of the pigment because all of the light is reflected, scattered or absorbed before it reaches the metal surface. Thus, paint is a method of coloring that is substrate-agnostic—whether silver, gold or copper, the metal will appear blue when covered with blue paint.

The situation is different for objects colored by thin-film interference. Oil films on water can appear as any color of the rainbow, even though small quantities of oil and water are mostly transparent. In this case, the optical properties of the substrate underlying the film matter, because light bounces back and forth in the film multiple times.

Usually one can visually determine whether an object is painted or colored by thin-film interference: A painted surface looks more or less the same from every viewing angle, whereas the reflection from optical thin films changes color and intensity depending on the angle at which you hold it. This is because the optical path length through the film depends on the viewing angle, and this path determines the interference condition.

However, this effect becomes less significant as films become thinner, until it is nearly impossible to discern the difference between a painted surface and one colored with ultra-thin interference coatings. Transparent films at such tiny thicknesses do not significantly affect the color of the substrate but highly absorbing films do. We determined that it is nearly impossible to use optical techniques to determine if an unknown sample is: 1) a solid block of material; 2) coated with smooth paint; or 3) composed of an ultra-thin film coating on a substrate.

This is related to a common problem in spectroscopic ellipsometry—a sophisticated technique used to determine complex refractive indices and thicknesses of thin films. While modern ellipsometers are sensitive to the presence of films down to a monolayer in thickness, they are unable to simultaneously determine the thickness and refractive index of an ultra-thin film if both are unknown.

Realizing dynamically switchable absorbers

Any active, dynamically tunable structure in photonics, such as a modulator or a display pixel, contains a tuning mechanism: some material or structure whose optical properties are altered with applied stimuli. We looked for a method to tune our thin-film absorbers and wavelength-selective coatings to create active devices.

Because the propagation distances are short and there is no field enhancement within these films, small changes in the complex refractive index are not sufficient to appreciably change the reflectivity of a sample. This rules out many common tuning mechanisms, including Kerr nonlinearity, carrier injection (at least at visible or infrared wavelengths), or liquid crystals.

To tune our thin-film structures, we turned to vanadium dioxide (VO$_2$), a well-studied phase change material. At room temperature, it is a semiconductor; however, when it is heated past about 70 °C, it undergoes a dramatic structural and electronic phase transition, resulting in bandgap collapse and a four-orders-of-magnitude increase in DC conductivity. This transition occurs gradually with increasing temperature, thus giving us access to a large range of optical properties.

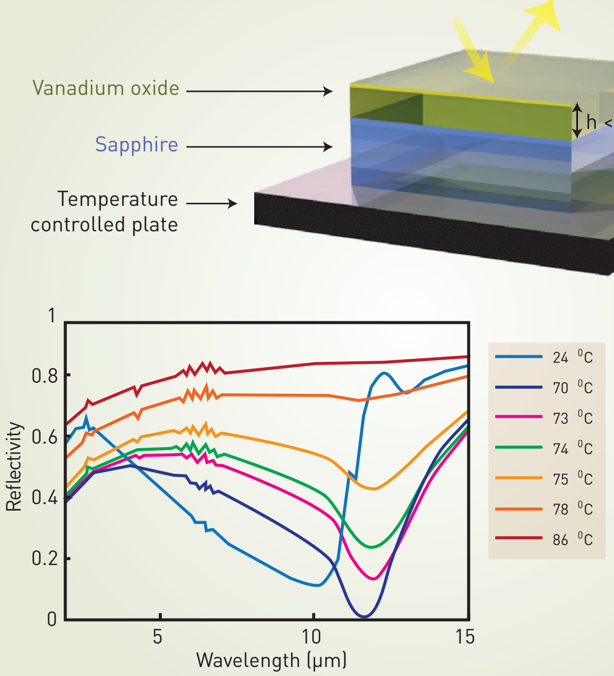
For this experiment, we worked in the infrared spectral range of 5-15 µm, which is important for thermal imaging and vibrational spectroscopy. Unfortunately, at these wavelengths, we could not use conventional metals (e.g., gold, silver, aluminum) as substrates because they behave too much like perfect electric conductors.

Instead, we turned to sapphire. Sapphire is a wide-bandgap dielectric whose complex refractive index at infrared frequencies has a large contribution from phonon resonances. Surprisingly, this effect is so strong that, at wavelengths between 11 and 15 µm, the optical properties of sapphire are quite similar to those of metals in the visible. Sapphire also happens to be an ideal substrate for VO_2 growth.

In our experiment, we monitored the infrared reflectivity of a 180-nm-thick VO_2 film deposited on a sapphire substrate as its temperature was swept from room temperature to 90 °C. At low temperatures, the VO_2 was basically transparent, and we could see the phonon features of sapphire, while at high temperatures the VO_2 was largely metallic and displayed a relatively large, slowly increasing reflectivity with increasing wavelength. However, at an intermediate temperature, when the VO_2 was neither purely semiconducting nor purely metallic, we observed that the reflectivity around 12 μm went abruptly to zero, corresponding to perfect absorption of light within the structure. At this temperature, VO_2 behaves as a highly lossy dielectric, thus allowing the destructive interference condition to be met and leading to greatly suppressed reflection and enhanced absorption within the VO_2 film.

> There are tradeoffs in device performance that may be overcome by managing and enhancing optical absorption.

Temerature-dependent reflectivity measurement



Reflectivity vs. wavelength for different temperatures. At an intermediate temperature (70 °C) the minimum in reflection corresponding to the perfect absorption can be seen.

Phil Saunders/Adapted and modified from Kats et al., Appl. Phys. Lett. **101**, 221101 (2012).

Applications of enhanced light absorption

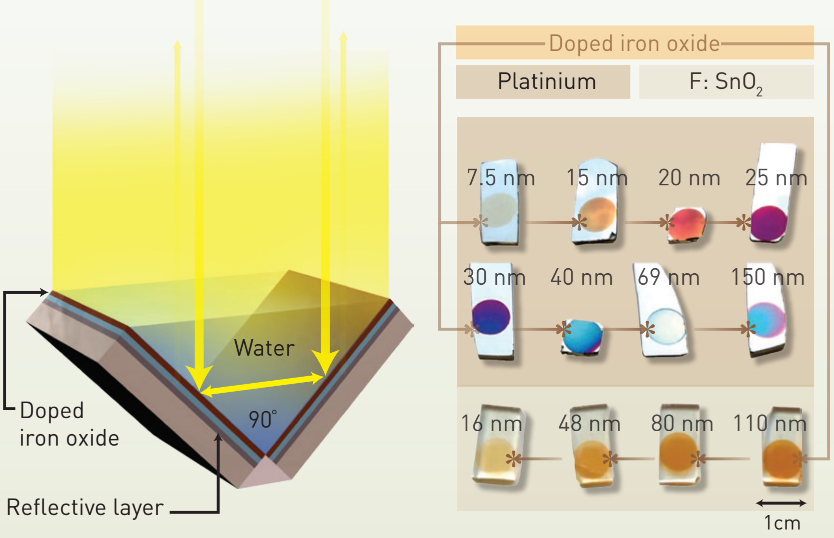
Conservation of energy maintains that light cannot just disappear: It must go somewhere or be absorbed. For the case of lossless thin films (such as soap bubbles), any destructive interference in reflection must correspond to constructive interference in transmission, and vice versa. When light shines on a sample with an opaque substrate, such as gold, any light that is not reflected must be absorbed.

While light absorption is often considered undesirable in optical systems such as microscopes and telescopes, there is a wide range of optical and optoelectronic devices for which absorption is a key feature. Most systems that require spectral (color) filtering use wavelength-dependent optical absorption. Perhaps more importantly, the efficiency of light-harvesting devices such as solar cells and photodetectors can benefit greatly from enhancement of the total amount of light that is absorbed in their active layers.

Recently, much research has been devoted to developing methods for enhancing absorption in such light-harvesting devices, especially solar cells. If light can be focused into smaller and smaller volumes to be absorbed, then less expensive and/or less rare semiconductor material is needed to create efficient devices, decreasing overall cost. Furthermore, there are tradeoffs in device performance that may be overcome by managing and enhancing optical absorption; for example, in thin-film solar cells, thicker films are typically required to absorb most of the incident light; yet thinner films are preferred to efficiently extract the generated electrical carriers as a current.

Researchers have pursued various approaches to enhancing light absorption in thin-film solar cells, including roughened surfaces, gratings, photonic crystals, plasmonic nanoparticles and dielectric nano- and microspheres with whispering

Doped iron oxide water-splitting films



(Left) Water-splitting cell. (Right) Doped iron oxide films of different thicknesses on two different substrates.

Phil Saunders/Adapted and modified from Dotan et al., Nature Mat. **12**, 158 (2013).

gallery and Mie resonances. Many have promise, but affordability remains an issue. While high cost may be tolerated for ultra-high-efficiency photovoltaics for specialized applications, one may question the practicality of breaking the bank on high-resolution lithography to improve the efficiency of cheap commodity solar cells.

From this perspective, our thin-film structures, which can absorb 70 to 80 percent of incident light in ultra-thin semiconductor films, are prime candidates for integration into light-harvesting devices. There are no nanofabrication steps beyond thin-film deposition, so large-area absorbing films can be created cheaply and efficiently.

Last fall, H. Dotan and colleagues of Technion published a study parallel to our own work, featuring 10- to 50-nm-thick iron-oxide films deposited on metallic back-reflectors and used as water-splitting cells that generate hydrogen from sunlight. Conventional iron-oxide water-splitting cells suffer from the poor electronic properties of iron oxide, significantly limiting performance. By utilizing the ultra-thin-film interference phenomenon, the Technion group enhanced the efficiency of the cells without using costly nanoscale fabrication techniques. We believe that many more light-harvesting devices using ultra-thin-film interference are on the horizon.

Thermal radiation applications: Absorption in reverse

Another set of potential applications arises when examining the thermal radiation properties of highly absorbing thin films. Thermal radiation, the phenomenon responsible for light emitted from a hot stove-top or an incandescent light bulb, is intrinsically linked by thermodynamical laws to light absorption: a heated object only emits light as efficiently as it absorbs.

In a recent work, W. Streyer and colleagues demonstrated that semiconductor substrates coated with ultra-thin transparent films can be used as selective thermal emitters. When such films were patterned and subsequently heated, an image arising from differences in thermal emittance could be seen with an infrared camera. We developed this concept further, and used our VO$_2$ thin films on sapphire substrates as tunable thermal emitters. Because of the phase change properties of VO$_2$ and the resultant tunable absorptivity (and hence emissivity) properties, we were able to demonstrate a thermal emitter that emits less infrared light and appears cooler on an infrared camera even as it is heated, in stark contrast to every-day experiences that hotter object glow brighter.

Outlook

The continued development of ultra-thin films featuring large optical absorption due to interference opens up possibilities in many areas of optical science and technology, including light detection, solar harvesting, coloring and labeling, and even novel light sources. We look forward to new directions in thin-film optics which are likely to come from the combined efforts of materials scientists, physicists and engineers. OPN

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