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Heat-induced perfect light absorption in thin-film metasurfaces for structural coloring [Invited]

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Abstract: Heating reflective metals is known to produce a wide range of colors due to oxidation of the metal surface. In fact, the most vibrant colors used in the pre-industrial era came from oxides, acetates and carbonates of metal ores and minerals. In this work, we show that heating low reflectivity metals, e.g., Ni and Ti, creates structural colors through perfect light absorption. We tune the absorption across the visible and NIR spectrum by changing the heating duration and, consequently, the oxide thickness. We demonstrate experimentally angle-insensitive perfect and near-perfect absorption in the visible and NIR regimes up to ±60°. The absorption is insensitive to the incidence angle due to the relatively high refractive index of the formed oxides, which create iridescent free coloration. We demonstrate that the oxide layer thickness, with refractive index n, is $< \lambda/4n$ due to non-trivial phase change at the oxide/metal interfaces, which makes these systems the simplest example of meta-surfaces based on thin films. The results show that oxidized metals can have applications beyond producing vibrant colors.

1. Introduction

Perfect light absorbers are devices where most of the incident radiation (>99%) is absorbed within a given frequency range [1, 2]. While nanostructured photonic materials enable perfect light absorption by matching the free space impedance to suppress reflection while critically coupling light to a material with finite losses, these materials are impractical for many applications due to the high cost and low throughput of the required nanofabrication [3]. On the other hand, thin-film based light absorbers consisting of a lossless [1] or lossy dielectric [4, 5] offer a large area, and significantly cheap alternative to realize tunable perfect light absorption.

However, these optical absorbers require a minimum of two separate material depositions, one for the metallic substrate and another for the dielectric film. On the other hand, perfect light absorption (PLA) is not possible with a homogeneous substrate comprising only of a single material due to the strong impedance mismatch with the surrounding medium for materials with high losses [1]. Here, we show that PLA is possible using a single metal film via heat-induced oxidation of an ultrathin ($< \lambda/4n$) oxide layer on the surface, removing the need for a second deposition. The oxide layer thickness is below that required for anti-reflection coatings due to abrupt phase changes at the oxide-metal interface. Our work revives an old observation, i.e., colors generated on heated metal surface, and shows that these colors can be due to materials exhibiting properties of modern metasurfaces. The generated colors on heated metals are usually angular independent which is uncommon in interference-based phenomena. We show that light absorption in heated Ni and Ti is insensitive to the incidence angle due to the relatively high refractive index of the formed oxide. We will first discuss the conditions of PLA in thin-film

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coatings and thin-film metasurfaces. Then we show that the structural colors are produced due to PLA. We finally discuss the angular independence of PLA and the ultrathin thickness of the oxide layer.

Critical light coupling takes place when the resonator absorption and reflection rates are equal. In thin films, this takes place due to amplitude splitting destructive interference such that light is entirely trapped inside the resonator and is dissipated due to the existence of losses [6]. Accordingly, two conditions must be simultaneously satisfied to realize PLA; the interfering waves must be out of phase (phase condition), and the out-of-phase waves must be of equal amplitude (amplitude condition) [7]. The phase condition is satisfied either by ensuring that the thin dielectric film thickness is $d = \lambda/4n$, i.e., antireflection coating condition, or by ensuring a non-trivial phase shift (ϕ) upon reflection from the dielectric film, the metallic substrate or both, i.e., ($\phi \neq 0$ or π), with $d < \lambda/4n$ [1, 4, 7]. While a lossless dielectric or a perfect electric conductor metal introduce a trivial phase upon reflection, a lossy dielectric or a metal with low reflection can introduce a nontrivial phase shift. On the other hand, the amplitude condition is determined by careful balancing between reflected light from the dielectric film (hence its refractive index) and the amount of light dissipated inside the dielectric film and upon reflection from the metallic substrate. As we showed recently [1], this balance can be realized using various material combinations, e.g., a lossy dielectric on a reflective substrate (see Fig. 1(a)) or a lossless dielectric on a low reflectivity metal (see Fig. 1(b)) [4]. The balance can also be realized using a lossy dielectric on a low reflectivity metal, however, the lossy dielectric refractive index cannot be very high, e.g., Ge, otherwise the amplitude condition cannot be satisfied (see online supporting information for reference [1]). When the phase and amplitude conditions are satisfied using a dielectric film with $d << \lambda$ due to the existence of an abrupt phase shift and losses in the system, an equivalent semi-infinite medium can be defined that has the same absorptance as the combined thin-film/substrate structure. Accordingly, the thin-film/substrate structure can be regarded as a metasurface since the properties of the radiation in the farfield are tailored by controlling the nearfield phase and amplitude [8].

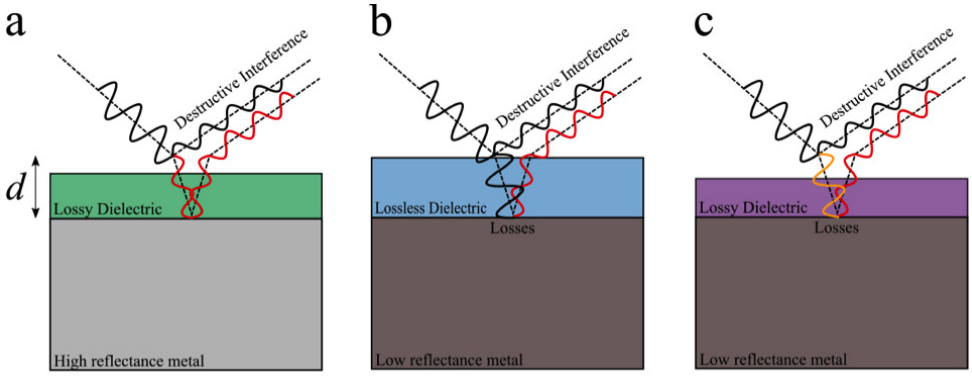

Fig. 1. (a) An optical absorber consisting of a lossy dielectric film of thickness d on highly reflective metallic substrate. Optical losses in the dielectric are responsible for PLA. (b) An optical absorber with a lossless dielectric where optical attenuation occurs in a lossy metallic substrate. (c) An optical absorber with a lossy dielectric on a lossy metallic substrate.

2. Experimental methods

To experimentally demonstrate the simplicity of this design, we deposited 150 nm of Ni and 150 nm of Ti at a rate of 0.5 A/s using electron beam evaporation on a silicone substrate. This single deposition creates an optically thick metallic base for the absorber, and is the only deposition

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required to build the perfect light absorber. We baked each sample at 400°C for 20-40 minutes in increments of 10 minutes for Ni and for 40-60 minutes for Ti, using a hotplate (IKA CMAG HS 7). The reflectance spectra for heated Ni and Ti samples (incidence angle = 15°) taken via JA Woollam VASE ellipsometer are shown in Fig 2.

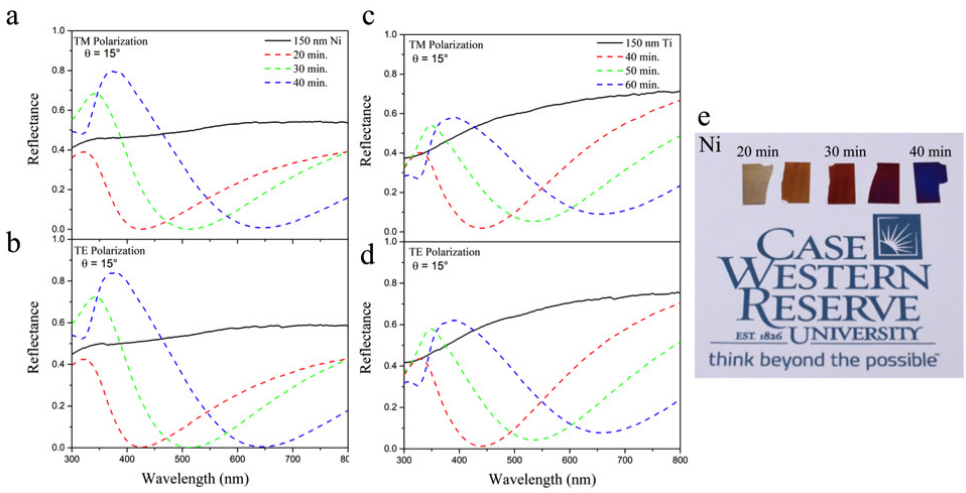

Fig. 2. The reflectance spectra for (a) TM, and (b) TE polarized light incident on an optically thick Ni film (black), the film heated for 20 minutes (red), 30 minutes (green) and 40 minutes (blue). Maximum absorbance of 99.93% is obtained. The reflectance spectra for (c) TM, and (d) TE polarized light incident on an optically thick Ti film (black), the film heated for 40 minutes (red), 50 minutes (green) and 60 minutes (blue). The absorptance is lower for heated Ti samples compared to Ni samples. For all measurements, the angle of incidence is 15°. (e) Shows an image of the color evolution of a 150 nm Ni film deposited on Thermo Scientific microscope cover glass (0.13 mm-0.17 mm) heated from 20 minutes (left) to 40 minutes (right) in increments of 5 minutes. Similar colors are obtained for Ti sample over longer time.

Fig 2(a) shows the reflectance spectra for the untreated Ni film as the well as the baked films for TE polarization at 15° incidence angle. Clearly, unheated Ni and Ti films have weak absorptance across the visible spectrum (50%). The Ni film that was baked for 20 minutes absorbs 99.7% of light at 425 nm. As the baking time increased to 30 minutes, the resonance red shifts to 510 nm where 99.94% of light is absorbed. Baking for 40 minutes further redshifts the resonance to 645 nm and 99.5% of light is absorbed. TM polarization (Fig. 2(b)) shows a similar trend. Similarly, Fig. 2(c, d) shows the reflectance spectra for an untreated Ti film as well as backed Ti films. Similar to Ni films, absorption resonance redshifts to longer wavelengths as the heating time is increased; however, perfect light absorption is not possible for the Ti-TiO_2 system at small angles. Fig. 2(e) shows photographs of heated Ni sample showing the color progression as a function of baking time highlighting the possible applications.

The absorption is clearly due to the creation of an oxide layer. To find the oxide thickness, spectroscopic ellipsometry measurements were fit against a model of a semi-infinite metallic substrate (either Ni or Ti) with a finite thickness of the associated metal oxide (NiO or TiO_2) on top using the transfer matrix method (TMM). For the oxide layers we used a modified version of the Tauc-Lorentz model [9], which has been widely applied to a variety of thin film semiconductors and insulators, including oxides [10-12]. To accurately extract the refractive index of the oxide layers, we had to fit the data over a large wavelength range, including in the near-UV region

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where absorption is non-negligible. This made the Tauc-Lorentz a convenient choice, since it works over a broad spectral range. Moreover, unlike many simpler models, the Tauc-Lorentz complex dielectric function correctly obeys the Kramers-Kronig relations. In order to account for the possibility of weak sub-bandgap absorption due to disorder, we used a variant of the Tauc-Lorentz model that includes Urbach tails [13]. The complex refractive index of NiO, $\tilde{n}_{\mathrm{NiO}}$, and TiO_2, $\tilde{n}_{\mathrm{TiO_2}}$ at 650 nm are $\tilde{n}_{\mathrm{NiO}} = 3.27 - 0.09i$, and $\tilde{n}_{\mathrm{TiO_2}} = 2.34$. The NiO thickness for 20, 30 and 40 minutes baking duration are 12 nm, 20 nm, and 30 nm, respectively, which corresponds to an optical length at the reflection minimum $\left(\lambda_{\mathrm{min}}^{\mathrm{NiO}}\right)$ of $\lambda_{\mathrm{min}}^{\mathrm{NiO}}/(11.5\tilde{n}_{\mathrm{NiO}})$, $\lambda_{\mathrm{min}}^{\mathrm{NiO}}/(8\tilde{n}_{\mathrm{NiO}})$, and $\lambda_{\mathrm{min}}^{\mathrm{NiO}}/(6.6\tilde{n}_{\mathrm{NiO}})$ respectively. The TiO_2 thickness for 40, 50 and 60 minutes baking duration are 18 nm, 36 nm, and 50 nm, respectively, which corresponds to an optical length at the reflection minimum $\left(\lambda_{\mathrm{min}}^{\mathrm{TiO_2}}\right)$ of $\lambda_{\mathrm{min}}^{\mathrm{TiO_2}}/(10.5\tilde{n}_{\mathrm{TiO_2}})$, $\lambda_{\mathrm{min}}^{\mathrm{TiO_2}}/(5.8\tilde{n}_{\mathrm{TiO_2}})$, and $\lambda_{\mathrm{min}}^{\mathrm{TiO_2}}/(5.5\tilde{n}_{\mathrm{TiO_2}})$ respectively.

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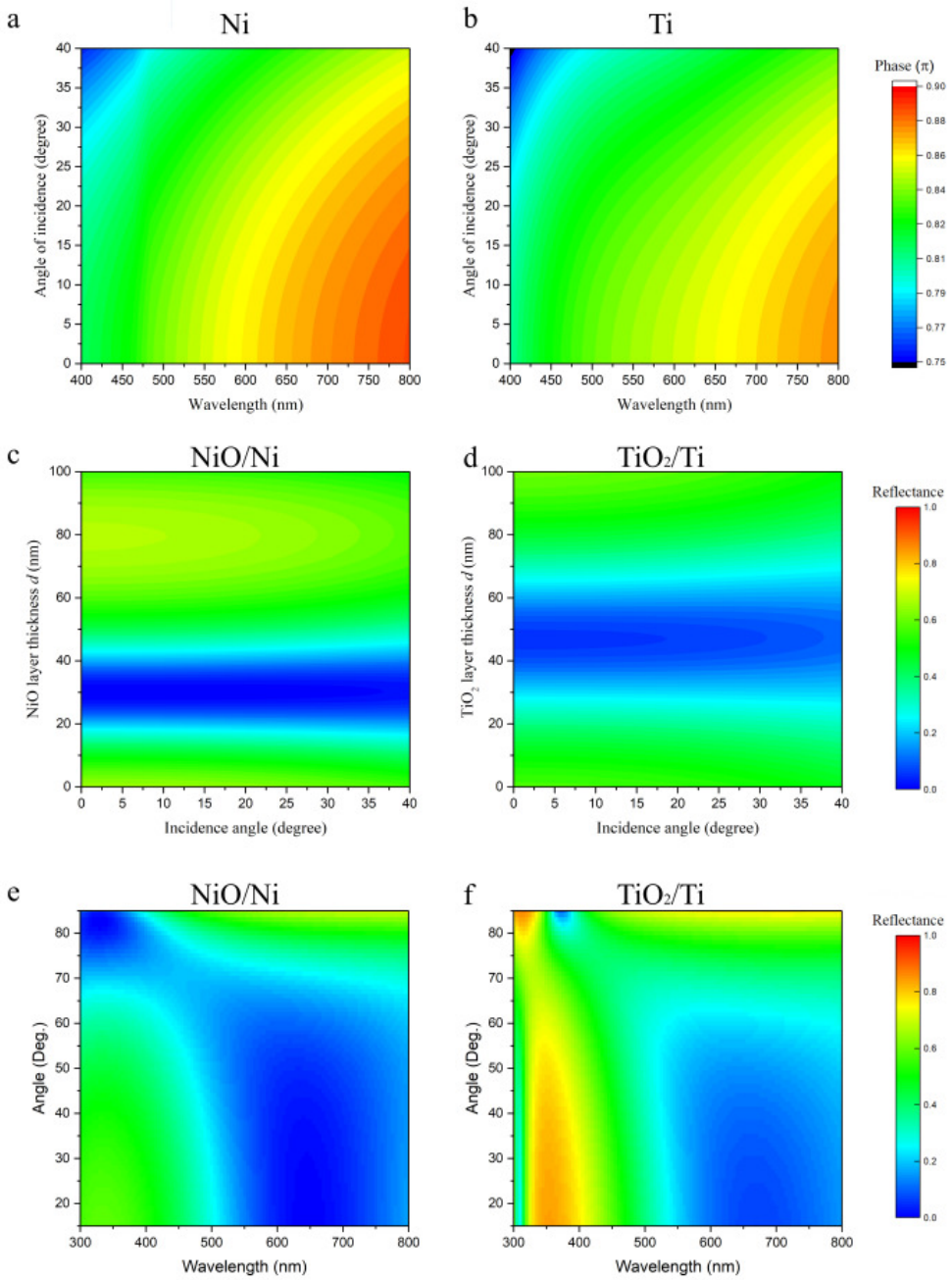

Fig. 3. The calculated reflectance phase shift upon reflection of TM polarized light from (a) Ni, and (b) Ti, as a function of incidence angle and wavelength. The acquired phase is $< \pi$ and approaches π as a function of wavelength. The calculated angular reflectance as a function of incidence angle and (c) NiO thickness and (d) TiO_2 thickness reflects the iridescence-free absorption of the absorber. The incident wavelength is 650 nm. The calculated reflectance curves for (e) 30 nm of NiO on Ni and (f) 50 nm of TiO_2 on Ti showing the broadband, wide angle range light absorption of our samples.

As we mentioned earlier, realizing PLA with ultrathin oxides ($d < \lambda/4n$) requires non-trivial

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phase shift at the oxide and/or the metal interfaces. Since the losses in both oxides are small, we expect the non-trivial phase shift to occur at the metal interface. Figure 3(a) and 3(b) show the phase shift, in units of π, upon reflection from Ni and Ti at different angles of incidence (0° - 40°) in the visible range. At longer wavelengths, the reflection phase approaches π as the metal reflectivity increases for lower frequencies, i.e., the metal approaches the perfect electric conductor condition. Furthermore, the high refractive index of the oxides means that very thin oxides can realize PLA. Figure 3(c) and 3(d) show the calculated reflectance of NiO/Ni and TiO_2/Ti for different NiO and TiO_2 thicknesses, respectively, as a function of incident angle at λ = 650 nm. The metal substrates are opaque, hence, absorptance is complimentary to reflectance. Strong absorptance is achieved over wide angular range for both oxides. NiO absorptance, however, is less angle-sensitive, for a given oxide thickness, as it has higher refractive index [14]. The calculated reflectance is shown in Fig. 3(e) and Fig. 3(f) for 30 nm of NiO on Ni and 50 nm of TiO_2 on Ti, respectively. The absorption is broadband and angular independent over ±60° .

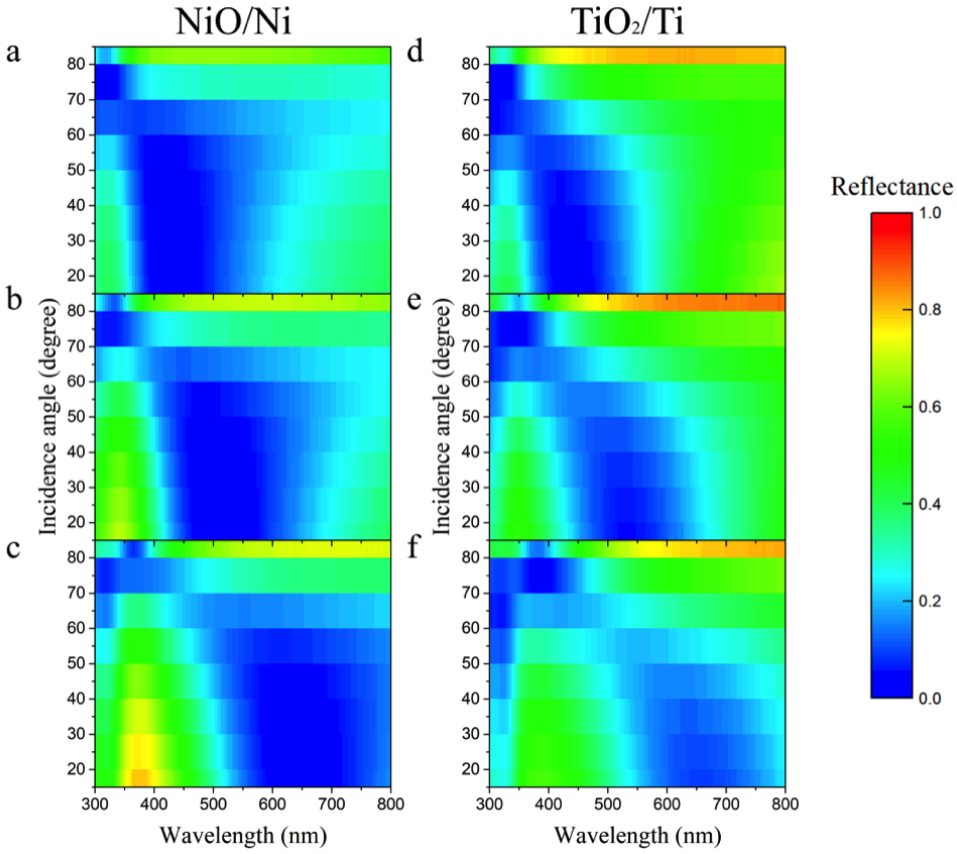

Fig. 4. The angular reflectance from 15° - 85° for NiO-Ni absorber heated at 400 degrees Celsius for (a) 20 minutes, (b) 30 minutes, (c) 40 minutes. The angular reflectance from 15° - 85° for TiO2- Ti absorber heated at 400 degrees Celsius for (d) 40 minutes, (e) 50 minutes, (f) 60 minutes. The angular insensitive of the absorptance is clear for both absorbers. The NiO-Ni has broader absorptance.

Figure 4(a), 4(b), and 4(c) show the experimental angular reflectance of NiO/Ni, for NiO thicknesses of 12 nm, 20 nm, and 30 nm, respectively. Figure 4(d), 4(e), and 4(f) show the

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experimental angular reflectance for TiO_2/Ti, for TiO_2 thicknesses of 18 nm, 36 nm, and 50 nm, respectively. The data presented are for TM polarized light; however, TE polarized light shows similar behavior. We note that the reflectance minimum for both samples is generally angle insensitive which explains the color persistence of oxidized metals at different angles. However, the NiO/Ni absorber is less angle sensitive, which is consistent with the results predicted by our model presented in Fig. 3(c) - (f). The theoretical model captures the qualitative features of the reflectance throughout the wavelength and incident angle range. Small discrepancies with respect to the experimental results in Fig. 4(c)-(f) are most likely due to the approximate treatment of the oxide layer in the model: for example, the degree of oxidation probably tapers off continuously away from the surface, rather than forming a perfectly homogeneous layer as in the model. The broadness of the absorption modes for the NiO/Ni absorber compared to the TiO_2 /Ti absorber is likely due to the existence of losses inside the weak sub-bandgap absorption in amorphous NiO layer.

3. Conclusion

We report structural coloring as a result of perfect light absorption by depositing single low-reflectivity metal layers exposed to controlled heat. The iridescence-free PLA can have applications beyond heat induced structural coloring. Perfect light absorbers, in general, can be used as a solar receiver for decorative solar thermal applications. In addition, palladium is a low reflectivity metal with a relatively high refractive index oxide. Accordingly, using a single deposition of Pd thin film it is possible to realize a hydrogen gas sensor, which is based on modifying the absorption modes corresponding to PLA. The realization of PLA using a single film deposition can have applications in thermo-photovoltaics where the absorbed heat from solar spectrum is transferred to a selective emitter/absorber, as well as stealth technology and electromagnetic shielding.

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