Nanometre optical coatings based on strong interference effects in highly absorbing media

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Additional photographs of samples

For visual clarity, we include an additional photograph of the samples shown in Fig. 4 in the main text in Fig. S1. The photograph was taken on a black background with diffuse white light illumination.

Figure S1. Another photograph of the samples shown in Fig. 4. (a) Bare Au surface before Ge deposition. The optically-thick (150 nm) Au film was deposited on a polished Si substrate (b-i) Colors formed by coating Au with 3 nm, 5 nm, 7 nm, 10 nm, 15 nm, 20 nm, 25 nm, and 30 nm of Ge, respectively. (j) 150 nm of Au deposited on a rough (unpolished) Si substrate. (k, l) 10 nm and 20 nm of Ge deposited over 150 nm of Au, on a rough Si substrate.

Partial-wave explanation of resonance

In this section, we focus on the physical mechanism of the ultra-thin film resonance and explain the conditions in which it can occur. We begin by analyzing the total reflectivity from a structure like that in Fig. 1(b), where medium 2 has complex refractive index \( n + ik \) and medium 3 is a PEC. We plot the reflectivity at \( \lambda = 532 \text{ nm} \) as a function of \( n \) and \( k \), and find that for a film with \( h = 10 \text{ nm} \) the reflectivity stays close to 1 for all values of \( (n, k) \) from 0 to 5, but for \( h = 50 \text{ nm} \) a zero in reflectivity occurs at \( 2.81 + 0.61i \), which corresponds roughly to the \( \lambda/4n \) (quarter-wave) film (Fig. S2). This can be understood as a critical coupling condition to the lossy asymmetric
Fabry-Perot cavity formed inside the film [S1] [S2]. No absorption resonance exists for a film thinner than this with a PEC substrate.

Figure S2. (a, b) Reflectivity for a film with complex index $n + ik$ and $h = 10$ nm and 50 nm, respectively, on a PEC substrate, at $\lambda = 532$ nm.

When the conductivity of the substrate becomes finite, however (as is the case for metals at visible frequencies (Fig. 1(d)), the situation changes significantly. For example, in Fig. S3 we plot the reflectivity vs $(n, k)$ of the films given that the substrate is Au at $\lambda = 532$ nm ($n_3 = .44 + 2.24i$). We observe that when the index of the film is $4.3 + 0.71i$, the reflectivity drops to zero even though the film thickness is only 10 nm, corresponding to $\sim \lambda/12n$.

Figure S3. Reflectivity for a film with complex index $n + ik$ and $h = 10$ nm on a gold substrate at $\lambda = 532$ nm.
To better understand the mechanism leading to the reflectivity minimum at 4.3+0.71i, we expand Eqn. 1 into partial waves to get \( r = \sum_{m=0}^{\infty} r_m \) where \( r_m = t_{12} r_{13}^{m} r_{32}^{(n-1)} t_{21} e^{2m\beta} \) for \( m > 0 \) and \( r_0 = (\bar{n}_p - \bar{n}_q)/(\bar{n}_p + \bar{n}_q) \), \( t_{pq} = 2\bar{n}_p/(\bar{n}_p + \bar{n}_q) \), and \( r_0 = r_{21} \). With this formulation, we can plot the reflectivity taking into account only the first \( m' \) partial waves to see how the reflectivity evolves as more and more partial waves are included. We do this in Fig. S4 (a) and (c), where we assume that the substrate is a PEC or Au at 532 nm, respectively, \( h = 10 \) nm, and \( n_2 = 4.3 + ik \) where \( k \) can vary from 0 to 2.1 (see legend). We see that in the PEC case the final reflectivity is close to 1 for all values of \( k \). The partial reflectivity goes above 1 when only the first 1-2 secondary waves are taken into account, but the value drops back down below 1 when the other partial waves are included, preserving energy conservation. In the case of Au, however, the reflectivity changes significantly with changing \( k \), even reaching precisely 0 at approximately \( k = 0.7 \). Note that for all cases with significant loss (\( k >> 0 \)) the partial reflectivity reaches its final value of after only 3-4 partial waves are accounted for (corresponding to 3-4 passes through the lossy medium).

Figure S4. (a) Partial reflectivity from the sample taking into account the initial reflection between mediums 1 and 2, and also 0, 1, ... secondary partial waves where the first partial wave comes from a single round trip through medium 2, the second from two round trips, etc. The substrate is a perfect electric conductor (PEC), with \( n_3 = \infty + i\infty \). Medium 2 has index 4.3 + ik, where \( k \) is given in the legend.
of (b), \( \lambda = 532 \) nm, and \( h = 10 \) nm. (b) Phasor diagram corresponding to (a), showing graphically how all values of \( k \) within the range of 0 - 2.1 lead to roughly the same overall reflection coefficient \( R \) (close to 1). The circles each represent a particular reflectivity (\( R = 1 \): solid line, \( R = 0.2 \): dashed line, \( R = 0.1 \): dot-dashed line, \( R = 0.05 \): dotted line), which is reached if the phasor trajectory terminates on a particular circle. (c) Partial reflectivities as in (a), but with \( n_3 = 0.44 + 2.24i \), the complex index of Au at 532 nm. (d) Phasor diagram corresponding to (c). The resulting values of \( R \) can be read off by using the circles as a reference. In particular, the \( k = 0.7 \) trajectory ends up at the origin, yielding \( R = 0 \).

Since the partial wave amplitudes are all complex quantities, we can plot them in the complex plane, where they are represented as vectors (referred to as "phasors") (Fig. S4 (b, d)). The first phasor \( r_0 \) begins at the origin, \( r_1 \) begins at the end of \( r_0 \), etc. The total reflectivity \( R \) is the magnitude-squared of the final value of the phasor trajectory in the complex plane (\( R \) is identically zero if the trajectory returns to the origin). In the case of the PEC substrate, the first few partial waves all move away from the origin, indicating constructive interference and therefore a large final value of \( R \) (Fig. S4(b)). With the Au substrate, however, the phasor trajectory makes a sharp turn after the first partial wave, a result of the near-zero phase shift that the light experiences reflecting from a lossy dielectric into a low-optical-conductivity metal (such as Au at 532 nm), opening the possibility that the complex sum of the secondary partial waves could partially or totally cancel \( r_0 \).

In the phasor diagrams in Fig. S4(b, d), we drew circles centered on the origin corresponding to reflectivities \( R = 1, 0.2, 0.1, \) and \( 0.05 \) (solid line, dashed line, dot-dashed line, dotted line, respectively). This allows us to visually identify the reflectivity by using the circles as references; for example, since the \( k = 1.4 \) (red) trajectory terminates between the dotted and dot-dashed circles, we know that \( R \) is between 0.05 and 0.1. We see that varying \( k \) results in a wide range of reflectivities. In particular, the \( k = 0.7 \) trajectory terminates precisely at the origin, resulting in \( R = 0 \) (corresponding to 100% absorption). The reflectivity minimum in \( n-k \) space is very broad (Fig. S3), so even when the values do not precisely match those of the minimum-reflectivity condition, a significant absorption resonance can still be observed. This is what happens for evaporated Ge films in our experiments (Fig. 2(b, c)), which at 532 nm correspond to the cyan curve in Fig. S4(a). We note that while the \( R = 0 \) condition cannot be achieved with the Ge/Au material system in the visible at normal incidence due to the limited degrees of
freedom ($k_2$ and $n_2$ can be tuned by controlling the incident wavelength, but not independently of each other), such a condition can be found for some incident angles. For example, the reflectivity in Fig. 3(b) drops to 0 for $\theta \sim 70^\circ$ and $\lambda \sim 535$nm.

Absorption in the substrate

We performed analytical calculations in the same manner as in the main text (following the textbook matrix method such as that of ref. [6]) to obtain separate plots of absorption in the Ge layer and absorption in the Au substrate (Fig. S5(b) and (c), respectively). We observe that the vast majority of the absorbed power is dissipated in the Ge film, with only a small fraction of the light dissipated in the underlying Au substrate.

Figure S5. (a) Calculated reflectivity spectra from the Au/Ge geometry for various thicknesses of Ge given a 7° angle of incidence and mixed polarization (reproduced from Fig. 2(c) in the main text). (b, c) Calculated fractions of the total power absorbed in the Ge film and in the underlying Au substrate, respectively, corresponding to the reflectivity spectra in (a).

Surface profile of samples

We performed AFM measurements on some of the bare and coated substrates to obtain an estimate of the surface roughness post-deposition. For the films deposited on polished Si wafers (Figs. 2, 3, and 4(a-h) in the main text), we found that the RMS roughness was ~1.24 nm for the uncoated Au sample, ~0.47 nm for the sample coated with 7 nm of Ge, and ~0.37 nm for the sample coated with 20nm of Ge (Fig. S6). We also performed contact profilometer measurements on the samples deposited on the rough back-sides of Si wafers (Fig. 4(k-m) in main text), and found that the RMS roughness was ~680 nm, with the lateral feature size of approximately 5-10 µm.
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Stability of the films

Long-term stability of the highly-absorbing films may be a concern for some applications. In the case of our experiments, the measurements were within 1-2 days of the deposition, and the samples were then stored in gel-boxes outside of any cleanroom environment. No special care was taken to protect the samples, which were also periodically completely exposed to ambient conditions. We observed no perceptible change in the colors of the samples over a four month period, indicating that they are relatively stable. We also performed another set of reflectivity measurements corresponding to that of Fig. 3 on the same sample, and observed very little change over these four months (Fig. S7).
Figure S7. (a, b) Experimental reflectivity spectra for s- and p-polarization, respectively, for angles of incidence from 20° to 80° for an Au film coated with 15 nm of Ge, as taken one day after the deposition of Ge. This is the same data as presented in Fig. 3 (a, b). (c, d) Experimental reflectivity spectra corresponding to those in (a, b), taken ~4 months after the deposition.

For long-term stability, however, a variety of methods may be required to passivate and protect the semiconductor surface. If Ge is used as in the present work, then this can be achieved by chemical passivation methods (e.g. sulfide functionalization) [S3], which will not significantly affect the optical properties of the films. Alternatively, a capping layer may be deposited on top of the semiconductor to protect against chemical or mechanical damage. One possibility is sputtered hydrogenated amorphous germanium (a-Ge:H), which has been used to protect, for example, Ge-based nuclear radiation detectors and can be tens of nanometers thick [S4] [S5]. Another is the hard carbon coating, also known as the diamond-like coating (DLC), which adheres well to germanium and silicon, and is extremely resistant to both chemical and abrasive environments [S6] [S7].

A capping layer with a thickness of tens of nanometers or more may significantly affect the observed optical properties, depending on the optical properties of the material and its thickness.
To test this, we performed 4-layer transfer matrix calculations, including a 10 nm DLC layer on top of the Ge. This thickness was chosen because it was the thinnest DLC layer that was analyzed as a protective coating in ref. [S7], and the complex refractive index was interpolated from the data provided in ref. [S6]. The resulting reflection spectrum was nearly unaltered (Fig. S8). A thicker layer may change the reflectivity properties significantly; however based on our calculations the ultra-thin absorption resonances can still be successfully designed. In fact, the capping layer can be seen as an additional degree of freedom in the design of these thin optical coatings.

Figure S8. Normal incidence reflectivity calculations of a Au/Ge system for Ge thicknesses between 0 nm and 25 nm as in Fig. 2(c) in the main text with (a) no protective coating and (b) a 10 nm diamond-like coating (DLC)

Equivalent reflecting material

The following point was raised by one of the referees: since the presently-demonstrated semiconductor layers have a thickness much smaller than the wavelength of light, an equivalent semi-infinite medium can be defined which has the same reflectivity spectra as the combined substrate/film structure for various angles of incidence.

To explore this, we used the concept of "input optical admittance or "surface optical admittance", which is sometimes used to analyze optical thin film assemblies (e.g. ref. [1] in the main text). For any arbitrary collection of films, one can define a single surface admittance at an interface between medium 1 and medium 2, which takes into account the effect of all of the layers underneath (2, 3, 4, etc..). This is analogous to defining a single electrical admittance (or, equivalently, impedance) for a circuit comprising many elements. For materials without a magnetic response (permeability \(\mu = 1\), which is usually small at optical frequencies (ref. [1])),
the surface optical admittance is directly proportional to a surface refractive index, and we will limit ourselves to this case.

For example, we analyzed the structure comprising an Au substrate with 15 nm of Ge (blue dot-dashed curve in Fig. 2, and the data of Fig. 3 in the main text) and calculated the normal incidence reflectivity (Fig. S9(a)) as well as the surface refractive index (Fig. S9(b)). The extracted values for the surface refractive index ($n$ and $k$) are such that one could reasonably imagine a real material (or a metamaterial) with these parameters. We used these values of $n$ and $k$ to calculate the reflectivity at several oblique angles for both s- and p-polarization, and compared them to the actual calculated reflectivities from the layered system (Fig. S10).

Figure S9. Calculated reflectivity for normal incidence from a gold surface coated with 15 nm of Ge (a) and extracted surface refractive index (b)

Figure S10. Calculated reflectivity spectra for oblique incidence ((a) s-polarization and (b) p-polarization) from the layered geometry (blue) and from a flat infinite half-space with complex refractive indices ($n$, $k$) given in Fig. S9(b) (red). The reflectivity data for $\theta = 0^\circ$ is shown with the dashed curves, for $\theta = 40^\circ$ with the dot-dashed curves, and the $\theta = 80^\circ$ with the dotted curves.
The match is not perfect, which means that strictly speaking one cannot define a homogeneous semi-infinite medium which is completely equivalent to the layered system when looking at the reflection properties. However, the reflectivity curves actually match reasonably for both p- and s- polarization for all incident angles, indicating that it is possible to define a semi-infinite medium which nearly reproduces the optical properties of the layered system. This means that, to an approximation, one can also define quantities such as the pseudo-Brewster angle [S8] for our layered surface.

Supplementary references


